Vapour Phase HF and XeF$_2$ Etching Methods with Improved Selectivity for MEMS Manufacturing

Daniel Drysdale

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Abstract

Fast and high selectivity vapour phase etching techniques for silicon dioxide and silicon materials are necessary for cost-effective and high precision manufacturing of future MEMS devices. The thesis describes the development and characterisation of vapour phase HF etching methods for silicon dioxide films and XeF₂ based etching processes for silicon.

In studies of vapour phase HF etching of silicon dioxide films the effects of catalyst choice, water and alcohol, are investigated in terms of etching rate and selectivity against silicon nitride films. The former is commonly used as the sacrificial material to release the fabricated microstructures from a substrate while the latter is used as the structure or passivation material. The dependence of etching rates and selectivity on gas flow, pressure and temperature were studied. It has been found that the best etching rate and selectivity for a water based catalyst can be achieved at low temperature and high pressure conditions while for the alcohol based catalyst high temperature is preferred. Selectivities of 26:1 and 12:1 have been obtained for the water and alcohol based catalysts respectively.

In order to improve the selectivity, the effects of deposition and post processing conditions for silicon nitride on the resultant etching behaviour have been investigated. The silicon nitride films were made to contain more silicon (silicon-rich) than in the standard nitride films by increasing the gas ratio between silane and ammonia in the deposition process. The effect of annealing was also studied. It was found that the etching rate by HF vapour is reduced by a factor of 3.6 from 9.5 nm/min to 2.6 nm/min. After annealing at 500°C the etching rate can be reduced further to 1 nm/min. The total reduction of etching rate is by approximately an order of magnitude indicating that the selectivity can be improved by a factor of about 10.

XeF₂ based vapour phase etching of silicon has also been studied since silicon is also used as a sacrificial material in MEMS manufacturing. The undercut etching behaviour was investigated for both single crystal silicon and polysilicon films produced by the PECVD method. An improvement in undercut etching rate by almost a factor of 2 has been achieved for polysilicon, 18 µm/min over the value of 10 µm/min as in the previous work. A new etching process by adding hydrogen in the reaction gas was studied showing significant improvement in selectivity from 500:1 to 1000:1 between the single crystal silicon and the PECVD silicon dioxide films, and it is from 19:1 to 10000:1 between single crystal silicon and the PECVD nitride films.
Dedication

I dedicate this to my Grandparents who looked forward to the day I completed my thesis.

I’m sorry I took too long for you.
The ability to express the gratitude I feel for a number of people who helped me during the course of this research is a very difficult thing, especially over the course of 6 years. I shall try my best in as succinct a way as possible.

I’d firstly like to thank Dr. Changhai Wang. As my academic supervisor, you have been invaluable. You’ve kept me on the right path throughout this thesis when I’ve been moving every direction but forward. Your guidance and advice on how to make this thesis more than just a paperweight has been in may ways, life saving, and I can’t thank you enough for all your support.

Dr. Tony O’Hara, my industrial supervisor. There have been numerous occasions where I was ready to pull out my fast disappearing hair and your experience, guidance and calm eased my worry. I came to MEMS almost by accident and knew very little in real-world experience. Your vast knowledge and patience in passing this onto me over these last few years has been greatly appreciated and has likely saved me from a mountain of mistakes and manufacturing faux-pas in this time.

I couldn’t have finished this without your help and will be forever grateful to both of you.

To Tony McKie, CEO of memsstar. A massive thanks for your support in all this work, as well as multiple beers at the end of some very long days.

A number of the process and technical team at the Scottish Microelectronics Centre, Edinburgh, are owed a huge debt of gratitude for teaching me so much regarding manufacturing processes, especially Dr. Andy Bunting, Ewan MacDonald, Richard Blair and Stewart Ramsay, thank you.

Finally, to my family: The perpetual words of support were heard. I know I don’t look like I’m listening most of the time, but I heard every word. Thank you for everything.

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## Nomenclature

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<td>Hydrogen Fluoride</td>
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Chapter 1 Introduction

1.1 Introduction
In this thesis, vapour phase etching processes are discussed, developed and further improved. Fabrication of semiconductor integrated circuits and recently, micro electromechanical systems (MEMS) devices, relies on multiple processing steps. These steps involve the generation of functional and sacrificial layers that must be built into the device to allow for manufacturing of functional devices. Once all layers have been deposited, the sacrificial layers must be removed to allow the device to be realised. Commonly in semiconductor processing, wet chemical processes have been used due to convenience and lack of any damaging effects to the final devices on product wafers. This has been the process of choice for decades in the semiconductor industry and it has developed to include large arrays of options depending on the process requirements, be that specific etch solutions for a material, an etchant for specific geometries or even rinsing solutions to ensure clean samples.

In MEMS processing however, this same simple approach is not suitable. The main reason is due to the existence of the stiction phenomenon. This phenomenon causes the adhesion of freestanding structures to a substrate in the presence to moisture. This is due mainly to the formation of Van der Waals forces, hydrogen bonds or electrostatic forces [1]. This is a major problem at the micron scale in MEMS manufacturing, as the restoration force of these structures at the MEMS scale is small enough that the force overcome the force applied by these three forces, thus leading to permanent adhesion and a reduction in yield. For this reason, stiction is one of the major causes of low yield in device, making it harder for device manufacturers to enter the MEMS industry with reliable products. This ultimately leads to the re-development of the product cycle as devices move from one processing technique to another. In devices for industries such as automotive, any change may require 6-18 months of re-development and re-qualification before being accepted as a viable product.

There have been many proposed methods to remove moisture when releasing sacrificial layers in a wet chemistry method. These involve processes that have a final dry method designed to remove any moisture that may still be present including standard evaporation steps, supercritical drying or sublimation drying methods. Most recently, the development in vapour phase etch processing has become a more prevalent and
viable method for sacrificial release etching. Both anhydrous hydrogen fluoride (aHF) [18] and Xenon Difluoride (XeF$_2$) processes [50] have been investigated in industry and academia. These options are now becoming key processes in minimising the presence of moisture during the etching process. This requires that the wafers be placed in an environment where the etching chemical can be introduced in vapour phase. The logical presumption being that in this phase, the formation of moisture is much harder, which reduces the likelihood of stiction occurring resulting in a greater yield of working devices.

In MEMS devices, some predominant material combinations are: silicon with silicon dioxide and silicon nitride or one of these films on a substrate surface for one of the functions: passivation, insulation, structural or sacrificial materials. In any case, designers look to have as high a selectivity result as possible between these films. In silicon etching, selectivity towards both silicon dioxide and silicon nitride is important. In HF etching, selectivity of silicon dioxide towards silicon nitride is the most prevalent requirement and the slower a nitride film can etch the better. Throughout this thesis, understanding selectivities between these three primary materials is investigated and understanding the factors influencing these behaviours is determined.

This thesis aims to study new technologies and define behaviours that will be used in manufacturing foundries and research groups alike for production of next generation MEMS and nano electromechanical systems (NEMS) devices. By developing the understanding between the three key materials silicon, silicon dioxide and silicon nitride, a greater capability can be used to produce smaller devices with increased functionality. This thesis describes the development and characterisation of two etching methods: using anhydrous hydrogen fluoride as an etchant for silicon dioxide and xenon difluoride for etching of silicon.

**1.2 Thesis Layout**
Chapter 2 describes the current state of the art for these vapour phase etching methods, including wet release techniques used both in current and past manufacturing of MEMS devices.
Chapter 3 summarises the fabrication techniques including film deposition and patterning techniques used in this work and describes the basic principles of each process as it relates to its role in the manufacturing sequence.

Chapter 4 investigates the differences in between both alcohol and water as the process catalyst and highlights not only the similarities based on the same process parameters, but also the differences that can be seen between silicon dioxide and silicon nitride films.

Chapter 5 further investigates means to increase the robustness of silicon nitride films. Silicon nitride is a fundamental material that for either structural or electrical reasons must be preserved. With MEMS and NEMS devices becoming more commercially prevalent, the increase in fabrication levels and the push to smaller and smaller device sizes has pushed critical dimensions much smaller. This ultimately means that the effect of etching on these critical layers and their critical dimensions becomes ever more important. By developing the deposition process to improve film robustness, the means to increase etch tolerances can also be better improved.

Finally in chapter 6, the characterization of continuous flow XeF$_2$ etching is developed. In XeF$_2$ etching, a common architecture has become prevalent within the XeF$_2$ systems available: the use of pulse processing. The systems developed by memsstar utilize a very different configuration, which is still largely undefined in mainstream literature and industry. Chapter 6 defines both the fundamental reaction mechanisms of XeF$_2$ etching as well as the reaction capabilities of the system and the benefits gained from a system design such as this over alternative means of running this process. It also includes investigation into alternative sacrificial materials while looking at silicon dioxide and silicon nitride films as in previous chapters.
Chapter 2 Literature Review in the State of the Art

2.1 Introduction
Throughout the thesis, etching technologies for MEMS and the Semiconductor industry will be discussed. With such a developed industry and knowledge base in the semiconductor world, which is largely transferrable into the MEMS world, there are many processes, skills and methods that have been developed and have become accepted design methods for developing devices and their respective process flows. The move to smaller scale device features due to the increase in manufacture of microelectromechanical systems (MEMS) devices has seen the application of many existing processing methods such as: thin film deposition, lithography processing, reactive ion etching (RIE) processes, transferred to MEMS manufacturing without problem. Many of these processes are considered as the front-end processes, in which thin films required for active devices including buried layers and dopant diffusion are deposited. Back-end processing, which includes interconnect formation and metal deposition, have again largely been transferred to MEMS device design process flows. However the interesting but occasionally troublesome integration has become apparent during the etch steps required for the release of the critical layers in the devices, such as accelerometers, pressure sensors or microphone type devices. Currently in the semiconductor industry, a standard wet etch process could be used but this process can be disastrous for MEMS devices.

The increased focus in the MEMS sector during the last decade has brought with it a whole host of challenges: no longer can these characterised wet etch techniques be carried across from the semiconductor industry without subsequent processing issues being found. The development of devices with micron and nanometre sized features demand that these processes, still frequently utilised for larger feature sizes, require vast improvement or be replaced altogether when tackling the modern design issues of large scale device manufacturing.

Two such methods investigated in the body of this thesis are the etching of silicon dioxide sacrificial layers by with vapour phase anhydrous hydrogen fluoride (HF) gas and the etching of silicon with xenon difluoride (XeF₂). The move to MEMS devices and the stricter requirements of these etch processes has called for investigation and ultimately a full transition in some cases into vapour phase etch processing in research
and development groups in industry and academia. In this chapter, a review of the current state of the art and the research that has led to current technology options is discussed.

2.2 Sacrificial Etching by Hydrogen Fluoride

The first process to be discussed is the etching of silicon dioxide films by hydrogen fluoride. This has been an established wet etching process for wafer cleaning for a long period of time. As the semiconductor and MEMS industries move to small-scale devices, these wet processes have exhibited limitations in their capabilities. There are two main problems with wet etching of silicon dioxide in HF solutions: stiction and control of selectivities towards key materials.

In modern MEMS fabrication, stiction has been one of the key factors impeding the full commercial rollout of devices. Stiction is the phenomenon whereby the released structures permanently adhere to the substrate of a wafer after the removal of the sacrificial layer such as silicon dioxide, silicon nitride, polysilicon or any material in which moisture is not instantly repelled from its surface. The primary cause of the stiction can be attributed to Van der Waals forces, electrostatic forces and hydrogen bonding as well as coulombic attraction [1-4]. The primary mechanisms of stiction formation are described as follows:

**Electrostatic forces**

Electrostatic forces occur due to the internal charges in a released structure. This charge will naturally generate an electric field in an air gap, for example between two released plates. Electrostatic stiction in comparison to other causes can be considered as temporary since the effects of the charge transfer tends to equalise over time between the two surfaces. The problem however, is that the initial stiction could be caused by these electrostatic charge transfers but then maintained by one of the other mechanisms.

**Van der Waals forces**

Van der Waals forces are weak attractions between molecules, which can be polar or non-polar in nature. These molecules will have a small non-static dipole moment to them, which can cause a small attraction between the two surfaces or between a surface and liquid interface. The non-static dipole moment of the molecules means that the electrons in their electron shells are unable to screen the atomic nucleus charge in all
directions at all times. This presumes that the surfaces that allow this attraction to exist are flat and uniform. On rough surfaces where peaks and troughs may exist, this roughness generates focused points of possible attraction that may not be strong enough on their own to cause the permanent attraction.

**Capillary forces**
Capillary forces exist between liquid and solid surface interfaces. When the contact angle between them is less than 90°, a pressure variance forms between the inside and outside of the droplet where the external pressure is greater than the internal pressure. This generates an attractive force between the two plates and causes them to be attracted to each other, causing stiction.

**Hydrogen bonding**
Hydrophilic surfaces will naturally contain an amount of water in them below a temperature of 150°C. When these water containing surfaces come into contact with each other, the water within the films will begin to form hydrogen bonds between the hydrogen and oxygen atoms on opposing surfaces. Breaking these bonds is easier than a typical chemical bond with the adhesion energy of these bonds having been measured to be in the region of 100 mJ/m² [5]. This process can lead to a silicon surface forming a small oxidised layer where the silicon surface is terminated by hydroxyl groups (-OH) which is then susceptible to further hydrogen bonding from another hydrogen atom within a molecule.

The effect can cause two structures to touch or come into close proximity in the presence of moisture [5]. Semi-permanent or fully permanent adhesion can occur when the restoration force of the freestanding structure is lower than that of the stiction force. The removal of this sacrificial layer in many cases, is realised using a wet etch solution in which the devices are placed. After this process removes the material, the device can be rinsed and dried. It is during this rinse and drying process step that stiction commonly occurs. This is when one or more of the above-mentioned mechanisms for stiction will come into play and thus cause stiction. This is known as release stiction and considered to be one of the main causes for low yields in the production scale release process in MEMS manufacturing.
There have been many methods developed for minimising the level of moisture in the development process and thus minimising the occurrence of stiction. Some of these methods seek to bypass the traditional phase boundaries as can be seen in the phase diagram in Fig. 2.1 by making sure that moisture does not form and instead forces the reaction to shift directly into the gas phase. This has been performed with such techniques as elevated temperature drying processes [6], evaporation drying, sublimation drying and supercritical drying [7, 8, 9]. These studies discuss the selective etching of the substrate area underneath the released structures after the removal of the sacrificial layer by means of increasing the gap between the freestanding structures and the substrate. This method is effective due to the increased distance making it harder for the released device to not only deflect enough to touch the surface, it also increases the force within the released structure. This leads to an increase in the restoration force within the structures than those found with smaller gaps between the beam and substrate, which means the structure is capable of overcoming the force applied to it by residual moisture. This idea is based on a similar concept as described in the literature [10], that discusses roughening the surface of a device substrate to reduce the effective surface contact area with the released devices. An Nd-YVO₄ laser was used to roughen the surface and demonstrate the effectiveness in small scale fabrication, large scale integration of this process would be too costly as a process step and some alternative methods that can generate the same effect were subsequently developed [9]. Structures with rounded cross-sections were described as an alternative solution [11]. This design has the effect of reducing the amount of force that can be applied to the surface of the released structure in a different way to that reported previously [9]. The curved cantilever is an uncommon design in the device from the previous literature [10], but does not require a different process for the device to be realised, thus reducing development time and costs.

Supercritical drying of wet etched samples is another commonly used and effective means of overcoming the issue of residual moisture [9]. The concept is founded on the standard phase diagram for solids, liquids and gasses as shown in Fig. 2.1. When the environment in which the sample is placed is moved into a high pressure, high temperature regime, the residual liquids can bypass the typical phase boundaries and cause the moisture to be removed without residues or causing effects such as stiction. This is a very effective method of moisture removal, but adds a number of additional process steps into the manufacturing stage for a device. If there were processes in which
release could be achieved without additional long steps such as this, then processing batches of wafers would be completed in less time.

Another method has been developed to use the wet etch process to release MEMS structures [12], through iterative rinse steps to remove the HF and replace it firstly with an alcohol based rinse agent like methanol or isopropanol and then to displace that liquid with a solution with self assembled monolayers, which are naturally hydrophobic. In coating the whole device, both the lower and upper surfaces of the freestanding device can resist the interaction with the external forces. This leads to a reduced likelihood of stiction occurring. There has been much work in the field of self-assembled monolayers, not only for the ability to make a surface hydrophobic [13], but also to make them corrosion resistant [14]. The techniques have also been used as a means for binding enzyme and DNA strands for medical analysis [15], chemical sensors [16] and allowing the transfer of electrical charge at small dimensions for use in nanoscale field effect transistor (FET) devices [17]. The field of self-assembled monolayers (SAMs) and its applications is substantial in itself. It offers great opportunities for the development of anti-stiction, anti-fouling and bioactive surfaces.

In recent years however, a direct replacement method for wet etching processing has become more prevalent and is now an area of increasing interest: vapour phase hydrogen fluoride (HF) etching. An initial viability study has been presented previously [18]. Primarily, many etch processes have been focused on replacing the wet
hydrofluoric acid etching process used for the etching of both native oxides and sacrificial oxide layers. Once in the vapour phase, this can no longer be considered hydrofluoric acid, as the process is not in a liquid phase, but a gas phase. It is this move to gas phase processing that is crucial for controlling the environment in which the samples or wafers are etched. The hydrogen fluoride source is anhydrous and is typically 99.9995% pure or even higher (where the contaminant itself is made up largely from water). Many attempts to dry wafers involve bypassing standard phase diagram boundaries in an effort to reduce the moisture residues on the released devices. While effective at increasing yields, vapour phase processing can be easily integrated into the standard manufacturing process flows which is repeatable with a low relative cost. The reaction of hydrofluoric acid with silicon dioxide is described in equation (2.1) [18].

\[
\text{Catalyst} \quad \text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \quad (2.1)
\]

The reaction for HF in either acid or vapour phase reactions requires a catalyst to initiate and sustain the etch process. Most commonly, there are two types of catalyst: water and alcohol. The role of the catalyst in both cases is to allow for the dissociation of HF into H\(^+\) and F\(^-\) radicals. The rates at which the HF can dissociate can be affected by the choice of the catalyst used. In the wet processes, water was used as the catalyst in some cases but as the process moves on, it is largely replaced by alcohol. In the early development of the vapour phase method, water, which was inherent in the ambient atmosphere, was the available catalyst. As the move to environment control under vacuum regimes developed, two very different branches have since been developed. While the wet and vapour phase methods outlined above have both had varying yet reasonably good results, showing improvements in yield and reduction in contaminants over a standard wet etch process, it is the HF vapour phase etching method that shows the greatest promise in reduction of device failure due to stiction.

Since its inception for use as a vapour phase etchant for silicon wafer cleaning process in 1966 [19], hydrofluoric acid has been used as a wet etch solution for removal of native oxide layers. More recently and more importantly, it has been used as a vapour etchant for removing sacrificial structural layers in MEMS device fabrication. One of the key benefits of vapour processing as described previously, is its high level of
environmental process control. This control is more precise at maintaining the
evironment than the wet etching methods that occur in ambient atmosphere conditions.
This process is still in its relative infancy compared to many of the processes used in a
standard foundry and is still in the stages of being characterised. The industry already
has suppliers of vapour phase etching tools using HF but there is still much that has yet
to be understood. Recently direct comparisons of HF etching in acid baths and in
vapour phase etching systems have been performed [20]. A comparison has been made
between an HF etch process using a 1% solution with silicon dioxide samples and an
atmospheric vapour phase etch process where oxide samples are etched by vapours
from an HF: H₂O solution bath. The samples etched in the vapour process are observed
to have a cleaner surface finish than those submerged in a solution of HF. Other studies
have also discussed the comparison of wet and vapour phase etching [21]. It was found
that there are process benefits to move to the vapour phase processing from the wet
processes, but that there are some issues when scaling the process to production level.
Residues in the form of reaction by-products from silicon nitride films that would be
rinsed away during a wet process step are no longer removed in the vapour phase. As
such, additional processing steps are necessary to overcome this problem. The
repeatability of these processes parameters requires a number of measures to ensure
consistency. These are critical control parameters that are considered throughout the
etch processes. The control of the HF vapour phase etching process and its effectiveness
is primarily carried out by chamber pressure, sample temperature and reactant gas
flows.

These main parameters can control the etching of sacrificial layers in many ways. The
use of chamber pressure is a means to control the residence time of the etchant gasses
and their by-products in the vapour phase. By maintaining a higher pressure, the gasses
are removed from the chamber more slowly than at lower pressure where environment
removal is faster. Due to the gasses residing in the chamber for longer at higher
pressures, this allows for reactions taking place to be more readily reacted for longer
periods thus giving a faster etching process.

The sample temperature is another crucial process factor within the HF vapour etching
process. As with any system where temperature control is common, this controls how
much moisture is present in and around the surface of the device and the chamber
atmosphere. A higher temperature reduces the amount of moisture and with the vapour
HF etching process in mind, a lower moisture presence causes a slower initiation of etching, resulting in a slower overall etch as moisture is not as readily available to initiate the etching process. This has been discussed previously [18, 22]. Early vapour phase development systems were based on the atmospheric processes where the ambient air was the source of process catalysts in the form of moisture. For better control of the etching rates, the systems are incorporated with temperature controls to improve repeatability.

The final controlling factor is the reactant gas flow. Gas flow is a term that can constitute a number of conditions. In general however, etch behaviours dictate higher HF and catalyst gas flows and the concentrations will provide a higher etching rate for films.

While stiction is the primary limiting factor to mass production, the other focus in this work is selectivity. Selectivity refers to the ability of an etch process to remove one material selectively over another. This does not necessarily mean that one film is etched while the other is not, but rather that one film etches considerably more than the other. Knowing the selectivity effects also allows designers to modify film thickness to compensate for the expected etching of specific films. An ideal scenario would be an etch process that leaves the important materials unaffected while fully removing the sacrificial layer. In both acid and vapour phase etching process with HF, careful consideration of the selectivity effect is required.

In the future as the device feature sizes decrease, the focus will shift from etch rates to selectivity as the need to remove films preferentially and maintain critical dimensions becomes prevalent. The most common of the sacrificial films in an HF etch process is silicon dioxide. This can be deposited in a number of processes, from the plasma enhanced chemical vapour deposition (PECVD) to the thermal growth techniques. Silicon dioxide layers are used for a number of reasons, from the dielectric layers in active devices to passivation layers. However, the most recent emerging use is as a sacrificial layer to be removed at the end of the manufacturing process to release the device structures and realise the functionality of the design. The recent MEMS fabrication trends have also seen greater interest in the deposition methods of films and the etch process behaviours. As designers move away from certain materials due to device requirements, the materials available have come under higher levels of scrutiny.
As such, PECVD oxides and nitrides are now the films of choice for MEMS manufacturing due to their lower deposition temperature requirements when thermal budgets are a consideration.

It is intended that during this literature review, the results from both wet and vapour phase processes can be analysed to show the behavioural trends. Explanations into these behaviours, while looking into the comparison of the catalysts used and the effects of etching based on the choice of the catalyst will be discussed. Further analysis will focus on the film deposition techniques and how the differences in deposition methods impact the etching of the films are also described.

2.2.1 Effects of Catalysts on Etching Behaviour

It has already been shown in equation (2.1), that HF will react with silicon dioxide in the presence of a catalyst. In the late 1960’s, HF etching was typically performed in wet processing baths at atmospheric pressure which was mixed to approximately 48% HF to 52% water. The use of an alcohol as the process catalyst began to develop as devices began to reduce in feature size. As the dimensions began to decrease and devices started being fabricated using more complex methods, some layers would be removed in the atmospheric wet bench process. This led to stiction where the released layers would adhere to the lower surface layers causing a failure of the devices and reduction in yield. This problem was overcome whereby after the HF etch step, a rinsing solution consisting of de-ionised water mixed with an isopropyl alcohol (IPA) solution was used. It was found that stiction occurred less frequently and that yields therefore increased to levels where mass production of small-scale devices was possible. This method relied upon the ability of the IPA, as an alcohol, to harvest and displace the remaining water at the surface of the released structures. By mixing water with IPA, the water could be more readily removed than in the standard rinse procedure.

As feature sizes decreased with the onset of MEMS devices, an alternative solution to wet etching became a priority as wet-etching processes saw the increase of stiction. With the development of vapour phase etching, these problems could be overcome. By utilising low pressures in the tens of Torr while atmospheric pressure is approximately 760 Torr, it is possible to keep both the etchant gasses and catalysts in vapour phase thus reducing the formation of moisture. Early research into true vapour phase HF etching used alcohol based processing because the wet process used isopropyl alcohol
to reduce the stiction effects in both the etch and rinse steps to produce the best yield results [23]. It is not clear if it was considered that these solutions still contain water, however early research appeared to show that the aim was to completely remove all traces of water from the etch process. This is clearly not entirely possible due to the by-product of the oxide etching process being water as described by equation (2.1). However, making the reactant gasses exclusively HF and an alcohol based catalyst, it was expected that this would provide improved results. No work has been found in comparing the effects of vapour phase etching of silicon dioxide films with water or alcohol as the catalyst or the specific differences in their behaviours under the same physical hardware configurations. This will be one of the key topics of this work: a study on the behaviours of these two catalysts and their respective behaviours when etching oxide films as well as the behaviours relating to selectivity between the oxide and nitride films under vapour HF etch conditions.

2.2.1.1 Water Based Catalysts
The etching of silicon oxides with hydrofluoric acid vapours utilising small amounts of ambient moisture in the air was discussed [19]. This interaction with the vapour from a bath of hydrofluoric acid also has water as a constituent part of it. The work showed high etching rates can be achieved, but the control of the parameters such as uniformity was difficult due to the uncontrolled nature of the ambient moisture acting as the catalyst.

The most common etching reaction involving HF is with silicon dioxide. This is described in both [19] and [24] and is given, depending on the number of moles of HF represented, as either the reaction described in equation (2.1), or expanded in equation (2.2).

\[
\text{Catalyst} \\
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \quad (2.2)
\]

\[
\text{H}_2\text{SiF}_6 \rightarrow 2\text{HF} + \text{SiF}_4 \quad (2.3)
\]

This shows the difference in the reaction when there are increased levels of HF in the reaction, which result in different reaction by-products. In this case four moles of HF in equation (2.1) gives silicon tetrafluoride (SiF\textsubscript{4}), but six moles results in the formation of
fluorosilicic acid ($\text{H}_2\text{SiF}_6$), which further dissociates into $\text{SiF}_4$ as shown in equation (2.3).

In the previous studies of the reaction of a silicon surface held above the vapours during the reaction with water, it was pointed out that the reaction will only take place once an adequate moisture layer is formed on the silicon surface. It was proposed that the solution is fluorosilicic acid described in equation (2.3). The reaction of the fluorosilicic acid and $\text{SiO}_2$ can itself cause etching to occur which creates water as a reaction by-product thus feeding the etch reaction further. The work was performed on thermally grown oxide layers that are grown at temperature of 1200°C. This design used a method to etch the exposed areas of oxide using photolithography; this method however, does cause problems when performing vapour phase etching. The HF vapour was able to penetrate the photoresist to etch the areas that were to be protected by the photoresist, which does not occur in HF acid solutions. Further improvement was found using masking photoresists used in metal etching processes. These photoresists used substantially more robust polymer materials in the formation of the resist, allowing them to be robust in harsher environments. While these can act as a partial mask, it was insufficient to fully protect the oxide from etching,

Further work continued to discuss the mechanisms needed to explain HF/H$_2$O reactions [24]. These reaction mechanisms are based on the assumption that etching is only initiated if a thin liquid layer containing HF has formed over the surface of the material to be etched. It is stated that since the concentration of the reactants is dependant on the HF fraction that can be altered by adding more hydrogen or fluoride (by adding HCl or NH$_4$F respectively), then control of the reactants is necessary to balance the products and minimise the effect on the structures. A problem lies in trying to add extra fluorine to the process. In doing so, it creates an ammonia by-product that can cause stiction issues in the released structures. This residue is thought to be ammonium fluoride (NH$_4$F), which can be removed by the application of heat at 200°C. A point to note is that $\text{H}_2\text{SiF}_6$ can react with $\text{SiO}_2$ to increase the etch rate within the reaction chamber. By observing the effect of the mixture of HF and H$_2$O with regards to their partial pressures, it can be found that there are regions where equal pressures for both materials exist in a stable condensation layer, which can be formed as previously mentioned [19]. This means that the pressures of HF and H$_2$O must be at the point where there is more of a moisture level than the level of evaporating mixture. This was shown to be possible
at a range of different pressures for both HF and H₂O but in both cases one of the reactants must be at high pressure for condensation to occur. These steps show that although the reaction is performed in the vapour phase, a condensation stage is needed to initiate the etching process, thus showing that a small amount of water in high HF partial pressure is enough to create a condensed phase and etch the sacrificial layer.

Another study described the methods of wafer preparation and methods used for vapour HF etching [25]. Differences can be observed in etch rates for different types of oxides from silicon such as the thermally grown material as well as doped and undoped PECVD deposited oxides. A point is also made that vapour HF etching of silicon nitride layers is relatively slow in comparison to the oxide layer etching and as a possible application the latter can be used as an etch protection mask under the conditions outlined within the work.

The etch process highlights an important step: the time taken to form an initial condensation layer as discussed in literature [24]. It was found that higher nitrogen carrier gas flow rates and therefore a presumed higher HF partial pressure, the incubation time is lower. This incubation time is the time needed to fully form the condensation layer over the wafer and the time in which essentially no etching takes place. A longer incubation time is reported to be due to a lower water partial pressure from the reduced carrier gas flow rate and hence the increased time for the formation of a condensation layer on the wafer.

The difference in etching rates on the other films was shown due to their processing methods. While phosphosilicate-glass (PSG) had a high etch rate compared to borophosphosilicate-glass (BPSG), it had a longer incubation time as well. It was also observed that an annealing stage for the BPSG film densified the layer, which increased the incubation time. As described previously, the addition of hydrochloric acid (HCl) can affect the etch rate of oxide layers [25]. The etch rate and incubation time both increased with the addition of HCl so it is shown to be a trade-off for the system. The study discussed the addition of HCl in an HF/H₂O process with a higher water ratio. It was found that the etch rate decreased greatly from the azeotropic mix which was determined to be caused by the drop in HF concentration due to additional water and HCl. The reaction proposed in these studies involves an intermediate stage as shown in equations (2.4) and (2.5).
On reaction with the oxide layer leads to:

\[
\text{SiO}_2 + 2\text{H}_3\text{O}^+ + 2\text{HF}_2^- \rightarrow \text{SiF}_4 + 4\text{H}_2\text{O}
\]  

(2.5)

This shows how the formation of the condensation layer begins: water can catalyse the reaction and is also a reaction by-product. This closed-loop feedback nature of this reaction allows the growth of the condensation layer to the point where the reaction then begins to etch the oxide layer. The overall effect of adding HCl is the slowing down of the creation of HF_2^- groups giving a slower incubation stage. This reduces the pH at the same time which leads to an increase in the etch rate of the oxide layer. The inverse can be said of a reaction to HF and H_2O in favour of HF.

Another study further discusses the effect of the etch rate by controlling both the incubation time and the temperature of the wafer [22]. In these experiments, the wafers were first cleaned in an oxygen and ozone mixture to minimise any effects caused by contaminants. The effects of temperature on these wafers for both PSG and BPSG show a small decrease in etch rate with a higher temperature whereas the thermally grown oxide shows a noticeable drop in etch rate. This effect was more clear with doped native oxides though it was noted that a higher content leads to a higher etch rate. In these examples, it is seen as detrimental to the etch rate to have a high sample temperature.

While the process requires that water is necessary to catalyse the reaction, at increased temperatures, the level of water available is reduced as it evaporates from the film interface and so the etching rate drops. It was therefore concluded that high temperatures, which cause a higher incubation time, are detrimental to the etch process. The deposited oxides annealed at high temperature as part of the process, suffered from decreased etch rates due to the oxide becoming denser and more resistant to the etching initiation step.

A further study also discusses the effects of temperature of the wafer on the resulting etch rate [26]. The wafers used were silicon with thermally grown SiO_2 and a further polysilicon layer deposited above this. Much like the previous studies [19], the wafer was held in place above the HF/H_2O solution where the vapour was produced at
atmospheric pressure in a polytetrafluoroethylene (PTFE) box in which a heater was placed on the wafer to heat it. It was found that the difference in temperature of the wafer with respect to the HF solution ambient temperature was a key interaction factor. The smaller the difference between the wafer temperature and HF solution, the more effective the etch process was found to be. The problem with a small temperature difference is that an abundance of moisture can build up on the surface, which leads to stiction of the released structures. A balance must be found whereby the etch process is constant, yet not so slow that there is enough moisture to cause stiction.

The reactions with these different materials and many others have been considered [27]. This work characterised different types of films to assess their ability to be etched in HF vapour as well as possible issues that may arise from these selected materials. While previous reaction systems are acknowledged [24], they propose an alternative reaction method to the etching setup which is very similar to production systems involving an etch chamber with independent gas supply lines for the catalyst, HF source and carrier gas. A large number of films commonly found in CMOS processing, from various forms of silicon dioxide and metal were studied. The type of deposition process used, especially for silicon dioxide films is of great importance, as being able to produce the films for specific requirements is something many devices require. Specifically, it was noted that doped oxide films, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG) and borosilicate glass (BSG) leave residues under the released structures in the vapour release process, but they have a significantly higher etch rate than the standard PECVD and thermally grown oxide films.

US Patent application 5567332 A discusses an interesting means of etching silicon with HF that involves first etching a portion of the silicon dioxide with wet processes to etch down to the silicon at the bottom of the device [28], before being placed into a vapor phase HF and H₂O process for the final undercut and release of the device. This is a very simple way to overcome a key concern on full device wafers: etching a large area of silicon dioxide on the surface of a wafer. From reaction (2.1), every mole of SiO₂ that is consumed, leads to two moles of H₂O being generated. This will ultimately lead with a large open area of oxide, to a very fast etch as the process is being enhanced by the increased catalyst generation of the water. By etching only the open field area of oxide in a wet process, this makes the undercut more controllable as there is no requirement to control the field oxide etching stage. Its main drawback is of course, the need for two
etching systems to complete the release fully, but the increase in control may make it viable in some facilities.

Work has been reported describing the advantages and disadvantages of both the wet and dry etch methods using HF for different types of sacrificial layers such as thermal oxides, PSG, TEOS and nitrides as well as metal layers [29]. When describing HF vapour etching methods performed with an HF and H$_2$O based process, the merits and disadvantages for some of these key factors mentioned are also described. The initial results of the experiments for wet etching with a 1:1 ratio of HF and H$_2$O process showed that it had a high etch rate with the annealed phosphosilicate glass (PSG). This is due to the reaction of the phosphorus in the etching process which itself is converted to phosphoric acid bringing about the increased etch rate. Again, residues formed during the etching of these PSG films are difficult to remove and lead to stiction of released structures. Etching of tetraethylorthosilicate (TEOS) was shown to be similar in etch rate, whereas the thermally grown oxide for the silicon wafer was shown to be the slowest due to the fact that to grow the oxide layer, the wafer had to be heated to the highest temperature of all the samples prepared. When observing nitride layers, there are two common methods of creating the nitride layers: low-pressure chemical vapour deposition (LPCVD) and plasma enhanced chemical vapour deposition (PECVD). Each of these methods has its advantages and disadvantages as discussed in the literature where each of the methods is compared and contrasted [30]. A major difference in these two methods is the lower deposition temperature of PECVD films. Whereas control of layer deposition in LPCVD systems is simpler using low pressures as it reduces the unwanted gas-phase reactions, it still needs a high temperature to ensure sufficient deposition speeds.

While studying a 1:1 mix of HF and H$_2$O [29], experiments were also carried out with a buffered HF (BHF) glycerol mixture which is a 2:1 mixture of buffered HF, a 7:2 mixture of NH$_4$F to HF with 1 part NH$_3$, and glycerol for a comparison. The solution of BHF and glycerol has a lower concentration of HF and hence results in a slower etch rate. It was shown to also have a more preferential etch towards silicon dioxide films and thus a better selectivity towards nitride and metal layers.

As discussed previously, when dealing with HF vapour, many factors contribute to the effectiveness of the etching of sacrificial layers. These were also considered during the
comparison of the wet and vapour HF etching processes [29]. It was noted that if the wafer was not left long enough to reach the “true” processing temperature, then there would be an over abundance of moisture on the wafer etch interface. This raises the risk of etching too quickly, or if left too long at the set temperature, then surface moisture will be driven out leading to a reduced etch rate. The second aim of the pre-treatment was that of nitrogen flow rate. Since the flow of nitrogen introduces the reactants, low flow rates result in lower levels and hence a lower etch rate, but a maximum flow of 1 l/min showed no major improvement over a flow of 0.8 l/min.

Higher temperatures drive out more of the moisture content within the etching chamber, and since water is needed to catalyse the reaction, this lowers the etch rate. As moisture is minimised, the chance of stiction in released structures is substantially reduced. Lower process temperatures result in higher etch rates increasing the chance of stiction due to the increased moisture levels at the etch interface. It has been found that while the nitrogen bubbles through the 1:1 HF: H\textsubscript{2}O solution, more HF is evaporated than H\textsubscript{2}O thus the HF levels decrease faster and the constituent solution in the bubbler gradually becoming a more water based solution. A decrease in HF concentration is observed over prolonged periods of time, resulting in the HF: H\textsubscript{2}O solution requiring recalibration periodically.

Similar results from the wet etch process have been found in the literature regarding oxide layers where the thermally grown oxides are etched the slowest and the annealed PSG is still the fastest etched film [29]. However, one of the by-products of this reaction, phosphoric acid, which would have been washed away in a wet etch process, was found to remain on the wafers after etching in vapour HF. This remains as the vapour process occurs at relatively low temperatures. As such, the acid residue cannot evaporate as it is known to evaporate at 200°C. This suggests the use of the annealed PSG as a sacrificial layer in HF vapour etching would not be suitable, as this residual by-product may have the potential to induce stiction. TEOS showed comparable etch rates to the annealed PSG without the problems of residual by-products. It was found that during vapour etching of silicon nitride layers, a secondary compound was formed. This secondary compound was thought to be Si-NH\textsubscript{2} or an ammonium product such as NH\textsubscript{4}F, which could be removed by heating the wafer after etching. It was noted that only some metals can be etched in HF vapour and that their respective etching rates were very slow. While it has been shown that HF vapour provides many benefits, such
as a major reduction in the occurrence of stiction and an increase of selectivity with some materials, it is clear there is a lot of work required to fully characterise nitride layers in these regimes.

Selectivity within an HF and H₂O vapour process is discussed by studying the absorption and desorption processes on the BPSG and thermally oxidised films [31]. The methods to improve the selectivity of one material over another by adjusting the mechanisms that promote the etching of the individual materials are described. The etching rate of thermal oxide drops with an increase in temperature on the wafer or a decrease in the water partial pressure. However, these factors do not affect the etching of BPSG very much due to the different etch initiation conditions. It was found that both PSG and BPSG can be removed without etching any of the thermally grown oxide layer on the same wafer. This was also complimented with the results that high temperature etching with HF vapour gave an improved etch rate towards these materials. To measure the differences of these etch parameters, experiments were carried out at a range of temperatures and partial pressures for the water based catalyst on both BPSG and thermal oxides while the HF partial pressure was fixed along with the etch time. The results show as expected, the etch rate of the thermal oxide decreases as the temperature rises whereas for BPSG, as the water partial pressure increases, the etch rate follows the trend but the increase of temperature shows no change in the etch rate. This shows that greater selectivity of BPSG over thermal oxide can be achieved by increasing the etch temperature. For the experiment looking at the selectivity for BPSG and thermally grown SiO₂, at room temperature of 20°C, both the BPSG and SiO₂ were etched but raising the temperature to 65°C decreases the thermal oxide etching rate to very low levels while the BPSG was unaffected. This shows a capability to control and increase selectivity dependence on the films chosen by the design requirements in the device, and something that can be considered in the work of this thesis. The effects of raised temperatures of 45°C and 65°C on the etch rate were described. Once the HF vapour is added, its partial pressure begins to reduce slowly while the generated SiF₄ and H₂O partial pressures begin to increase and show an exponential change over time but the etch rate of the oxide does not rapidly increase like the etching rates at room temperature [29]. While HF and H₂O are both absorbed by SiO₂ during its initial reaction, condensation forms high ionisation layers on the surface of the oxide that react in the proposed reaction described in equations (2.4) and (2.5) [31].
It was observed that greater water levels at the oxide surface will influence the ionisation energy and that the etch reaction is generally limited by the amount of water absorbed. Though it is observed that the rate at which the H$_2$O product is formed is much slower than that of SiF$_4$. Based on equation (2.4), there should be a noticeably greater amount of H$_2$O produced. This lack of generated water therefore means that the water is not desorbing from the oxide surface to the gas phase, as it should be but remaining in the oxide surface and slowly building up. The generation of H$_2$SiF$_6$ as described in equation (2.2) in the HF and H$_2$O based system is known to reduce the vapour pressure. The absorbed H$_2$O in the oxide layer reacts with the HF and causes a large increase in the etch rate and a drop in the HF partial pressure. It was found that by adding HF vapour to a chamber filled with H$_2$O vapour, the etching rates increase in contrast to the situation where both gasses are added at the same time. The liquid layer is one reason that a high etch rate exists. It is easily formed when either or both the HF and H$_2$O partial pressures are high and is formed only after the SiF$_4$ partial pressure reaches a critical level. As described in previous examples however, having a very fast initial etch can also continue to etch at a fast rate and cause stiction with released devices, which must be avoided.

Selectivity issues occur on many materials and another common requirement is the need to remove a native oxide from a wafer while causing negligible effect to other materials on the wafer. Native oxides grow naturally when silicon is exposed to atmospheric conditions. The native oxide is less dense and so is easier to remove and minimise its effect on the thermal oxide layers. While this material is sometimes considered to be very useful in processing due to its high electrical insulating abilities and chemical resilience. Nevertheless, it is much less than that of the thermal oxide and PECVD oxides. This is due to the fact that it grows at room temperature in atmospheric conditions while PECVD oxides are deposited between 300°C up to 900°C depending on the source gas and hardware configuration used. Thermal oxides are commonly grown between 800°C to 1200°C. A proposed method of removing native oxide while avoiding the etching of both thermal and CVD oxides has been described [32].

The etch process is carried out by placing the wafer within a vacuum environment that is able to control pressure for anhydrous HF from 5.9 Torr to 59 Torr. The reaction within the chamber was monitored continuously using the absorption spectra for SiF$_4$ and HF. The reaction was observed when the IR transmittance for HF increased and
SiF$_4$ decreased. During one experiment, it was found that the native oxide etch rate decreases as the temperature increases and at higher temperatures, the thermal oxide etching rate was one order of magnitude higher. One factor known to affect the reaction rate is the concentration of the HF used in the reaction. In this case, it was found that beneath a critical concentration level, the thermal oxide would not be etched and above this level, it would be completely removed. This critical concentration is dependant on the moisture level as well as the HF concentration and increases when there is less moisture and is also dependant on the type of oxide. Dry thermal oxide has a critical concentration level when H$_2$O concentration is less than 0.4 ppm (volume). The critical level for the native oxide is also dependant on the factors that led to its formation. Formation in hot air and hot HNO$_3$ is much higher than in other formation methods. With all this information, it is possible to selectively etch different oxides by controlling the HF concentration used in the etch reaction.

### 2.2.1.2 Alcohol Based Catalysts

An alternative mechanism for vapour HF etching is described in literature between HF and methanol as the process catalyst [33, 34]. Methanol has the same functionality as water; it acts as a catalyst and is used to aid in the dissociation of the HF molecule into H$^+$ and F$^-$ radicals. Alcohols were introduced into vapour phase etching was due to its use in rinse solutions, it was possible to absorb excess water at the etch interface and therefore give better control of the process.

The initial reaction begins with the interaction of HF and alcohol catalyst methanol as described by equation (2.6) [33].

$$2\text{HF (ads)} + \text{M (ads)} \rightarrow \text{HF}_2^- \text{(ads)} + \text{MH}^+$$  (2.6)

where M is methanol, CH$_3$OH, and (ads) stands for absorbed state, describing the state of the reactant during reaction. The hydroxyl (-OH) group within the methanol is known to dissociate the HF molecules to create the HF$_2^-$ molecules in a similar fashion to the water catalysis, which is key for the etching process. Upon reaction with an oxide layer such as silicon dioxide, the reaction is different as described by equation (2.7).

$$\text{SiO}_2(s) + 2\text{HF}_2^-(\text{ads}) + 2\text{MH}^+(\text{ads}) \rightarrow \text{SiF}_4(\text{ads}) + 2\text{H}_2\text{O(ads)} + 2\text{M(ads)}$$  (2.7)
Unlike the reaction of HF with silicon dioxide in the presence of the water catalyst, equation (2.7) shows that there is not only the original methanol catalyst used for process initiation, but there is also water present. This results in two possible catalysts in the etch environment at the same time. This leads to much stricter process control requirements, otherwise the use of the alcohol-based catalyst becomes redundant once the reaction has stabilised and the amount of water generated by the reaction overwhelms the supplied alcohol, resulting in process behaviours similar to those of a water only based process.

Depending on the temperature and pressure, there can be an issue with the by-products. These come from a reaction creating fluorosilicic acid. As shown in equation (2.2), this can be further decomposed into SiF₄ and HF, but care must be taken to ensure that its formation is limited or this could induce stiction at sites across the structures. This reaction has the benefit of leaving no residual product on the wafer after etching.

Further study into the HF and methanol based process has been discussed [23]. In this work, the method was described by incorporating methanol into the HF vapour etch process as a substitution for water. The effective pressure for the process to take place was chosen by the analysis of the pressure where reactants remain in the gas phase. This reduces the likelihood of release stiction and suggests that if there is any water by-product created, then the water evaporates as it is also in the gas phase at the low-pressure levels. This is not always the case such as in the case for BPSG where it was thought that moisture from the oxide itself may be released faster than it can be driven out and in fact increases the etch rate on the wafer. The results obtained from the experiments confirm many of the expected results from the previous work. For thermal oxide films, when the temperature increases, the etch rate decreases due to the evaporation of the absorbed moisture which would otherwise help to catalyse the reaction and increase the etch rate. This was different to the results obtained from the BPSG etching work where the etch rates were very high. It was thought this may be due to the formation of some phosphoric acid from the BPSG itself which is known to drastically increase the etch rate of oxide films. They also showed that when there was no methanol present and hence no chance for the water molecules to be formed, there was no etching. This agrees with the observations that HF needs a catalyst to initiate the etch process. The results are different enough from HF and water catalyst etching to conclude that there is a different mechanism at work.
Further work using methanol as a substitute for water was carried out at Toyota [35, 36]. The main body of the work consisted of the development of HF and methanol etching of silicon nitride layers. The work discussed the ability to etch SiO$_2$ without etching polysilicon. This was performed with the HF and methanol solution through a different etching mechanism in which the methanol flow rate was varied to observe the difference in the etch rates. The etch rate was found to be dependant upon gas flow and pressure as well as the temperature which are the three known factors affecting the etching process. The work was based on etching of Si$_3$N$_4$ layers using the HF/methanol process and analysis of the reaction by-products [36]. A summary paper of the work describes their attempts to improve the cleanliness of the nitride layers that have been in reaction with HF and methanol. After reaction, a residue was found which was identified as ammonium hexafluorosilicate ((NH$_4$)$_2$SiF$_6$). This compound could be broken down into less harmful components, first breaking down to NH$_4$F and SiF$_4$ then decomposing further at an elevated temperature. It was also discovered that the amount of by-product increases as the reaction continues. Above 100°C, the formation was much less and a heat treatment at 200°C removed all contamination. This shows that while it is possible to remove the by-product by thermal treatment, the temperature may need to be moderately high which could cause some issues if the structures on the wafer require to be at a low temperature to maintain certain characteristics.

The work described in [37] discusses the use of an alcohol as a substitution for water in the HF etching process. However it was based on isopropyl alcohol (IPA) as an alternative. As previously discussed, the reaction between the HF and alcohol will result in the formation of H$_2$O which is useful in catalysing the reaction as it dissociates the HF molecules which is key to the etch process but also produces more water molecules. This results in a higher HF concentration than is preferable to give a higher etch value as the process then generates a high level of catalyst material in both water and alcohol. The high level of volatility of IPA and methanol give rise to evaporation when mixed with water and this alcohol vapour as a catalyst has been shown to aid in the removal of other products from the wafer surface. The reaction as described in [33] and [34] is said to remove the by-products by desorption during the heating process. The residues on the etched wafers are discussed. It was found that there is a formation of phosphoric acid during the etching of PSG as has been discussed previously. It was also shown that residues were found when etching the TEOS (tetraethoxysilane) and LTO (low temperature oxide) on a nitride layer but that etching of these on a polysilicon layer
showed no formation of residues or effects of stiction. This therefore shows that there is a possible link between contamination and residue formation with the nitride layer.

These examples provide a reason why alcohols are sometimes preferred over the H$_2$O based catalysts. With methanol or IPA, the condensation stage is slower which initiates the reaction of oxide etching at a reduced rate. This results in a reaction that still has a small amount of water present which can be controlled more easily to maintain the reaction. This allows the reaction to be catalysed without causing stiction of the free structures.

Since vapour-phase etching can be a slow process with the alcohol catalyst based process, a two part process can be used. Firstly by wet etching of the wafer with a buffered oxide etchant (BOE) and then using vapour phase etching to reduce the total etch time considerably [33]. This provides an initial fast etch but has the ability to release structures in such a way that the chance of stiction is reduced. It could be considered the best of both aspects: the high speed of a wet etch initially with minimal chance of stiction and also condensation and vapour etching in a controlled manner.

The released structures for the tests, made with a TEOS sacrificial layer on the wafers, were found to be completely released and the detachment length was far greater than those released using only the wet etch process. The pressure of both the HF and methanol also provide ways to improve the etch rate by mixing both of these chemicals at their own relative pressures. For example, by having a higher partial pressure for HF, the etch rate increases.

### 2.2.1.3 Selectivity of silicon dioxide to silicon nitride films

It is well known that the basic reaction between HF and silicon nitride (Si$_3$N$_4$) is given in equation (2.8) [29].

\[
16\text{HF} + \text{Si}_3\text{N}_4 \rightarrow 3\text{SiF}_4 + 4\text{NH}_4\text{F} \tag{2.8}
\]

However, ammonium fluoride (NH$_4$F) is formed, this is observed as a crystalline build up on the surface of the device after etching. This must be heated to above 200°C to remove it as described in previous sections, since it could be damaging to the final product either by causing some device damage or partially causing damage when being
heated for removal. The sudden change in stress of a material could be just as damaging as the stiction itself. This reaction does not require a process catalyst in the same way as the silicon dioxide films require an initiation period.

Hence the issues arising with silicon nitride layer etching comes from the formation of nitride-specific reaction by-products where the formation must be either be reduced or completely avoided. The current method to remove silicon nitride is the use of hot phosphoric acid in a wet etching process. The problems associated with this method are that particles are formed which can severely damage the released structures. The process is also conducted at temperatures between 150°C and 180°C. This combination of high temperature and long processing time due to the low etch rates raises safety issues for the users of the process. The hot phosphoric acid etching method as reported [38, 39], can be performed at a lower temperatures of 135°C, which reduces the risk to the users. An improvement of this method is to look at etching the nitride by using a number of different methods. Patents exist that describe nitride and oxide etching using plasma with a mixture of ammonia and nitrogen trifluoride (NF₃) or a secondary mixture of tetrafluoromethane (CF₄) and oxygen with hydrogen and nitrogen. This is primarily for use in cleaning CVD chambers and furnace deposition tubes, although applications into material etching have also been considered [40]. Plasma is generated with the ability to selectively etch the oxide and nitride layers in an anisotropic direction. Depending on the gas flows, the oxide and nitride films can be selectively removed. This process is slow and would not likely be suitable for large scale manufacturing however as the plasma would remove some other materials that may be required as part of an active device. This does however provide a means of increasing the selectivity of the oxide layers on a nitride film. Heating samples to a temperature of 100°C allows the layers to be etched without the chance of stiction and so increases the yield of useful devices in practice. Silicon nitride etching has also been reported in HF acid baths, [41], and described in a regime in which an HF etch system could be made to preferentially etch silicon nitride over silicon dioxide films.

The results show the contrary in most cases, the etch rate of the silicon dioxide layers is not dependant on the concentration of the F⁻ ions. It has been described that the reaction with HF₂⁻ ions is one of the key reactions for etching specifically silicon dioxide layers [102]. This is because the Si-O bond is different from the Si-N bond and is broken with a different etching mechanism. This suggests that difluoride molecules, HF₂⁻, are better
at breaking the silicon-oxygen bonds, whereas monofluorides HF$^-$ or ionised fluorine F$^-$ are the active species in breaking the silicon-nitrogen bonds. The bond must be severed completely and therefore the monofluoride ions are best suited to do this but the etch rate is reduced as there is a decrease in the ease of breaking the bonds and hence, etching, with difluorides. The formation of monofluorides with an abundance of water is very difficult, this means this reaction is very hard to enhance while the reaction of the difluorides takes control, causing oxide etching at an increased rate. Another view is to recognise that in more diluted HF solutions, a monofluoride reaction will take precedence over a difluoride reaction. Thus the etch rate of SiO$_2$ decreases much faster than Si$_3$N$_4$ when the HF concentration is lower and the selectivity towards nitride layers increases. Also, the higher the temperature, the more prevalent the monofluoride reaction is. While the removal of the excess moisture will lower the etch rate of oxide layers, this does not affect the nitride etch rate in the same way and so the selectivity towards nitride over oxide increases. A similar method to achieve a high selectivity of silicon nitride to silicon dioxide but with a slight modification is discussed [42]. In this case an additional solvent mixture called EDGE (diethylene glycol propyl ether), was used. This improved the selectivity and allowed for lower process temperatures than the previous example by 50°C. It was found that if EDGE is included in such a way that the total gas mix has a cumulative small dielectric constant, the etch selectivity is improved. If the dielectric constant was larger, the selectivity dropped further. What both of the series of experiments show however, is that temperatures greater than 50°C shift the behaviour of the etch process from a preferential high selectivity process in favour of silicon dioxide to a process where silicon nitride is more preferentially etched. This is interesting in that it agrees with the other studies where the etch temperature is kept at the room temperature region as the process etch rates begin to slowly decrease as the temperature rises.

2.2.1.4 Commercial design based examples

When dealing with more complex and commercial designs and structures, it is not always possible to choose the materials of a device to make sacrificial etching easier. Certain materials will need to be used due to the properties they possess. An example of this is given in [43], where a structured polycrystalline silicon membrane is to be released by HF vapour etching. The device was fabricated using multiple processing steps such as LPCVD polysilicon deposition and an RIE step also. There were also multiple annealing steps at high temperature that would drive out much of the moisture
form the device. A membrane was built on top of a PSG sacrificial layer. This was to be etched away once a polycrystalline silicon material was deposited. The membrane material was shaped such that there were open entrances to allow HF vapour to etch the PSG layer and free the membrane. The previous studies [29] described issues with the etching of PSG using HF vapour due to the production of phosphoric acid which only evaporates at temperatures above 200°C. In this work, the issue was avoided by firstly etching the PSG layer, then using a wet BOE to remove any remnants of the breakdown of the PSG material and finally rinsed by IPA and methanol. To remove the moisture that would be left by all the wet rinse methods, a CO₂ critical point dry stage was used. This provided high temperature and pressure to remove the solutions by passing the liquid-gas phase barrier and super-critically heating them. This also removed all final traces of rinsing solution to give a complete and released membrane. This specific example shows there are methods of getting round the problems that are known to exist already by using other means such as supercritical drying.

In the latter part of IC chip fabrication and from the beginning of microsystems fabrication, the idea of being able to keep a wafer completely free from contaminants during the different processing stages has been of critical importance as any external contaminants can cause failure of the devices on a wafer. To this end, processing units known as cluster tools were developed which act as complete processing systems that keep the wafer under vacuum during the key release stages. This system is the subject of another paper [44]. The work discusses the effect of oxide etching within one of these etching process modules, referred to as PM’s, with an HF and methanol based process. The etching mechanisms utilised here are much the same as in the previous work [33]. The steps needed to initiate etching in a cluster tool are discussed. The key differences between HF and methanol etch based processes and the HF and H₂O etch based processes are discussed. As described previously [24], the etching of a wafer will not begin until a layer of condensation has formed on the surface.

The first difference is that the condensation layer in the methanol based etching processes will be thinner than the water based etch process due to the higher pressure needed for methanol processing. This means that there will be fewer OH⁻ ions in the layer to react with the oxide to remove it. It is also observed that the temperature at which the process occurs of 100°C is much higher than that of the HF and H₂O based etch process. This high temperature will aid in reducing the chance of release stiction,
but it can substantially reduce the etching rate. To remove any particulates, the wafer was cleaned by a UV/O$_3$ and UV/Cl$_2$ process to remove any hydrocarbon and metallic contamination respectively. The key parameters known to affect the etch rates and their repeatability such as the mixture ratio, process temperature and chamber pressure are all considered here. The greater the water flow or the speed which OH$^-$ ions can be introduced into the process module, the faster the etch process will be as there will be more of a reaction with the oxide. This would be useful where a higher temperature is used as this causes reduced etch rates. As described earlier, H$_2$SiF$_6$ can be formed as a by-product of the etching process. This product can also break down into SiF$_4$, which is useful in limiting the amount of generated particles. The generation of a by-product and its subsequent desorption rate will define whether there will be an accumulation of particles on the finished product. If the generation of by-products is much greater than that of the desorption rate, then particle generation occurs. The reaction by-product is generated by the etch rate and as such, its rate of formation and subsequent desorption can be controlled by the process pressure and temperature up to high temperature and low pressure giving the best desorption rates for the by-products. Tables 2.1 to 2.5 show the highest reported etching rates for oxide and nitride films in both liquid and vapour phase processes.
<table>
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<th>Film Type</th>
<th>Etch Rate (Å/s)</th>
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Table 2.1 Comparison of etching rates for silicon dioxide films in standard wet etch processes using water as catalyst.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Process Temperature (°C)</th>
<th>Film Type</th>
<th>Etch Rate (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Judge et. al. [95]</td>
<td>30</td>
<td>Thermal Oxide</td>
<td>36.2</td>
</tr>
<tr>
<td>Monk et. al. [92]</td>
<td>21</td>
<td>PSG</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>PSG</td>
<td>150*</td>
</tr>
</tbody>
</table>

*Surfactant added to BHF to increase etch.

Table 2.2 Comparison of etching rates for silicon dioxide films in standard wet etch processes using alcohol as catalyst in BHF solution.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Process Temperature (°C)</th>
<th>Film Type</th>
<th>Etch Rate (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS Lee et. al. [96]</td>
<td>25</td>
<td>Thermal Oxide</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>TEOS</td>
<td>6.7</td>
</tr>
<tr>
<td>YI Lee et. al. [33]</td>
<td>25</td>
<td>Thermal Oxide</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>TEOS</td>
<td>37.5</td>
</tr>
<tr>
<td>Shimaoka et. al.</td>
<td>30</td>
<td>Thermal Oxide</td>
<td>16.7</td>
</tr>
<tr>
<td>[35]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hanestad et. al.</td>
<td>25</td>
<td>Thermal Oxide</td>
<td>116</td>
</tr>
<tr>
<td>[27]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WI Jang et. al.</td>
<td>35</td>
<td>TEOS</td>
<td>206.7</td>
</tr>
<tr>
<td>[37]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3 Comparison of etching rates for silicon dioxide films in a vapour phase etching processes using methanol as catalyst.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Process Temperature (°C)</th>
<th>Film Type</th>
<th>Etch Rate (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wong et. al. [97]</td>
<td>25</td>
<td>Thermal Oxide</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>PSG</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>BPSG</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>Thermal Oxide</td>
<td>0.08</td>
</tr>
<tr>
<td>Witvrouw et. al.</td>
<td>25</td>
<td>PSG</td>
<td>48</td>
</tr>
<tr>
<td>[29]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>TEOS</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>PECVD Oxide</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>Thermal Oxide</td>
<td>2.5</td>
</tr>
<tr>
<td>Cao et. al. [43]</td>
<td>25</td>
<td>PSG</td>
<td>22.2</td>
</tr>
</tbody>
</table>

Table 2.4 Comparison of etching rates for silicon dioxide films in vapour phase etching configuration using water as catalyst.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Liquid/Vapour Phase</th>
<th>Catalyst Used</th>
<th>Type of Oxide</th>
<th>Reported Etch Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Witvrouw [29]</td>
<td>Liquid</td>
<td>Water (49% Conc.)</td>
<td>PECVD Nitride</td>
<td>16.3A/s</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>Water (49% Conc.)</td>
<td>LPCVD Nitride</td>
<td>2.1A/s</td>
</tr>
<tr>
<td></td>
<td>Vapour</td>
<td>Water</td>
<td>PECVD Nitride</td>
<td>71.8A/s</td>
</tr>
<tr>
<td></td>
<td>Vapour</td>
<td>Water</td>
<td>LPCVD Nitride</td>
<td>0.9A/s</td>
</tr>
</tbody>
</table>

Table 2.5 Comparison of etching rates for silicon nitride films in liquid and vapour phase etch processes at 25°C.

2.2.2 Summary

The development of vapour phase etching of silicon dioxide films using hydrogen fluoride gas shows substantial improvements over the wet etching methods commonly employed and its future capabilities show much promise.

From the initial development as a means of cleaning wafers for manufacturing of IC’s, its move to a means of patterning masks in wet etching processes helped HF etching become a standard process in semiconductor fabrication. As discussed previously, in MEMS manufacturing, the standard HF etching processes began to suffer from reliability issues in the form of stiction. The released devices could no longer overcome the forces applied to them due to the residual liquid remaining on the wafer after HF etching and the subsequent rinse steps. This led to the introduction of alcohols as part of the etch process to draw water away from the wafer by iteratively rinsing it with alcohols. As both water and alcohols are capable of acting as the process catalyst for the HF etch, there is no issue in initiating and sustaining the etching of oxide films in the wet etching processes as the reduced levels of water on the devices after rinsing keep the likelihood of stiction to a minimum, leading to the use of alcohols exclusively as process catalysts. In this thesis, the use of water as the process catalyst will be the key factor. While the reasoning for alcohol is clearly justified, the realities of operating in a vacuum system suggest that the enhanced control, even with water as the sole catalyst could be further controlled and as such, the process would benefit from this. An unavoidable process behaviour appears to be that regardless of the catalyst, water is generated. This generation of water using alcohol is partially controlled by using the alcohol to draw the water away from the surface, but this leads to the regimes where the
water acts as a double catalyst reaction in the etching process. Determining the effects of each catalyst would be useful to quantify their advantages and drawbacks as described in Chapter 4.

2.3 Sacrificial Etching of Silicon by Xenon Difluoride

The second sacrificial etching technique investigated in this thesis is etching of silicon materials by Xenon Difluoride (XeF₂). XeF₂, which was first reported in 1962 [45, 46], and since then a number of methods in bringing this molecule species to a more practical and functional use have been developed. The wet etching processes for silicon removal to this day are still the preferred route for many semiconductor and MEMS devices with many options available to meet the specific requirements. These processes can require additional processing to remove the residual contaminants from wafer surfaces such as the KOH based processing method discussed herein. Dry chemical processes for silicon etching certainly exist, but these are largely anisotropic etches. XeF₂ processing is the first dry process for isotropic etching of silicon. The reaction is described by equation (2.9) [47].

$$2\text{XeF}_2 + \text{Si} \rightarrow 2\text{Xe} + \text{SiF}_4$$

(2.9)

Today, its primary use is as a fluorinating agent for the etching of silicon as part of the manufacturing of devices. Xenon difluoride is the most stable among all compounds containing Xenon. While it is a halogen and considered to be inert, it is capable of reacting with fluorine form compounds. It forms a white crystalline structure which appears similar to sugar. The basic structure of the XeF₂ molecule is shown in Fig. 2.2.

![Figure 2.2 Basic structure of XeF₂ molecule][75].
Its synthesis requires the reaction of fluorine gas and xenon with a suitable energy source. This energy source can be an electrical charge, radiation such as a UV source or the application of heat and is shown in equation (2.10) [46].

\[ \text{Xe} + \text{F}_2 \rightarrow \text{XeF}_2 \]  

(2.10)

Care must be taken with xenon difluoride, as it is a strong oxidiser and will begin to decompose in the presence of moisture and light. When it begins to decompose, it will slowly break down into minute molecules of HF gas so care must be taken in its handling.

The most important factor is vapour pressure, which is approximately 4 Torr at room temperature. The xenon difluoride will sublimate at pressures above 4 Torr. In the silicon etching system used throughout, the xenon difluoride is contained in a solid source container through which nitrogen carrier gas flows. This carrier gas is saturated by the xenon difluoride as it passes through the material. The saturated carrier gas then flows into the process module where it is introduced to the silicon surface to be etched. The reaction of silicon and xenon difluoride is a multi-stage process. Firstly, the XeF\(_2\) molecule is absorbed into the surface of the silicon where the xenon then dissociates from the fluorine and is then released.

The current wet processing technologies for etching silicon are based on the use of potassium hydroxide (KOH) baths. These processes have a good level of selectivity to other structural and functional materials. Vapour phase etching of silicon must have these same high selectivity properties for the process to be viable in a process fabrication procedure. Xenon difluoride can in small amounts react with other materials. During the initial reaction with silicon, fluorine dissociates from the xenon. Not all SiF\(_4\) will be fully formed and not all F\(^-\) released during the reaction, which will break silicon-to-silicon bonds. Some of these unreacted molecules will find their way to other device surfaces and react if possible. Silicon nitride and silicon dioxide are common materials in many devices as discussed in section 2.2 and design groups require good silicon selectivity capabilities.

The first systems utilised the natural vapour released from the XeF\(_2\) crystals under vacuum, further configurations that are more efficient have since been developed. In
this section, the existing processes, their general reaction mechanisms and primary uses will be discussed as well as the transition to the vapour phase processes.

2.3.1 Wet Process Etch Techniques

In MEMS processing, the etching of silicon is typically carried out in wet etch processing baths. These processes are commonly also anisotropic etches and allow precise structures to be realised. These processes gain their anisotropic behaviour with the help of masking materials on the surface of the silicon layers. Over time, a range of chemicals have been developed for wet etching of silicon. These have come from the specific requirements for the surface finish. Primarily KOH requires a more thorough rinse stage due to the metal contamination by the residual potassium and as such, tetramethyl ammonium hydroxide (TMAH) and ethylene diamine pyrocatechol (EDP) were introduced. These processes are still used and have desirable properties that allow for each of their uses in a process flow for manufacturing.

Another study describes the use of three other wet etching solutions: HNA (HF/Nitric Acid/Acetic Acid), KOH and EDA (ethylenediamine, catechol and hydrazine). The EDA etches the <100> silicon plane with an etch rate of 1.1 µm/min at 100°C in contrast to silicon dioxide at less than 1 nm/min in the same process [47]. Due to the lack of potassium residues, this is ideal for semiconductor manufacturing.

Another of the <100> etchants used was a mixture of KOH with water and propanol. This solution etches the <100> plane about 100 times faster than the <111> plane. Removal of the propanol from this mixture allows the solution to etch the <110> plane approximately 600 times faster than the <111> plane. The understanding of the etch rate differences by plane is associated with the silicon packing densities shown in each plane and is discussed in Chapter 6 of this thesis. The benefit of crystal orientation dependent etching (ODE) processes, is a very fine control in the structures that are fabricated. If a mask and the subsequent open region on the wafer is able to exploit a specific orientation such as described in this work, then fabrication of some structures is made easier. It allows the designers to compensate for the known etch rates in specific planes and design devices more accurately by knowing at which regions the specific planes will intersect and act as an etch stop region. In the most common plane <100>, the measured etch rates have been reported as high as 1.4 µm/min.
The use of TMAH has also been reported in literature [48]. TMAH falls under the quaternary ammonium hydroxide (QAH) group of wet etch solutions. Some work has been carried out on tetraethyl ammonium hydroxide (TEAH) [49]. However the main QAH solution used in modern manufacturing is TMAH. The use of TMAH as another alternative to the KOH process is due to its higher compatibility with MEMS processing with the measured etch rates of up to 1 µm/min in some cases. The etching mechanism is similar to that of the KOH process, but without the residual potassium contamination that follows. While TMAH has been measured to have an etch rate less than both of the KOH and EDP processes at 0.5 µm/min in the <100> plane, the surface roughness of the silicon was negatively impacted by this process. The etch drop may not be the critical concern during process development when there are no further post processing steps required to remove the contamination as is required by a KOH step for example. It was also shown that the selectivity between oxide and silicon films with TMAH was substantial by four orders of magnitude of difference. Like KOH etching, as the concentration was increased, the etch rate decreased. It was also shown to increase as the temperature increased, similar to KOH etching. Silicon nitride was used as the masking material showing a good selectivity. The other process capability shown, similar to the other wet etchants, is the etch preference in specific crystal planes. TMAH etches <100> orientation planes approximately 25 times faster than <111> planes, again allowing for good control for structure design and fabrication.

A review paper has discussed some additional options along side the above-mentioned silicon wet etch solutions [50]. It also provides a brief review of some of the future vapour phase etching techniques for dry etching of silicon. These vapour phase options will be discussed further in this chapter. One option they discuss is the HNA etch solution. The primary reaction mechanism, like KOH and some other wet etch processes, is to oxidise the surface of the silicon such that the silicon is consumed in the formation of the oxide which is then removed by the hydrofluoric acid in the etch solution. It shows high silicon etch rates of up to 20 µm/min in some cases. The acetic acid reduces the dissociation of the nitric acid into less reactive molecules, thus maintaining a sufficiently high oxidation rate for the silicon surface. The full reaction path with silicon is described in equation (2.11) [50].

\[ 18HF + 4HNO_3 + 3Si \rightarrow 3H_2SiF_6 + 4NO + 8H_2O \]  

(2.11)
It has been reported previously that the \( \text{H}_2\text{SiF}_6 \) can further dissociate into HF and SiF\(_4\) thus further catalysing the reaction with any available oxidised surfaces. HNA is also susceptible to a drop in etch rate in doped regions. HNA has the benefit of being one of a very small number of isotropic wet etchants due to the oxidation of the surface and its subsequent removal by the HF etching stage.

For EDP, there is a similar instance to the other anisotropic wet etch processes, a preference to etch in the <100> orientation over the <111> plane with lower etch rates than TMAH of 0.75 µm/min. Like EDP and HNA, it shows a drop in etch rate in the presence of doped regions. The selectivity between the etch rates of the doped and undoped regions are unaffected such that the ratio of selectivity between <100> to <111> is 35:1 in both the doped and undoped regions. It shows similar process behaviours as KOH and TMAH in terms of temperature and concentration.

In summary, the wet etching processes are largely anisotropic etch processes. Solutions are typically preferred for specific silicon etch planes as an anisotropic etchant of silicon. The nature of having to submerge devices and samples in these etch solutions leaves devices open to the problems of stiction as outlined in the motivation for vapour phase HF etching process development. The major limitation in some cases with these wet processes is in fact their behaviours, their orientation dependency does not allow etching in all planes at the same rate. The next steps in this process would be to seek out isotropic etching processes.

2.3.2 Vapour Phase Etching of Silicon by Non-XeF\(_2\) Based Processes

Similar processes to those of the wet processes that provide high levels of anisotropic etching behaviour are the processes based on the plasma systems such as reactive ion etch (RIE) systems. Fluorine has always been an effective method of breaking down materials such as silicon. In [51], the etching of silicon devices was discussed with fluorine dissociated in a down stream plasma system. The process was carried out at low pressures of up to 0.6 Torr. They highlighted an issue specific to vapour phase processes: natively grown oxides on the silicon surface. By the very nature of the wet processes such as KOH and TMAH, the thin film would not inhibit etching as was observed in the vapour phase. The native oxide as described previously is a naturally formed thin oxide layer. The native oxides need to be removed before etching can take place. One common way to overcome this effect is to place the wafers in a buffered HF
(BHF) solution for a few seconds prior to the removal of the native oxide. It is easily removed in an HF bath and the wafers can be rinsed and ready for vapour phase etching. It was observed that the delays by native oxide growth could hinder the initiation of etching by a number of minutes. It was also noted that close to the silicon-oxide interface, the silicon would etch faster as the presumption that the native oxide in this region of the sample was more readily cleared than in a large open area of silicon since the mask would draw reactions towards it. A selectivity of 42:1 between the thermally grown silicon dioxide and the etched single crystal silicon structures was found.

In another study [53], the etching of silicon using the same reaction chamber as previously described was investigated [51, 52]. In this case a mixture of multiple fluorine containing compounds was used, including bromine and chlorine trifluoride (BrF₃, ClF₃), bromine and iodine pentafluoride (BrF₅ and IF₅), as well as nitrogen and bromine trifluoride (NF₃, BF₃) and phosphorous trifluoride and pentafluoride (PF₃ and PF₅). The first group of gasses showed good etching of silicon and a very high level of selectivity towards the oxide films. The latter group of compounds NF₃, BF₃, BrF₅ and IF₅ showed no reaction with oxide layers. It is also noted that these gas reactions leave a much smoother surface finish in comparison to the reaction of silicon with XeF₂ [52].

A method of etching silicon in vapour phase without the use of an RIE process or that of XeF₂ is described [54]. The wafers were placed in an enclosed box, the vapour from a liquid mixture of HF and HNO₃ was used. This solution of liquids acts in a similar fashion to HNA based wet processing but in a vapour phase. It was found that by controlling the mixture and process temperature it can be a suitable means for silicon etching. An alternative mixture of HF vapour with solvents with ozone bubbled through the solution at atmospheric conditions was also described [55]. It shows that many of these vapour phase silicon etching processes attempted to replicate the etching mechanisms of such processes as KOH by generating OH⁻ groups which will react and etch the silicon surface in the vapour phase, thus reducing the side effects observed in wet processes.

**2.3.3 Vapour Phase Etching of Silicon and other Materials by XeF₂**

The early development of the XeF₂ material was aimed at increasing the stability of XeF₂ as XeF₄ was also produced during the formation process, which was known to be explosive when reacting with water in the atmosphere by forming XeO₃. The early
systems for etching with xenon difluoride under vacuum relied on either allowing the vapour to sublimate from the crystals and etch the silicon when the vapour is exposed to the surface, or building up the pressure inside what is referred to as an expansion chamber before being exposed to the wafer to be etched. This chamber allows pressure to be built up to a value of typically 3 Torr before being introduced into the etch environment. The etch chamber is sealed and the gas reaction takes place until either a set time is reached or the XeF₂ is fully consumed at which point, the etching chamber is pumped out with a vacuum pump. This is repeated a number of times and is typically described as a pulsed process. A typical system diagram is shown in Fig. 2.3.

![Diagram of etch system](image)

Figure 2.3 Typical configuration for a pulse process etch system.

The early work to discuss the interaction of xenon difluoride as a means of etching silicon was discussed [57]. It described the etching of electron beam deposited silicon films, typically polycrystalline in structure. The process was run at very low pressure in the region of 14 mTorr at 27°C. In this regime, no surface etch or change could be measured in silicon dioxide, silicon nitride or silicon carbide films. The very low process pressure was suitable for etching silicon readily as the energy required for initiation of silicon etching is lower than that required for etching of these other films. The key factor in controlling the etch selectivity towards these films is in the control of the etch by-products and the intermediate reaction by-products such as unreacted fluorine. The surface etching reaction steps of xenon difluoride with silicon have been described as a multi-stage reaction and involve the following:

**Non-dissociative absorption**
The XeF₂ is absorbed on the surface of the silicon to be etched in a physisorbed layer.
Dissociative absorption
The XeF₂ dissociates into Xe and Fluorine along with the silicon surface

Product formation
Silicon tetrafluoride (SiF₄) is formed at the silicon reaction interface

Product desorption
SiF₄ is released from the silicon surface

An increase in etch rate of silicon films was found with an increase in the process pressure, with etch rates of up to 0.7 µm/min at 14 mTorr. This also defined the selectivity data towards the selected materials. A 5:1 etch ratio of titanium to silicon and 2:1 etch ratio of molybdenum to silicon were obtained.

A further study [53] discussed the same hardware configuration as used in the tests described in [51] with a fluorine etching of silicon by plasma breakdown. This work describes the use of the natural vapour released from xenon difluoride crystals under the vacuum conditions. Unlike the previous work, increased pressures were used for the etching process. The temperature at which the sample was processed was varied. It was found that with increasing sample temperature, the etch rate of silicon begins to drop. This would show that as the temperature increases, the ability for a physisorbed layer to exist is reduced as temperature drives away more of the XeF₂ from the surface thus reducing the absorption and SiF₄ formation which is part of the reaction process. Similar to previously reported work [57], there was no observed etching of oxide films, but this did not rule out a very small etching effect occurring.

Improvements in the pulsed process etching of silicon by etching under higher process pressures inside the expansion chamber and during the etch process itself are described [58]. The samples were etched at pressures up to 0.9 Torr in contrast to the 14 mTorr and this led to a marked increase in the etch rates from 0.7 µm/min to 15 µm/min. The work reported previously [52] was repeated, where the natural vapour from the XeF₂ source was used as the etch material, but consistent results were not obtained. No etch or surface change for aluminium, chrome or titanium nitride films was found although roughening of tungsten films was observed. The work also showed an improvement in selectivity for Ti at 85:1 and Mo at 6:1 as improvements on work reported previously.
[57]. This suggests that as the pressure increases, the silicon is capable of being etched much faster than the respective metal films. It was also shown that the positive photoresist AZ5214 can be used as a successful etch mask as it appears to be inert in the etch process. It was found that the surface roughness increases with increasing pulses or etching cycles. The effects of mask openings with respect to etch rates were studied and the results showed that as the mask openings increase, the etch rates drop.

Integration of the isotropic nature of XeF$_2$ etching with the other anisotropic etch processes was also investigated. The vertical anisotropic etching of silicon trenches by RIE was combined with an isotropic etch process using XeF$_2$, [59]. The high selectivity effects towards SiO$_2$ films were used as a means of protecting the structures during the release phase. Another example described in [60] uses XeF$_2$ as an initial silicon removal step before using an EDP wet etch to produce the exact specific structures based on crystal orientations.

In the same period, similar research was reported [61]. The effects of performing pre-treatments on the silicon surface prior to etching silicon was studied. The results for etch selectivities agree with those in [58], but this work continued the trend of increasing process pressures by working at 1 Torr. The pre-treatment of the samples by heating to 140°C for 12 minutes prior to etch in an attempt to remove any moisture on the silicon surface was studied. It was found that this step helped to improve the horizontal and vertical etch ratios. But this came with the problem of a rougher surface finish however. Another method of compensating the lateral and vertical etch rates has been reported [62], in which large open silicon areas are added to the design to act as the buffers and attract more of the XeF$_2$ away from the main device sites so that the lateral undercut to vertical etch depth could be matched. Having large areas of silicon, 19 times larger than the device to be etched improved etch performance. However, in real terms this would provide a problem for fabrication as the large open areas required on a wafer would reduce the number of active devices on the wafer thus impacting on the cost efficiency of the device itself.

One parameter not frequently described in literature is the effect of etch uniformity using the XeF$_2$ based etching processes. The trenching and loading effects when etching deep silicon layers have been discussed [63]. There is a large inconsistency in the etch rates across the devices when deep trenches of greater than 20 µm are created. This
shows that for smaller mask openings, wide etch windows should be used in order to reduce the effects. A simple etching model to predict these effects was developed [64], but not for the process as a whole. A modified form of the Deal-Grove model as a means to explain some of the behaviours was reported to describe the etching of polysilicon films. This was able to contrast against the samples that had photoresist masks and those with oxide layers as the masks with various openings.

While most of the previous studies stated that the etch of silicon dioxide, silicon nitride and silicon carbide films could not be measured, an etch 12 nm/min was measured for LPCVD silicon nitride films [65]. The etching of PECVD and low temperature oxide films of SiO₂, titanium and tungsten films were also observeable. This was probably due to the availability of more accurate metrology equipment. One family of films with the reported etching behaviour, but without comparable data are germanium (Ge) and silicon germanium (SiGe) based films [65]. The results of these functional materials as fast etching sacrificial layers were reported [66]. It was shown that SiGe alloys etch 1.3 times faster than silicon and Ge films etch twice as fast as silicon thus giving merit to further investigation of germanium as a sacrificial layer.

The previous work in the etching of silicon by fluorine gas was described [51]. A selectivity of 42:1 of silicon to thermally grown oxide films was reported but it was required to place the samples in an HF solution to remove natively grown oxides from the surface. Different apparatus and gas delivery methods for etching silicon with fluorine gas as well as a comparison to XeF₂ have been described [68]. This was in relation to trying to release a MEMS fuel processor. The interesting difference is the lack of plasma in dissociating the fluorine and allowing the complete F₂ molecules to etch and interact with the silicon directly in a similar reaction mechanism as defined previously for XeF₂ with silicon. The N₂ gas was used as a means of diluting the total gas mix to around 25% fluoroine gas. The samples were placed under vacuum at 5 mTorr and were heated to 100°C for 1 hour prior to etching taking place at near ambient atmosphere and temperature. The XeF₂ etching work was carried out in a pulsed etching system as already described, at 3 Torr and ambient temperature for 2-minute pulses. While fluoroine etching showed high levels of inert behaviour towards platinum, nickel, aluminium and tantalum but some etching towards oxide films, the XeF₂ etch was less selective towards some of these films. The etch rate was 30 times slower with the F₂ gas and caused a much rougher surface however, both these results would not be ideal in a
full fabrication run. It was also found that fluorine did not etch silicon nitride films but roughened the surface while with XeF$_2$, a selectivity of 200:1 for silicon was measured against nitride.

As has been highlighted previously, one of the largest benefits from moving away from wet silicon etchants was the reduction in stiction of the released devices. The aim is two-fold: to increase yield in the current generation designs, but also to allow for the fabrication of next generation devices with much smaller dimensions where a wet etch process would fail. This outcome is observed when describing a micro-bridge design [69]. While there is no need to use vapour phase etching for such large device dimensions, on the other hand, it is necessary move away from wet processing for future designs with reduced feature sizes.

Recently, work on pulse processing at higher process pressures has been reported [70]. It was reported to be operating at pressures of up to 5.5 Torr with an improvement in the etch rates from 0.08 µm/min at pressures below 1 Torr to 1.9 µm/min. This agrees with a number of studies regarding the effects of aperture size and describes the effects of pulse processing while etching in the higher pressure regimes. An aluminium mask patterned onto the single crystal silicon wafer was used due to the non-reactive properties of aluminium with XeF$_2$. It was found that the vertical etch depth was approximately 70% of the lateral etch depth. This ratio has not been reported previously; so it may be specific to this system and is certainly worth investigation on other systems at even higher etch depths. The lateral etch rates are higher as the XeF$_2$ molecules underneath the structures are retained in the proximity of silicon for longer than in the open areas and as such, increasing the probability of molecular interaction by absorption which leads to the increase in the etch rate. It was believed that the interaction is random but higher as the increase in reaction probability is increased. A rough surface on the silicon was observed due to the increasing pressure and process time. A recent interest with XeF$_2$ in relation to the surface roughness has been to investigate the viability of using XeF$_2$ as a means of generating porous silicon films for solar panel applications. A pulsed process has been used to generate rough surfaces and assessed for the quality of porosity [71]. The previous attempts used HF vapour with ethanol as discussed in previous sections as a means of etching silicon. The interest in XeF$_2$ is to avoid stiction and damage to the sensitive layers which would be damaged in the presence of HF.
In the previous literature, there have been numerous studies which show that the level of etching of silicon dioxide films is small and the selectivity to be substantial. Many of these studies however, have worked in the regimes where the etch rates are very low and in the very low-pressure regimes where silicon will be more preferentially etched over an oxide film. The recently published work on silicon dioxide etching in the XeF$_2$ pulsed processing regimes [72] shows no oxide etching when the film is a bare wafer without any pattern or design. On the other hand, when the oxide is close to an open area of the exposed silicon, it was found that there is an interaction at the interface region of oxide and silicon causing an etching effect. The source of the etching effect was possibly coming from a formation of high energy fluorine based molecules released as part of the desorption of by-products of XeF$_2$ reactions with silicon. The incomplete reaction to form SiF$_4$ molecules such as SiF$_2$ and SiF$_3$ is considered to be a strong component in the etching of oxide films on silicon. These etching processes are again in a pulsed process system at pressures between 0.1 to 4 Torr at ambient temperatures. This work was limited by the inability of the pulse process systems to run processes at pressures above 4 Torr. Whereas the absorption of XeF$_2$ and the desorption of fluorine from the silicon surface may in fact have a further intermediate stage, whereby XeF is released from the Si surface first and can either subsequently be absorbed again by the silicon material or fully react. It was noted that with the thicker oxide films of 180 nm and even on an extended etch process of up to 36 hours, no etch on the oxide surface was observed. On the thinner oxides of 7.3 nm, the small nanometre defects on the surface can allow XeF$_2$ to diffuse into the substrate beneath the oxide due to the low thickness of the oxide and begin to form pinholes in the oxide. The interaction mechanism is similar to the reaction at the exposed regions of silicon and the oxide interfaces: subsequent etching of the silicon beneath the oxide layer generates SiF$_4$ and XeF as already described during the etch process. The etch process is able to react with the dissociated XeF and further etch the silicon or fluorinate the oxide layer and allow for greater etching of the oxide and silicon layers. This highlights a need to ensure designs to have an adequate thickness of the oxide layer.

One of the more common alternatives to silicon when it comes to sacrificial material that can be etched in a vapour system is molybdenum. The chemical reaction mechanism differs from the reaction between XeF$_2$ and silicon as described in [73]. While it has been discussed that the reaction of XeF$_2$ with silicon requires an initial absorption of the XeF$_2$ to initiate the reaction and sustain the generation of the F
species, the reaction with Mo is a direct surface reaction as described in equation (2.12) [73].

\[
\text{Mo} + 3\text{XeF}_2 \rightarrow \text{MoF}_6 + 3\text{Xe} \quad (2.12)
\]

The etching process was carried out at up to 1.2 Torr in comparable etching tests. It was found that the etch rate of Mo takes longer to stabilise than the reaction with silicon, but the etching process appears to be more efficient in the use of XeF\(_2\) than silicon. It was discussed that as in the silicon etching progresses, more and more of the XeF\(_2\) vapour is not used and this creates an excess of F which eventually reacts and generates fully reacted SiF\(_4\) by-product. Similar to the previous work in describing oxide etching in silicon [72], the intermediate etch step of XeF molecules either further reacts at the surface of the silicon or react away from the etch site. This is a dynamic behaviour of etching and fluorosilyl generation which ultimately generates the SiF\(_4\) molecules as expected. In terms of the temperature effect, the difference between Mo and Si etching is negligible with temperature.

2.3.4 Summary

Based on the current processing methods for silicon etching, there is a case for understanding the benefits of etching in vapour phase processes. While wet processing still offers a very useful platform for many designs, the move to the MEMS devices with smaller dimensions will make the option less viable. Effective dry release technologies will ultimately be required for the final release of the functional devices. It has been shown that the use of using wet processes such as KOH, EDP and TMAH are useful where specific features are required. However, where fast etching rates and isotropic etch profiles are required, these etch solutions are no longer suitable.

The move to vapour phase fluorine based etching technologies also appear incredibly useful. The only real drawback observed with these plasma based etching technologies is the surface modification caused by the plasma species. The XeF\(_2\) based etching technology appears to offer the speed and flexibility of the wet etching processes while avoiding the surface modification associated with the plasma based methods. The majority of vapour phase XeF\(_2\) etching is based on pulse processing techniques. This configuration imposes certain limitations such as the natural vapour pressure of XeF\(_2\) as well as the need to use pulses as the expansion chamber can only hold a finite amount of
XeF$_2$ vapour. In this thesis work, an etch method based on a commercially available continuous flow system by memsstar is characterised for vapour phase XeF$_2$ etching of silicon, oxide, nitride and other materials and will be described in Chapter 6.
Chapter 3 Fabrication and Characterisation Methods

3.1 Introduction
The creation of structures to be used for the etching studies in Chapter 4-6 was performed at the Scottish Microelectronics Centre (SMC), based at Edinburgh University. The facility is able to produce a large variety of thin films used in silicon integrated circuits and MEMS devices since it is a small-scale production facility. Three main thin films are investigated throughout this thesis: silicon nitride ($\text{Si}_3\text{N}_4$), silicon dioxide ($\text{SiO}_2$), and both single crystal and polycrystalline silicon materials. The films are commonly used for various uses in industry ranging from passivation layers in active devices to dielectric materials for RF devices. Crucially though, these films are also used as masks and sacrificial layers for device fabrication depending on the requirements. This means that the ability to understand how they are affected in an etch process is vital when designing devices. A range of test structures and samples were generated in both basic thin film layers and stacked layers to help better understand the behavioural characteristics of these materials. This chapter discusses the fabrication of these structures and the available processes for each film.

Selected metal films are also deposited. While nitride, oxide and silicon based films are the fundamental structural layers for many of today’s devices, etch process must also be compatible with the functional materials of the devices. Many of these are metals, which must retain their high quality characteristics after the etching process. Some layers require “stacks”: implying that a number of layers are used since certain materials cannot simply adhere to the surface of the base layer. In the case of tungsten deposition as an example, the stack typically consists of tungsten deposited on titanium nitride, titanium and silicon dioxide, as each layer requires a suitable adhesion layer upon which to build. Thus, considering the fabrication of a device, deposition of many different materials may be necessary.

3.2 Material Growth and Deposition
The deposition methods for structural and functional layers in MEMS and semiconductor fabrication are established and characterised methods within the manufacturing industries. Due to the range of required films, a number of different fabrication techniques are necessary. An overview of the common deposition techniques for MEMS and semiconductor manufacturing are discussed in this chapter. The
chemical vapour deposition (CVD) method is a standard means by which both oxide and nitride films are deposited. As will be shown, there are many ways in which these depositions can be performed. Most commonly wafers are exposed to a reactant gas under specific process conditions that will lead to film formation. The process and hardware configurations are described in this chapter.

3.2.1 Single Crystal Silicon Growth and Crystal Planes

Silicon is the most important material in microelectronics and MEMS. The growth of high-purity silicon for the semiconductor industry is most easily performed using the Czochralski (CZ) method. It is also the most cost effective method for the production of high volumes of silicon wafers. First, silicate materials are collected and converted to high purity silicon gasses. These are typically either silicon tetrachloride (SiCl₄) or trichlorosilane, (SiHCl₃). These gasses are then converted into single crystal and polycrystalline ingots with a reaction involving hydrogen gas as described in equation (3.1) [85].

\[
\text{SiHCl}_3 \text{(gas)} + \text{H}_2 \text{(gas)} \rightarrow \text{Si (solid)} + 3\text{HCl (gas)}
\]  

At this stage, these polycrystalline silicon ingots are placed into a quartz crucible and melted at 1415°C. Dopants are added if required and are selected to make the silicon material p-type or n-type. A seed crystal which has the same crystal orientation as is required for the final single crystal ingot is dipped into the melt and slowly pulled out. The molten silicon will orientate itself in the crystal plane of the seed. There are multiple control systems in place to ensure that dopant uniformity along with crystal quality and other material properties are consistent throughout the crystal growth process.

![Diagram of the CZ method for single crystal silicon growth](image)

Figure 3.1 Diagram of the CZ method for single crystal silicon growth [79].

The unit cell of single crystal silicon is shown in Fig. 3.2. The crystal plane of the silicon ingot seed dictates the crystal orientation of the resulting silicon boule. It is a highly organised and rigid structure and has the same lattice as diamond.
While the final formed silicon boule will be a single crystalline structure, its crystal orientation can dictate many properties such as atom count and binding energies as well as electrical properties. These properties have been used to develop specific silicon devices by utilising orientation dependent etches (ODE), to create specialised designs and achieve performance requirements that may not be possible in other regimes [76]. Crystal directions and planes are described using the miller indices based system with basic definitions shown in Figs. 3.3 and 3.4. The most common crystal planes used in the semiconductor industry are the <100> and <111> planes.

Figure 3.2 Structure of single crystal silicon [80].

Figure 3.3 Diagram of basic Miller indices directionality [81].
3.2.2 Polysilicon and Amorphous Silicon

Manufacturing of semiconductor grade silicon for wafers is a very controlled process from the orientation of the crystal plane to the level of dopants within the silicon ingot itself. Multiple small crystals with different crystal orientations form polysilicon or polycrystalline silicon. While polysilicon ingots are melted down in the early stages of the CZ method, there are other applications where silicon is used as an active device layer or mask. In this case polysilicon or amorphous silicon can be deposited during the manufacture of a device. The deposition techniques for these films will be discussed later in this chapter.

Amorphous silicon by its very name describes its lack of crystalline state. The arrangement of silicon atoms in the material is completely random. Untreated amorphous silicon can be prone to electric defects that may not be suitable for some devices. Passivation to reduce these defects takes place in a hydrogen environment and allows for better consistency in electrical behaviour. A major positive effect in using amorphous silicon is that the deposition process can be carried out at 75°C which allows deposition on many materials that may not be compatible with the high temperature conditions in polysilicon deposition thus allowing for a greater scope of devices that could potentially be developed.

Polysilicon deposition occurs in a low-pressure chemical vapour deposition (LPCVD) tube furnace. The basic arrangement is common for many types of deposition processes. There are differences in the reactant gas, temperature and pressure controls depending on the material required. A tube furnace design with a three-stage temperature control is used which maintains a nitrogen atmosphere by both a nitrogen flow inside the reaction tube and at the entrance to the furnace. Although polysilicon deposition is an LPCVD,
process, additional process pressure controls are in place such that the deposition process can take place at a low pressure of 550 mTorr. The reaction gas used for polysilicon deposition is silane (SiH₄). The silane decomposes into silicon to deposit on the wafer surface while the hydrogen by-product is readily removed from the reaction by a vacuum pump. The reaction process is given by equation (3.2) [86].

\[ \text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \quad (3.2) \]

This reaction is a very simple yet effective way of growing polysilicon films on surfaces such as silicon dioxide or silicon nitride which may be acting as a passivation or etch stop layer on top of electronic circuitry.

### 3.2.3 Silicon Dioxide

Silicon dioxide (SiO₂) is a commonly grown functional and structural layer within the semiconductor and MEMS industry. Silicon dioxide is a well-established material with many different applications depending on its structure and purity. The oxide used in semiconductor and MEMS is of a much purer quality than the glass for windows. The reason oxide is so useful among the semiconductor and MEMS industries is because of the properties that arise from the natural material properties of the silicon and the natural dielectric properties of the oxide. The common applications of the oxide films are as follows [87]:

**Passivation layers**

Due to the high density of silicon dioxide films, the film can be a physical barrier resistant to particle build up and also as a chemical barrier due to its inertness.

**Surface, device and inter-layer dielectrics**

As silicon dioxide layers behave as dielectric layers, they can either be used as insulation layers or allow charge to flow in a device. If the layer is thick enough, charge building between a metal layer and the silicon can be avoided.

**Dopant barriers**

The movement of dopants within oxide layers is very slow in comparison to exposed bare silicon. Thus oxide can act as protection to specific areas of a wafer in a process
that should avoid doping. This is ideal for doping p and n regions as part of the transistor fabrication process.

Two types of silicon dioxide films were used in the fabrication of samples in the thesis work, these being thermal oxidation and plasma enhanced chemical vapour deposition (PECVD). Thermal oxide is a denser and more stable film. It can act as a high quality mask in the etching processes or act as a passivation layer that protects the complimentary metal oxide semiconductor (CMOS) structures such as interconnects for an active device. The ability to accurately control thickness allows accurate deposition of silicon dioxide films.

For the fabrication of test structures during this work, silicon dioxide was used either as a sacrificial etch layer for HF etching, or as a masking layer for sacrificial etching of silicon and polysilicon in XeF₂ etching processes. The two main methods of deposition for silicon dioxide films available are thermal oxidation and PECVD deposition, which are described in this chapter.

### 3.2.3.1 Thermal oxidation

Thermal oxidation is the most commonly used method for deposition of silicon dioxide films. While thermal oxidation can occur at room temperature to form what is known as a “native” oxide, it is an extremely slow process. The application of higher temperatures in the region of 1200°C increases growth rates to a higher level in terms of deposition time for production. Thermal oxidation of silicon has a number of process methods: by placing the wafer in a horizontal tube furnace at high temperature with one of either pure oxygen as described in equation (3.3), dry steam (3.4) or with vaporised water (3.5) [87]. While the growth of silicon dioxide with dry oxygen in (3.3) might appear to be the way to deposit films with high purity, it is a very slow process. The use of dry steam by creating vapour phase H₂O using hydrogen and oxygen at high temperatures (3.4) or directly supplying vaporised water (3.5) greatly reduces the time to reach a useful oxide thickness due to the dissociation of H₂O into hydrogen ions (H⁺) and hydroxyl (OH⁻) groups. There is a small difference in the film quality between the processes of equations (3.4) and (3.5) and as a trade-off for the slightly longer time for film growth using dry steam processing of equation (3.4) than the vaporised water approach in equation (3.5).
Pure growth process - $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2$ \hspace{1cm} (3.3)

Dry steam process - $\text{Si} + \text{O}_2 + \text{H}_2 \rightarrow \text{SiO}_2 + \text{H}_2$ \hspace{1cm} (3.4)

“Wet” process - $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + \text{H}_2$ \hspace{1cm} (3.5)

The oxidation method in equation (3.4) is the most effective process for film growth when considering time versus quality. Care should be taken when setting up the gas flows for the process however, if the hydrogen content of the gas mixture is substantially above 4% it can cause an explosion. Silicon dioxide growth is in two stages: a linear stage followed by the parabolic (diffusion limited) stage. As the names suggest, the initial stage of oxide growth is a linear process whereby oxide grows linearly with time due to the ease of access to the silicon surface. Once an initial layer of oxide has been grown to 1100 to 1200 angstroms (Å) or 110 nm to 120 nm, the deposition process changes from a linearly controlled reaction to a parabolic growth (diffusion limited) reaction, which is limited by the diffusion of OH$^-$ molecules through the existing silicon dioxide layer and forms new silicon dioxide. This is done by reacting with the silicon under the silicon dioxide layer that has grown in the linear growth stage. The thicker the silicon dioxide film required, the slower the process becomes as the hydroxyl groups have to pass through a greater thickness of silicon dioxide.

These silicon dioxide growth stages have been derived into standardised equations for growth of a silicon dioxide film on a silicon surface Deal & Grove [87]. The silicon dioxide growth process is described by equations (3.6) and (3.7) for the linear growth and parabolic growth of silicon dioxide films on a silicon wafer respectively, [87].

$$\text{Linear growth regime: } X = \frac{B}{A} t \hspace{1cm} (3.6)$$

$$\text{Parabolic (diffusion) regime: } X = \sqrt{B} t \hspace{1cm} (3.7)$$

where $X$ is the silicon dioxide thickness, $B$ is the parabolic rate constant, $\frac{B}{A}$ is the linear rate constant and $t$ is the oxidation time. Rearranging the parabolic regime
equation shows the parabolic growth relationship for silicon dioxide films with a thickness greater than 1200 Å, or 120 nm.

The hydrogen shown in equations (3.4) and (3.5) initially exists within the oxide film and is due to the reaction taking place below the surface of the linearly grown silicon dioxide, but is driven out by the high temperature of the growth process in the tube furnace. This means that there essentially exists a mixture of two oxide layers in the initial growth stages: the linearly created oxide film and the diffusion growth oxide that contains higher hydrogen content within. Initial silicon wafer processing within the SMC was carried out on the wafers with <100> orientation. The <100> wafers are the most common wafers used in manufacturing. For the <111> orientation wafers, the deposition rate would have been quicker due to the higher levels of silicon atoms available in the <111> crystal plane than <100> plane. This consideration is also applicable in silicon etching as the <111> plane etches faster than <100> plane due to higher silicon atom density in the <111> plane.

Silicon dioxide formation is described as being a growth process. Silicon is physically consumed and silicon dioxide is produced. For every 1 micron of oxide formed, approximately half of this thickness was originally the silicon wafer. The silicon dioxide films formed in a PECVD reaction are from direct deposition. This is a distinction and explains the reason that thermal oxidation processes are much slower in comparison to the PECVD technique. The horizontal tube furnace configuration is the most typical industry example of thermal oxidation equipment used to provide high purity film growth and deposition in industry.

![Diagram of a thermal oxidation furnace.](image-url)
Figure 3.5 shows the horizontal tube furnace configuration with a quartz tube, temperature controlled zones and a gas inlet at the end of the tube. The wafers are placed on a quartz boat. This allows a full cassette of 25 silicon wafers to be placed vertically into the furnace for film growth. The temperature-controlled zones allow a consistent temperature to be maintained throughout the furnace. The heating is provided by copper coils and is split into 3 sections, each with its own temperature controller. The tube including the heater then sits inside an outer layer whose purpose is to remove excess heat from one area of the tube and therefore provide a more consistent heat distribution across the tubes’ length. The furnace when in an idle condition, is maintained at a temperature of 650°C. This is because to heat up from room temperature to a required value takes time, especially to stabilise at such temperatures. This means that when placing wafers into the furnace, there is already a high temperature environment where inserting and removing the wafers must be done with care. Inserting or removing the wafers into the furnace too quickly can cause warping of the wafers. This is why a loading and pull rate of 1 inch/min is used for wafers in a horizontal tube furnace.

The wafers must first be cleaned prior to any deposition or growth process to ensure high quality films and also high uniformities across the wafer. Micron sized particles can cause severe damage even at this early stage by producing surface roughness, thin regions and short points, where the film could be thin enough to electrically short any subsequent CMOS design through the deposited film. After cleaning, the wafers are then placed onto a 25 wafer quartz boat and placed into the furnace such that the wafers sit directly in the centre of the 3-zone temperature controlled furnace. After the deposition of the oxide layer, it can be patterned as a mask layer or as a functional layer for deposition of other layers depending on the requirements.

3.2.3.2 Low Pressure Chemical Vapour Deposition (LPCVD)
LPCVD systems were developed as the requirements for film deposition techniques evolved and the reduction of deposition costs became an important factor. Atmospheric pressure deposition systems are thoroughly understood and very flexible for different film deposition processes. The cost of reactant gas used are extremely high as well as the high process temperatures that are required. The pressure for the LPCVD deposition occurs in the region of 0.1 to 1.0 Torr. The added benefit of running a system in a low-pressure regime is increased repeatability of critical factors such as uniformity. This
happens by increasing the mean-free path of the reactant molecules. The mean-free path is defined as the average distance a molecule will travel before interaction with another object. An increase in the mean free path by lowering pressure greatly improves the repeatability of wafer-to-wafer uniformity as the collisions between molecules during the process are reduced greatly. Another benefit of low pressure deposition is that a low process temperature can be used. Lower temperatures are crucial in the fabrication of multi-layer devices in both the semiconductor and MEMS industries as the lower temperatures avoid metal reflow during the deposition of other functional films and layers. This is a benefit of both the LPCVD and PECVD processes as a metal reflow effect could cause inter-layer contamination and alloying of materials thus causing device failure.

3.2.3.3 Plasma Enhanced Chemical Vapour Deposition (PECVD)
When silicon dioxide and silicon nitride layers were deposited in the early period of semiconductor processing, the primary option was the furnace based high temperature solution at temperatures as high as 1200°C. This is not ideal for deposition on top of existing films. As described previously, the existing layers may be damaged due to the deposition temperature being higher than the melting point of existing layers. The PECVD method allows for thin films to be deposited onto existing layers at reduced process temperatures in the region of 300°C. This lower temperature similar to the LPCVD process is more acceptable for deposition of a thin film, where higher deposition temperatures can cause problems in the metal layers such as melting or alloying. Additionally, the lower temperatures avoid inducing stress on these metal films which could cause them to delaminate from the device surface. The PECVD reaction chamber as shown in Fig. 3.6 is a typical parallel plate configuration where the silicon wafer is placed on a pedestal. An RF signal is generated across the upper plate and lower plate on which the wafer is to have the film deposited. Plasma is generated inside the chamber using RF charge. This plasma breaks down the reaction gasses and the deposition occurs at the surface of the wafer.
The pedestal, which also acts as the counter electrode, is temperature controlled in the region of 250°C to 450°C. This low temperature capability over LPCVD processing makes PECVD very beneficial in fabrication of multi-layer devices as films can be deposited over metals such as aluminium. Like LPCVD, due to the lower deposition temperatures, PECVD films tend to be less dense while maintaining a comparably high uniformity. A PECVD process can deposit both silicon dioxide and silicon nitride films depending on the process gasses used. The system used at the SMC is shown in Fig. 3.7.
3.2.3.1 PECVD Silicon Dioxide
Deposition of silicon dioxide films in a PECVD system will typically use silane as its silicon source as well as nitrous oxide, which acts as the oxygen source. PECVD deposition systems allow for deposition of oxide films on materials that would otherwise not stand up to the temperature required for thermal oxidation processes. PECVD oxide films in comparison to thermally grown oxide films are less dense due to the lower processing temperature required. In the case of polysilicon films, PECVD oxide can be deposited on the surface to act as a masking layer. Growing thermal oxides on polysilicon would cause stress in the film and densification of the film, which would lead to slower etch rates than two distinct layers of mask and sacrificial materials.

3.2.4 Silicon Nitride Deposition
Silicon nitride, Si$_3$N$_4$, is commonly used an alternative option for silicon dioxide due to many of the described properties it has as a thin film. It is a very hard film, resistant to moisture and due to its high dielectric constant, is a great material for use in devices requiring a dielectric layer that does not oxidise. The most common uses for silicon nitride are:

**Hard masks for photolithography**
Due to the hardness of the silicon nitride, it is possible to use this as a mask for building structures. The uses range from allowing selective RIE etching to the patterning and growth of oxide on silicon substrates such as the local oxidation of silicon (LOCOS) process which has been used in industry to grow sections of oxide on a wafer while keeping the rest of it free from oxidation by protecting these regions with a mask.

**Passivation layers**
In many devices, passivation layers are applied as a means to isolate the surface from any atmospheric effects such as ambient moisture or even as scratch protectors. The ability for silicon nitride to do this over other materials is due to the previously described characteristic of being a very hard material with high resistance to moisture.

**High temperature resistant layers**
This property is a significant benefit for many devices that are to be used in high temperature device (engine sensors, fire sensors etc.). The common deposition techniques for silicon nitride use high temperature and are usually acceptable for the
materials on which the silicon nitride is deposited. However, this can cause device failure in the worst case scenario but commonly can give lower device yields due to the reflowing of metal materials leading to alloying.

3.2.4.1 LPCVD & PECVD Silicon Nitride Processing
Low-pressure deposition of silicon nitride takes place in a tube furnace similar to the horizontal tube furnace used for silicon dioxide but the process itself as inferred by the name takes place in a low-pressure environment. It also uses a tube furnace with multiple temperature controls as shown in Fig. 3.5. Typically, silane gas (SiH₄) and ammonia gas (NH₃) are used for silicon nitride deposition, but in some cases, dichlorosilane (SiCl₂H₂) along with ammonium chloride (NH₄Cl), hydrogen and hydrogen chloride (HCl) gas can also be used for deposition.

This requires the addition of a vacuum pump to reduce the pressure, which also has additional gas inlets at the entrance to the furnace. These inlets provide a constant stream of nitrogen gas throughout the chamber during the idle condition. The nitrogen flowing both through the chamber and at the opening of the chamber generates a nitrogen atmosphere that stops the quartz tube reaction with atmospheric gasses. Processing at low-pressure, the need to periodically clean it becomes less, which in turn increases the life cycle of the tube furnace. The standard reaction in an LPCVD process to form silicon nitride requires ammonia (NH₃) and dichlorosilane (SiCl₂H₂) process gasses in the reaction described in equation (3.8) [88].

\[
3\text{SiCl}_2\text{H}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{H}_2 + 6\text{HCl} \tag{3.8}
\]

The reaction produces the silicon nitride required but also hydrogen and HCl gases. The process pump attached to the reaction furnace easily removes both of these additional reaction by-products. The silicon nitride films made by this method are some of the densest materials used in industry for passivation and protection of devices.

3.2.5 Polysilicon Deposition
Polysilicon deposition is performed in an LPCVD process as outlined for silicon nitride films. The standard process is again at 550 mTorr. The process conditions required are described in Chapter 6.
3.3 Photolithography

Once the initial layer deposition process has been completed, photolithography is the next stage of the fabrication process for patterning. Photolithography is a process used within the semiconductor industry to allow the patterning and modification of existing structures from deposited films or to create masked areas allowing for the addition or removal of materials at specific sites. Photoresists are available in two common types: positive and negative. These titles refer to the type of mask required for exposure to a UV source. Positive photoresists undergo photo degradation where the exposed areas begin to break down. The material can then be removed with the aid of a development solution leaving behind a photoresist pattern. Negative photoresists undergo a polymerisation reaction and begin to cross-link under the UV radiation. The exposed areas in this case can be washed away in a development solution. Spin coating requires that prior to processing, the wafers for coating are prepared with an adhesion promoter. Hexamethyldisilazane (HMDS), is used as the wafer primer and wafers are placed in a sealed box for ten minutes to ensure the HMDS vapour has adequately coated the wafer surface. This aids the photoresist adhesion to the surface of the wafer and as such, helps improve the uniformity of the coating across the wafer. A basic process flow is described in Fig. 3.8. The silicon dioxide layer was primed in an HMDS for ten minutes. The photoresist layer is then deposited on the silicon dioxide layer by spin coating and is exposed to UV light through a mask. Finally the photoresist layer is developed to obtain a patterned photoresist mask on the wafer surface.

![Diagram of photoresist deposition, exposure and development.](image)

All photoresists under exposure to UV light undergo a chemical modification. The change as explained previously is dependent on the resist material, however all resists need exposure to a UV light source. The exposure time is dependent on the resists used,
the type of exposure, whether that is an unfiltered UV source or an i-line (365 nm) filtered UV light depending on the UV response of the material. The exposure time can be calculated from the equation (3.9) [89].

\[
time(s) = \frac{\text{Exposure Dose (mJ/cm}^2\text{)}}{\text{Radiance (mW/cm}^2\text{)}}
\]  

(3.9)

In patterning the SPR350 positive photoresist in the SMC, an exposure time of 10 seconds was required with an unfiltered UV light source.

One problem in patterning photoresists on highly reflective surfaces is the effect of reflected exposure of UV light from the material surface. This reflection leads to over exposure of the resist. In Fig. 3.9, reflected UV (blue) comes from the grey metal layer to expose the red resist layer and reflects the UV into regions that are unexposed by the masking layer. This leads to development issues whereby the whole resist layer can be developed off the wafer. Exposure times must be substantially reduced to avoid such over exposure and therefore ruining of the resist layer.

![Figure 3.9 Example of accidental exposure by reflection.](image)

3.4 Test Structure Fabrication

To understand the etching behaviours of both vapour phase HF and XeF₂ based etching processes, test structures were fabricated to allow analysis of etch rates and selectivities. The initial work was based on blanket films to investigate selectivity values. The simple samples were used for developing a behavioural understanding of the etch process. Patterned structures were created in Chapter 6 to study the undercut performance and selectivity between selected materials. These samples also more closely relate to semiconductor and MEMS devices by having the layers deposited onto each other than
simply assessing basic blanket films. Both of these methods are viable means of analysis; blanket films can provide a wealth of information due to their simplicity, while advanced behaviours can only be discerned using more complex structures.

3.4.1 Blanket Film Experimental Samples

The silicon dioxide and silicon nitride samples were deposited using the processes shown in Tables 3.1 and 3.2. The films were low frequency plasma enhanced chemical vapour deposition (PECVD) layers. These were deposited using the STS multiplex CVD system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ Flow (sccm)</td>
<td>12</td>
</tr>
<tr>
<td>N₂ Flow (sccm)</td>
<td>392</td>
</tr>
<tr>
<td>N₂O Flow (sccm)</td>
<td>1420</td>
</tr>
<tr>
<td>Pedestal Temperature (°C)</td>
<td>350</td>
</tr>
<tr>
<td>Showerhead Temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>Process Pressure (mTorr)</td>
<td>550</td>
</tr>
<tr>
<td>Process Power (Watts)</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3.1 Process parameters for PECVD silicon dioxide deposition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ Flow (sccm)</td>
<td>40</td>
</tr>
<tr>
<td>N₂ (sccm)</td>
<td>1960</td>
</tr>
<tr>
<td>NH₃ (sccm)</td>
<td>20</td>
</tr>
<tr>
<td>Pedestal Temperature (°C)</td>
<td>350</td>
</tr>
<tr>
<td>Showerhead Temperature (°C)</td>
<td>250</td>
</tr>
<tr>
<td>Process Pressure (mTorr)</td>
<td>550</td>
</tr>
<tr>
<td>Process Power (Watts)</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3.2 Process parameters for PECVD silicon nitride deposition.

3.4.2 Patterned Samples

While the thin film samples are very effective at building a basic understanding of the etching behaviours in silicon dioxide, silicon nitride and polysilicon materials, they are obviously not an exact comparison to actual devices. Structured samples were prepared for the work in Chapter 6 for studying the undercut etching behaviours. The samples
have the materials under etching in close proximity and patterned to expose all the layers that are under investigation.

3.4.2.1 Mask Design

Test structures were designed that could be made for analysis of at least two material layers to represent a more real-world example of the etch process. The structures are required for measuring the amount of sacrificial material etched as well as the amount of material of the mask layer that may be removed during the etching process.

The patterned structures were made for investigation of etching behaviours. It was expected that by placing the access points across the wafer, different measurements and more understanding could be attained for behaviours such as uniformity, which is critical for wafer scale fabrication of devices. A chrome-on-glass photolithography mask was designed for this purpose that would allow the fabrication of a sacrificial layer covered by a masking layer with open areas that act as access points for reactant gasses. The mask can be used to fabricate the etch windows for either the resist itself or would allow the patterning of the underlying layers such as oxide or nitride to provide access for the process gas to enter and react with the sacrificial sites. The design would also allow for assessment of selectivity between films and uniformity, by providing a measurement of etch evenness across the wafer. Fig 3.10 shows the mask design. It is a 7” diameter mask intended for use on 6” wafers. It consists of 3x3 arrays of 100x100 µm squares. The separation between each square is 100 µm and each array is 1 mm apart.

The wafers fabricated for testing are used in the XeF₂ etching process and will have polysilicon sacrificial layers for etching. This allows oxide or nitride, which are very commonly built onto silicon layers in MEMS devices to be used and investigated under etch conditions. The mask defined herein was used in a fabrication process requiring multiple steps. The first test structures were fabricated to investigate the effects on patterned films using polycrystalline silicon and single crystal silicon as the sacrificial options with photoresist masking layers. Later designs replaced the photoresist layer with PECVD silicon dioxide and silicon nitride layers. The change in material added the requirement to also etch through the oxide or nitride mask by the reactive ion etching (RIE) method. Table 3.3 summarises the options for the sample designs to be used for this work.
Figure 3.10 Mask design, (a) at full size and (b) a magnified region.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Sacrificial Material</th>
<th>Masking Layer Options</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂</td>
<td>Single Crystal Silicon, Poly-Silicon</td>
<td>Photoresist, SiO₂, Si₃N₄, Al, Cu, Cr</td>
</tr>
<tr>
<td>HF</td>
<td>Silicon Dioxide:</td>
<td>Si₃N₄, Al, Cu, Cr</td>
</tr>
<tr>
<td></td>
<td>- Thermally Grown</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- PECVD Oxide</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.3 Mask Layer options based on choice of etchant.

3.4.2.2 Sample preparation

The sacrificial layers typically have a patterned masking layer to allow for better understanding of etching behaviours such as undercut etching rates. There are a number of configurations depending on the etching process. In subsequent chapters, the full
sample descriptions will be given. Here, the outline of basic sample preparation for XeF₂ and HF test samples are provided.

Wafer preparation is crucial in the deposition of photoresist as any contaminants from the environment can cause defects in the photoresist and cause defects in the final structures. Prime wafers are new and unused and are rinsed for 1 minute in a 10:1 HF bath, the HF deck is shown in Fig. 3.11. These wafers can then be rinsed and dried in the Marangoni system that uses alcohol rinse processes and drying with warm nitrogen gas to ensure a clean surface, as shown in Fig. 3.12.

Figure 3.11 HF rinsing decks.

After the wafers have been cleaned, a protection substrate layer may be required. In the case of HF etching, silicon is perfectly acceptable as a substrate as this does not react with the HF etching regimes under investigation. For polysilicon films to be etched in XeF₂, an initial thermally grown oxide film is required where polysilicon is to be deposited as XeF₂ has a very low etch rate to thermally grown oxide films. An oxide layer of approximately 100 nm was grown on <100> wafers. A wet oxidation deposition process as described in equation (3.4) was used.
The process parameters are described in Table 3.4. With a process time of 18 minutes, silicon dioxide layers of 100 nm and typical film uniformity of better than 1% are possible. Deposition of the LPCVD silicon nitride film is described in Table 3.5. A process time of 4 hours results in a film of thickness 1 µm. Once the wafers have been removed from the furnace, they are ready for the next steps in the process flow, for example the deposition of polysilicon on the oxide films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ Flow (SLM)</td>
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</tr>
<tr>
<td>N₂ (SLM)</td>
<td>3</td>
</tr>
<tr>
<td>Process Temperature (°C)</td>
<td>1100</td>
</tr>
</tbody>
</table>

Table 3.4 Process parameters for thermally grown silicon dioxide.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₂Cl₂ Flow (sccm)</td>
<td>5</td>
</tr>
<tr>
<td>NH₃ (sccm)</td>
<td>20</td>
</tr>
<tr>
<td>Process Temperature (°C)</td>
<td>650</td>
</tr>
<tr>
<td>Process Pressure (mTorr)</td>
<td>550</td>
</tr>
</tbody>
</table>

Table 3.5 Process parameters for LPCVD silicon nitride deposition.
The polysilicon is deposited by the LPCVD method. The oxidised wafers are placed into a tube furnace and pumped down to a pressure of 550 mTorr. The parameters for the polysilicon process are described in Table 3.6. With a process time of 2 hours and 30 minutes, a thickness of 1 µm is achievable. These samples now with an oxide and polysilicon layer can be used for deposition of a photoresist layer.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ Flow (sccm)</td>
<td>30</td>
</tr>
<tr>
<td>Process Temperature (°C)</td>
<td>650</td>
</tr>
<tr>
<td>Process Pressure (mTorr)</td>
<td>550</td>
</tr>
</tbody>
</table>

Table 3.6 Process parameters for LPCVD polysilicon deposition.

For photoresist deposition, the wafers are placed in a hexamethyldisilazane (HMDS) vapour box for ten minutes prior to spin coating of the photoresist later. The HMDS acts as an adhesion promoter for the photoresist to bind to and ensures a higher quality resist layer on the surface of the wafer.

Deposition of the photoresist layers in the SMC is done with a Brewer Science CE6000 spin coating tool, shown in Fig. 3.13. The photoresist used in all depositions was the MEGAPOSIT SPR-350 photoresist that was deposited to a thickness of 1.6 µm. SPR-350 is a positive photoresist and as such, the exposed areas will undergo a photodegradation process whereby the resist begins to break down. This allows for the removal of the exposed photoresist after exposure to a UV light source. The process used to deposit the resist to this thickness has the first step with resist dispensed for 22 seconds at 40 rpm then spun for a further 1 minute at 1900 rpm. The post spin bake has the wafers heated for 2 minutes at 110°C and the placed on a cool down station for a further 1 minute. At this point, the photoresist is then patterned using the Karl Suss KS-MA8 mask aligner, shown in Fig. 3.14. The radiance of the MA8 was measured to be in the region of 4 mW/cm². Using information from the photoresist datasheet and using equation (3.9), it can be seen that an exposure time of 10 seconds is required for satisfactory exposure of the photoresist. This exposure creates the areas where silicon dioxide will become exposed. After exposure, the wafers are placed back into the Brewer tool to develop the photoresist. The developer is a chemical wash that removed the photoresist, which has been exposed to UV light. At this point, there are now open areas of silicon dioxide that need to be removed, leaving only the final sacrificial etch.
areas for the test structure.

Figure 3.13 Brewer Science CE6000 spin coating system.

Figure 3.14 Karl Suss MA6/8 mask aligner system.

The patterning of the silicon dioxide and silicon nitride films allow for the creation of masking layers. The steps outlined are used for the creation of the test structures in this body of work and are well-established processes within industry as a whole. After resist patterning and development, the mask layer must be etched to open the access points to the sacrificial layer where the photoresist is not acting as the mask itself. The reactive ion etch (RIE) method is used to etch the exposed regions of the oxide or nitride mask layer after the photolithography stage.
3.4.2.3 Reactive Ion Etching

Reactive ion etching is a process in which a combination of chemical as well as ion beam and plasma etching techniques are used to generate an anisotropic etching profile in materials. While there are a number of configurations of this design, the tool used as part of this thesis, is described here and a basic schematic is shown in Fig. 3.15. Photoresists and other structural layers can be utilised as the masking layers depending on the chemistries used. This system utilises a dual plate design, which acts as a cathode/anode system to generate plasmas within the system. The argon plasma ionises a selection of feed gasses, from CF$_4$, CHF$_3$, SiH$_4$ and NH$_3$. These ionised gasses along with the ion bombardment at the exposed surface interface, allow the possibility to control the power of the plasma as well as the rate at which the feed gasses are ionised. This also leads to selective etching of silicon dioxide and silicon nitride films with particular affinity towards single crystal and polycrystalline silicon materials. Photoresists are adequate as masking materials, however if the process powers are set too high, the rate of ionisation means that photoresist mask layers are consumed as quickly as the materials that are to be etched, thus losing selectivity.

![Diagram of a reactive ion etch chamber](image)

Figure 3.15 Basic diagram of a reactive ion etch chamber [82].

Silicon dioxide etching in the RIE system utilises CF$_4$ as the primary etch gas. Under ionisation by the plasma, fluorine ions are utilised to break the Si-O bonds. In the sample preparation here, the SPR-350 photoresist is used as the process mask to protect the areas of silicon dioxide that will be the final mask layer. The process requirement for each material to be etched in the JLS RIE system shown in Fig. 3.16 are given in Tables 3.5 and 3.6.
Figure 3.16 JLS RIE system in the SMC.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHF&lt;sub&gt;3&lt;/sub&gt; Flow (sccm)</td>
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</tr>
<tr>
<td>Argon Flow (sccm)</td>
<td>20.1</td>
</tr>
<tr>
<td>Power (Watts)</td>
<td>100</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 3.7 RIE process parameters for etching silicon dioxide films.

A process time of 1 hour 45 minutes was required for etching through a masking layer of 900 nm of thickness, giving an etch rate of 8.57 nm/minute for the PECVD silicon dioxide films

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF&lt;sub&gt;4&lt;/sub&gt; Flow (sccm)</td>
<td>50</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt; Flow (sccm)</td>
<td>4</td>
</tr>
<tr>
<td>Power (Watts)</td>
<td>50</td>
</tr>
<tr>
<td>Pressure (mTorr)</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 3.8 RIE process parameters for etching silicon dioxide films.

For a 1000 nm thick layer of the PECVD silicon nitride, a process time of 35 minutes
would be required, giving an etch rate of 28.6 nm/minute.

The photoresist layer used as the mask in the RIE process must now be removed before continuing with the vapour phase etching of the structured samples. This is performed in a barrel ash etch system which utilises an oxygen based plasma to break down the organic materials as shown in Fig. 3.17. This is able to remove all residual photoresist from the surface of the wafer in 60 minutes.

Figure 3.17 Image of the barrel asher used for photoresist removal in the SMC.

While this is one way in which these samples can be fabricated, using the processes outlined, there are a number of processes and film combinations used in the semiconductor and MEMS industries. Some simple examples of the layers as described here are shown in Fig. 3.18 and 3.19.

Figure 3.18 Material stack options for XeF₂ etching test samples prior to RIE processing.
3.4.3 Film Measurement and Analysis

Throughout the fabrication and after all etching processes performed throughout this thesis, metrology tools were used to measure film thicknesses. These systems carry with them an inherent measurement error. At the SMC, analysis of films was performed on two main systems: a nanospec-3000 optical microscope for film thickness measurements, and a Zeiss Axiotron for optical measurement of the undercut profile on samples where the masking layer was optically clear. Figures 3.20 and 3.21 show the Nanospec3000 and Axiotron systems respectively.

The Nanospec3000 system is capable of film measurements up to a thickness of 30 µm. The best resolution is 50Å [77, 78]. This relates to a ± 5 nm error in all measurements made on films.
The Axiotron system is capable of optical zoom of 150x if required. The software package on this system is by Spot Imaging and has built in capabilities to show measurement based on the objective used.

![Zeiss Axiotron system](image)

**Figure 3.21** Zeiss Axiotron system.

### 3.5 Summary

The fabrication techniques required for sample preparation in this work have been described. Wafer preparation, as well as film deposition and photolithography have been used to generate unpatterned films for etching under vapour phase HF etching conditions. Also, patterned structures for the study of undercut behaviours in the XeF₂ etching method using a simple mask design developed for this study.
Chapter 4 Comparative Study of Process Catalysts in Vapour Phase HF Etching of Silicon Oxide and Nitride Films

4.1 Introduction
In Chapter 2, the literature review described the use of a catalyst for the initiation and control of the etching of silicon dioxide films by hydrogen fluoride in liquid and vapour phases. Alcohols were introduced into the wet HF etching process primarily as a rinsing method and later, as a means to finely control the etching rates were discussed. The natural progression towards vapour phase processing which took with it the “best known method” (BKM) from wet processes which utilised alcohol to catalyse and control the etch. A number of authors have described the removal or control of water on devices as being a critical factor of the etch process to reduce stiction in various hardware configurations [19, 23, 25, 26, 31, 44].

The memsstar Orbis Xeric oxide etch system used in this work is a novel hardware design. This system uses water vapour as the process catalyst at the etch interface as it can be sufficiently controlled in such a way that using alcohol is no longer required. In this chapter, comparisons of two options for process catalyst are examined. Ethanol (200% proof from SAFC chemicals) was used as the alcohol based catalyst while de-ionised water was made available from the Scottish Microelectronics Centre. Samples of plasma enhanced chemical vapour deposition (PECVD) silicon dioxide and silicon nitride films were etched under the same process conditions to assess the differences.

4.2 Experimental System Design
4.2.1 Hardware Configuration
Etching was performed on the memsstar etch system, which is a fully automated single wafer system and can be used as a research and development (R&D) system or as part of a commercial production manufacturing line. The system within the SMC is shown in Figs. 4.1 and 4.2. This system is an advanced system having had multiple hardware revisions.
The chamber is a single wafer system, which can process small samples up to 200 mm diameter silicon wafers and utilises a showerhead built into the top of the process chamber to spread the process gases. The chamber is solid aluminium and is also capable of using different temperatures on the process pedestal on which the silicon samples will be placed and this operates from 5°C to 45°C. This means that the system cannot be directly configured to match those described in previous literature due to the constraints of the hardware described here. The work presented in this, and subsequent chapters, report the relative behaviours of silicon dioxide and nitride films in process regimes that are possible within the system.
This chapter focuses on the choice of catalyst: the commonly used alcohol process in contrast to a lesser utilised water system as a means of etching silicon dioxide films in a vacuum equipment. While alcohol is seen as the best choice for process control, in part due to the greater levels of information available, key considerations as devices move into the MEMS and NEMS feature size domain are now important. This work will show the behaviours of both process catalysts and their effects on oxide and nitride etching rates under the same process conditions. Silicon nitride is a common material that is required to co-exist on devices and as these MEMS and NEMS feature sizes and aspect ratios become more important, the ability for these films to fulfil their purposes without adverse effects will become substantially more important.

Gasses are introduced and controlled by mass flow controller (MFC) units, made by MKS instruments. These have an upper and lower 5% tolerance based on their calibrated values: for example, a 100 standard cubic cm per minute (sccm) MFC can run as low as 5 sccm and as high as 95 sccm with steady control. The highest and lowest 5% can be used, but gas flow stability may be inconsistent. These MFC’s are used to control not only HF flow, but also used on separate gas lines for the N\textsubscript{2} carrier gas flows for the catalyst. Gas distribution of both the catalyst and the HF gas is done with a showerhead gas dispersal design. This ensures uniform distribution of the gasses across wafers up to 200 mm diameter.

The catalyst for the reaction is introduced via a liquid source bubbler shown in Fig. 4.3. This consists of a stainless steel vessel filled with the required catalyst. A dip tube introduces the N\textsubscript{2} carrier gas, which is “bubbled” through the liquid and carries the vapour into the process chamber. The bubblers were filled with either 100 ml of water or ethanol when filled and calibrated via the tool’s flow calibration program to ensure a consistent output from the bubbler for each experiment. Calibration of the bubbler output required an output of 50 sccm of catalyst when 50 sccm of N\textsubscript{2} carrier gas is provided to the bubbler.
The process chamber is made of aluminium, which does not etch under vapour phase HF etching conditions and the gas lines are made from stainless steel. Inside the chamber, the samples are placed on a temperature-controlled pedestal by a Thermocube temperature controller system produced by Solid State Cooling. For this series of experiments, temperatures of 5°C and 21°C are used initially as a low temperature option and a temperature at an ambient value. Pressure was monitored and controlled by MKS instruments automatic pressure controller (APC) in conjunction with a baratron, also known as a capacitance manometer, to control pressures at millitorr values.

4.2.2 Sample Preparation
Samples of silicon dioxide and silicon nitride were deposited by plasma enhanced chemical vapour deposition (PECVD). These films were deposited onto 150 mm diameters <100> silicon wafers to a thickness of 1 µm. The <100> wafers were diced by a Disco wafer dicing system into 2 cm x 2 cm square pieces for chip-based study. The samples can provide a high level of information about process behaviours. This, along with the number of 2 cm x 2 cm samples that could be generated from a single 150 mm silicon wafer meant that a large number of test samples could be generated quickly. The process flows for each film have been previously described in Chapter 3.

4.3 Experimental Method
In this section, the behaviours of silicon dioxide etching and its selectivity towards silicon nitride films based on the etch process parameters are investigated. The co-existence of oxide and nitride films in semiconductor and MEMS manufacturing is high. Oxide films are commonly used as sacrificial layers, while it is common to find nitride layers acting as either an etch stop layer beneath the oxide or a passivation layer
used for protecting the surface of the device. A functional layer must be a specific thickness to maintain the calculated performance requirement. In all three instances, the exposure of oxide in the presence of nitride films together is unavoidable during the etch step. The ability to selectively remove the oxide layer while leaving the nitride film unaffected is a key target in manufacturing. This requirement has become more difficult as device features decrease in size, leading to smaller tolerances than can be available with wet etch processes.

HF gas flows were fixed at 150sccm in the etch system. The process catalyst flows were to be the primary focus of the etching processes and as such, a fixed HF gas flow would allow the results to reflect the changes with respect to catalyst changes specifically. There were two sources of nitrogen in the process; one as an adjustable buffer gas and the other as the carrier gas for the catalyst bubbler. Both nitrogen supplies were VLSI grade high purity nitrogen (99.9995% purity). The water is deionised water supplied via the SMC’s in house supply, the ethanol used is 99.95% purity, 200% proof ethanol supplied by Sigma Aldrich UK (product number 459836).

The process designed using a water catalyst was developed such that oxide films would etch to two targeted depths of 180 nm and 560 nm. In setting process conditions to etch the same oxide depth in each process, the behaviours of silicon nitride under the same conditions could be determined. These depths were selected with advice from memsstar, as etch depths in this region have previously been seen as sacrificial oxide layer thicknesses in MEMS devices. An oxide film of 180 nm has been used as a surface protection layer for the wafers prior to release. In other devices, sacrificial layers have been seen in the region of 0.5 to 0.6 µm. The choice of using a fixed flow of HF with varying flows for the process catalysts and the buffer gas was decided upon to better understand the roles of the catalyst under investigation.

4.4 Results

4.4.1 Fundamental Reaction Mechanisms

The primary reason to use catalysts is to lower the activation energy of the chemical reaction, while remaining inert to the reaction itself [90]. Throughout Chapter 2, catalysts were discussed in relation to the etching of silicon dioxide in HF, as acids in both liquid and vapour phase. Catalysts allow for reduced energy reaction paths that would not be available without the presence of the catalyst, which is shown in Fig. 4.4.
Hydrogen fluoride was used as a silicon dioxide etchant in 1966 [19] and has since become the industry standard for wet silicon dioxide etching. It is primarily used for etching silicon dioxide films, including to a lesser degree, quartz and silicon nitride while showing good compatibility within the process flow of a standard CMOS production line for these commonly used materials.

Hydrogen bonding is considered an inter-molecular bond. As its name suggests, this bond is induced when there is a partially positive charge on the hydrogen due to the high electronegativity from its partner molecule. This results in hydrogen bonding occurring with a small number of molecules that contain fluorine, nitrogen or oxygen. Returning to the example of HF, due to the high electronegativity of the fluorine molecule, there is a positive charge on the hydrogen molecule and negative charge on the fluorine molecule. When two HF molecules interact, the positive charge within the hydrogen of the molecule is attracted to the negatively charged fluorine of another HF molecule. Hydrogen bonds between viable molecules are not technically bonds, but rather a very strong dipole-dipole attraction. Figure 4.5 shows the basic structure of hydrogen bonding between HF molecules.
The energy required to form or break a hydrogen bond is low. The energy to break these bonds and stop them from immediately forming new bonds is very high in comparison to molecules of similar design such as H₂S, H₂Se and H₂Te. These molecules are not able to form hydrogen bonds like oxygen can and as such boil at much lower temperatures in an atmospheric environment unlike water which has an unusually high boiling point comparing to elements with similar element column groupings as those above.

A series of intermediate steps that may take place during oxide and HF reaction including the effects of a water based catalyst from a liquid bubbler as shown in equations (4.1) to (4.4), have been described in literature [22]. These reaction paths are similar to those when using alcohol-based catalysts, and while many of the subsequent steps already shown are the same, the initiation is described in equation (4.5). It is clear from both sets of reaction equations that the mechanisms are very similar, however differences can be observed. While all these reactions show an ideal reaction involving 1 mole of each material, as already described in Chapter 2 when looking at the various processes used, there is no perfect process that utilises 1 mole of catalyst or etchant. In reality, most groups utilise very different process and hardware configurations depending on their focus.

\[ \text{2HF + H}_2\text{O} \rightarrow \text{HF} + \text{H}^+ + \text{F}^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ \text{HF}_2^- \quad (4.1) \]

\[ \text{SiO}_2 + 2\text{H}_3\text{O}^+ + 2\text{HF}_2^- \rightarrow \text{SiF}_4 + 4\text{H}_2\text{O} \quad (4.2) \]

\[ \text{SiO}_2 + \text{H}_3\text{O}^+ + 3\text{HF}_2^- \rightarrow \text{SiF}_6^{2-} + 3\text{H}_2\text{O} \quad (4.3) \]

\[ \text{SiF}_6^{2-} \rightarrow \text{SiF}_4 + \text{F}_2 \quad (4.4) \]

\[ \text{2HF} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OH}_2^+ + \text{HF}_2^- \quad (4.5) \]

\[ \text{Si}_3\text{N}_4 + 16\text{HF} \rightarrow 3\text{SiF}_4 + 4\text{NH}_4\text{F} \quad (4.6) \]

The main functional group causing the dissociation of the HF into its subsequent components is the hydroxyl (-OH) group in the alcohol and the H₂O molecules. In both cases, the fluorine of the HF molecule forms a hydrogen bond with the hydrogen of the
The etching of silicon nitride with HF is also a long established reaction, and is described by equation (4.6). The fundamental difference between oxide and nitride films however, is the lack of a required catalyst for nitride films. This mechanism is further described in literature [96].

The use of either water or alcohol as the process catalyst leads to the dissociation of HF as shown in equation (4.1). The intermediate stage shows that the dissociated HF is able to subsequently lead to the formation of H$_3$O$^+$ and HF$_2^-$, with HF$_2^-$ being the preferred reaction by-product, however the H$^+$ and F$^-$ are capable of etching in this form also. This leads to the breaking of Si-O bonds by substitution of H$^+$ ions forming -OH terminated bonds in the oxide layer as shown in Fig. 4.6, [100], while the F$^-$ takes the free position of the now released Si molecule thus generation of the by-product SiF$_4$ molecule is complete.

Figure 4.6 Breaking of Si-O bonds by H$^+$ substitution [100].

Knotter discusses another possible process regime in which the formation of the H$^+$, F$^-$ and HF$_2^-$ moieties could be formed [100]. The formation of these molecules show that hydrogen bonding of the HF$_2^-$ molecule would introduce fluorine directly into the Si-O position shown in Fig. 4.7, thus reducing the requirement for an initial H$^+$ interaction as shown in Fig. 4.6. This method of reaction appears to be more prevalent in process regimes where a greater amount of H$_2$O is available either supplied by catalyst or by reaction by-product.
The etching of silicon nitride films is described in equation (4.6) by the same author [96]. While Figs. 4.6 and 4.7 show the interaction of hydrogen bonding and its role in the breaking of Si-O bonds, silicon nitride films are not capable of this interaction. This means that all Si-N bonds must be broken by free F\(^-\) ions, which in this case, has been dissociated through HF interaction with the process catalyst. While the source of fluorine in this reaction is the HF itself, fluorine can also be introduced via reaction of fluorine containing gas sources with a plasma, which is the primary reaction mechanism of the anisotropic reactive ion etch (RIE) method. Figure 4.8 shows how the F\(^-\) ion must break Si-N bonds by substituting itself in the place of the nitrogen bonded to the silicon. This occurs at all Si-N bond sites until the Si is free from the main body of nitride material and has become an SiF\(_4\) molecule due to the F\(^-\) substitution.

For the HF\(_2\) molecule that is observed to enhance oxide film etching to be preferentially generated however, it was put forth that specific process conditions must be met in order for it to exist in the reaction environment [100]. The pH of the reaction must be in a certain range to enhance the formation of this specific molecule.

pH by definition is the relationship of H\(^+\) concentration and is described by equations (4.7) and (4.8):

\[ \text{pH} = -\log[H^+] \]
\[ \text{pH} = -\log([\text{H}^+]) \quad (4.7) \]

Where \([\text{H}^+]\) describes the concentration of \(\text{H}^+\) in mol/L, such that where \(\text{H}^+ = 0.1\), the pH could be calculated as such:

\[ \text{pH} = -\log(0.1) \quad (4.8) \]

Thus,

\[ \text{pH} = 1 \]

In the discussion, Knotter states that in pH regimes with a pH greater than 2, the formation of \(\text{HF}_2^-\) is most prevalent. This requires an \(\text{H}^+\) concentration of less than 0.01 mol/L to ensure a pH regime of 2 or more. This in turn shows that if HF etching processes can be placed into regimes where this is possible by control of the etch environment itself, then this could certainly enhance the etching of oxide films over silicon nitride films. There have been specific studies into the mechanism of silicon nitride films which also suggest that regimes where higher concentrations of the \(\text{F}^-\) molecule would enhance the etching of nitride films [41, 42, 96]. The alcohol is capable of removing water from the reaction environment by absorption, thus reducing the likelihood of forming the preferred \(\text{HF}_2^-\) molecule and increasing the formation of \(\text{F}^-\) which is better suited for nitride film etching.

### 4.4.2 Behaviours of Vapour Phase HF Etching with respect to Process Conditions

Within the chapter, the effects of process conditions and their roles in etching results are described. The etch processes focus extensively on the effects of process pressures, the carrier gas flow of nitrogen provided to the catalyst and the temperature at which the samples are etched. A description of these conditions and the control they impart on the process is described within to aid in the discussion of the results under both the water and ethanol processes, as described in sections 4.4.3, 4.4.4 and 4.4.5.

#### 4.4.2.1 Process Pressure

Process pressure is the primary control used during this work. As described in Chapter 2, a range of process pressures in which the etching of oxide films by HF and the etching of silicon films by XeF\(_2\) have been reported. Increasing pressure in terms of HF vapour phase etching results in increased etching rates. From equation (2.1), the reaction of HF with an oxide film generates reaction by-products, which also act as the process catalyst. As the process pressure is increased, the automatic pressure controller
(APC) described in Figure 4.2 and in section 4.2.1 is utilised to control the chamber pressure by opening or closing an internal control valve depending on the requirement. Pressure increases due to the gas flow into the process chamber. When the required pressure is achieved, the APC uses a built in control algorithm to accurately control to that pressure. At low-pressure requirements, the APC control valve inside the unit can be considered partially open to vacuum. It must remove the chamber environment to maintain a low pressure inside. If the pressure were to increase at this point, the APC would control to the new pressure. The opening of the control valve to vacuum would decrease to maintain a higher chamber pressure.

As a result of this reduction in the opening to vacuum, the process gasses remain in the chamber for longer, leading to an increase in the residence time of reactant gasses. A second effect of this increase in residence time is the increased exposure of materials to be etched with these by-products within the process chamber. In many cases, this would not cause a process modification, however, with one of the reaction by-products from the HF etch with oxide being H₂O, a key catalyst, the reaction can be drastically affected by an increase in process pressure. As the APC controls an increased pressure by reducing the speed of reactant removal from the chamber environment, the catalyst generated from the reaction can be utilised alongside the catalyst introduced for the process. Utilising both the provided and generated catalyst from the reaction can provide an increased HF dissociation rate in contrast to a reaction where only a single source of process catalyst is available, leading to increased etching rates as will be shown within the chapter.

Care however, should be taken. As the pressure increases, the reaction catalyst compounds its presence at higher pressures due to the reduced pumping speed required to maintain a high pressure. The level of by-product catalyst generated from the reaction can overwhelm the catalyst provided by the process itself. At this point, the reaction is no longer repeatable or controllable. As such, taking care when using process pressure is required. Along with other process controls, this is key to maintaining a fast and controllable etch.

4.4.2.2 Carrier Gas Flows
Throughout this work, the flow of HF was fixed at 150 sccm, while the catalyst and N₂ buffer flows have been adjusted to always maintain a total gas flow of 350 sccm. This
would show the effects of the catalysts used which is the primary focus of this investigation. Figures 4.9 and 4.10 shows the relative catalyst outputs based on the input \( \text{N}_2 \) carrier flow, indicating the change in catalyst flows for both water and ethanol at flows from 25 sccm to 90 sccm.

![Graph](image)

Figure 4.9 \( \text{H}_2\text{O} \) bubbler output with increasing \( \text{N}_2 \) carrier gas flow.

![Graph](image)

Figure 4.10 Ethanol bubbler output with increasing \( \text{N}_2 \) carrier gas flow.

It can be seen that while increasing the carrier gas flows leads to an increase in the output of the catalyst, there is a slight difference in both materials. Assessing the total gas flows for each process regime, the relative concentration of the gas mixture can be shown as percentage mix when the \( \text{N}_2 \) carrier gas flows increase as shown in Fig. 4.11.
In fact, with the overall process conditions being pre-determined, it is possible to understand the relative catalyst concentration based on the same gas flow configurations. Table 4.1 highlights this in the context of the overall processes and shows the catalyst concentrations for the whole process. It can be seen that for the same N\textsubscript{2} catalyst carrier gas flows, there is an increased concentration of H\textsubscript{2}O compared to ethanol. This is due to the lower vapour pressure of water than ethanol and its behaviour with higher carrier gas flows.

Table 4.1 Relative calculated catalyst concentrations for process gas flow configurations.

<table>
<thead>
<tr>
<th>HF Gas Flow (sccm)</th>
<th>N\textsubscript{2} Catalyst Carrier Gas Flow (sccm)</th>
<th>N\textsubscript{2} Buffer Gas Flow (sccm)</th>
<th>H\textsubscript{2}O Concentration</th>
<th>Ethanol Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H\textsubscript{2}O Output Gas Flow (sccm)</td>
<td>Catalyst Conc. H\textsubscript{2}O (%)</td>
</tr>
<tr>
<td>150</td>
<td>25</td>
<td>175</td>
<td>45.6</td>
<td>11.5</td>
</tr>
<tr>
<td>150</td>
<td>50</td>
<td>150</td>
<td>51.0</td>
<td>12.7</td>
</tr>
<tr>
<td>150</td>
<td>75</td>
<td>125</td>
<td>59.2</td>
<td>14.4</td>
</tr>
</tbody>
</table>
50 sccm of carrier flow, the partial pressure of water would be 0.127 Torr. At a higher pressure of 3 Torr, the water partial pressure would be 0.381 Torr. Table 4.1 allows a guide for the catalyst partial pressure based on different total process pressure values. The increase is not a linear relation with the N\textsubscript{2} flow however. Heavy focus was placed on the formation of a thin water layer on the surface of the oxide under etch as a means of etch initiation [99, 100]. While these studies describe this layer as water, this is not a fully condensed layer, but rather a hybrid layer consisting of both vapour and condensed water, which dissociates HF at the interface of the oxide layer. In this work and in others, it has been described that it is a necessary requirement for the water layer to form on the surface as a key stage in the initiation of the HF dissociation and subsequent etching of the oxide layer [22, 26, 31].

4.4.2.3 Process Temperature

The final process control utilised within this work was the temperature of the samples under etch conditions. Within Chapter 2, reference was made to the initiation of etching using a condensed layer of HF and the catalyst at the immediate etch surface interface. As the etch initiation requires the interaction of the HF and catalyst vapour locally at the etch material, the temperature can play a major role. The work described in Chapter 2 has concluded that higher temperatures typically result in reduced etching rates of oxide films. With a high temperature, the etch interface is less capable of resulting in surface catalyst vapour as its interaction and condensation is inhibited due to the temperature. As temperatures decrease, the catalyst vapour capable of condensing at the local etch surface is increased. This leads to an increase in the dissociation of HF, leading to faster etch initiation and increased etching of the oxide films.

Within the work of this chapter, two main process temperatures have been used of 5°C and 21°C. The effect of increasing or decreasing temperatures however also requires, under some conditions, a change in these other process parameters. As temperatures increase, typically, oxide etch rates decrease due to the reduction in catalyst available at the etch surface. To counter this effect, process pressures can be increased. As described in section 4.4.2.1, this increases the residence time of the reaction gasses and the reaction by-products and is a means of increasing etching rates to compensate for the increased temperature. Conversely, as temperatures are decreased, process pressures must be decreased. If the process pressure remains the same while temperatures are decreased, the level of catalyst both provided and by-product, are more readily available.
than in a room temperature regime as lower temperatures does not drive the catalyst from the sample surface. If the pressure remains the same at both temperatures, then a lower temperature leads to a regime where the reaction generated catalyst overpowers the supplied catalyst and causes an out of control process. Lowering the pressure opens the APC control valve further to remove excess gasses within the chamber environment which in turn, returns control of the etch reaction to the system rather than being controlled by the reaction by-product catalyst.

4.4.3 Water as the Catalyst

The process parameters for three process configurations are described in Table 4.2. These process parameters are the main etch recipe steps for etching to the target depths of 180 nm and 560 nm at both 5°C and 21°C under a 3 minute etch process time. As shown in equation (2.1), the reaction describes the use of a catalyst for the etching of HF and silicon dioxide to initiate and control the etching process. Typically, this reaction initiates with a surface layer of H₂O inherent in the oxide film. This H₂O catalyst is controlled by the constraints of the chosen process recipe. From the reaction, water in vapour phase is generated as a reaction by-product, which also acts as the catalyst. The process pressure can be considered as one of the main process control parameters in the HF etching process. In the case of a high process pressure, the control valve position causes the gaseous molecules in the chamber to be pumped away at a reduced rate, thus increasing the residence time of the gas in the chamber. This high residence time ensures an increased level of reactant by-product H₂O is also generated and utilised as part of the etching process. Controlling the process pressure therefore allows for the control of the process by-product and the rate of HF dissociation by the process catalyst, which determines the etching rate of the silicon dioxide films.

The initiation and further use of HF etching of silicon dioxide films using HF and water vapour have been studied by IMEC in Belgium [29]. They have reported process conditions that require the HF etching process to be configured with a solution of HF and H₂O bubbled through a container using nitrogen between 0.1 l/min and 1 l/min in ambient temperature and pressure. The aim was to control the flow rates and introduction of the HF flow. The process was carried out at sub-atmospheric pressures but not under true vacuum conditions; this in some ways is the closest hardware configuration to the memsstar-based process. The large range in flows used by the IMEC group for the bubbled HF/H₂O solution are substantially larger than those
described in Table 4.2. Their use of a HF solution mixed with H₂O solution is also different from the memsstar system, which mixes the HF and catalyst inside the vacuum chamber. Some values of selectivity can be found in Tables 2.1 to 2.5.

The processes used in this work in Table 4.2 are not only different from the IMEC work described [29], but also from much of the literature. HF flows at 150 scem are much lower in contrast to the HF flows described in literature within Chapter 2. Temperature is another parameter that can be seen to vary from author to author. While the alcohol-based processes focus on removing water vapour from the etch front and the process module almost entirely with the use of elevated temperatures above 21°C, the memsstar etch system operates at room temperature as a means to exploit the presence of water. Initially, the HF vapour phase etching of oxides and nitrides in the memsstar system occurred at 21°C which is the temperature at which many reports present their data. This temperature is the standard operating temperature of the memsstar HF release process. The lower etching temperature of 5°C was used after discussions with memsstar who have been developing this as a means to etch oxide films at faster etching rates than currently possible at room temperature.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard Recipe</th>
<th>Low Catalyst Carrier Gas Flow</th>
<th>High Catalyst Carrier Gas Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF Gas Flow (sccm)</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>N₂ Carrier Gas Flow (sccm)</td>
<td>50</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>Buffer N₂ Gas Flow (sccm)</td>
<td>150</td>
<td>175</td>
<td>125</td>
</tr>
<tr>
<td>Pressure at 5°C low/high (Torr)</td>
<td>3.5/4.5</td>
<td>3.5/4.5</td>
<td>3.5/4.5</td>
</tr>
<tr>
<td>Pressure at 21°C low/high (Torr)</td>
<td>8/11</td>
<td>8/11</td>
<td>8/11</td>
</tr>
<tr>
<td>Etch Process Time (minutes)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 4.2 Initial process parameters for H₂O experimentation.

Figure 4.12 Selectivity of oxide to nitride with increasing carrier gas flows both 8 and 11 Torr and 21°C with an H₂O catalyst.
Figure 4.13 shows the etching results for oxide and nitride films at 21°C, having been etched for 3 minutes. The results describe etching behaviours as the catalyst carrier gas flow is increased from 25 sccm to 75 sccm. Two etch pressures were used to match target etch depths of 180 nm at 8 Torr and 560 nm at 11 Torr. Figure 4.12 highlights the selectivity effects that can be drawn from the results of the etching observed in Fig. 4.13. The HF gas flows remain constant at 150 sccm while the catalyst carrier flow increases from 25 sccm to 75 sccm and at the same time, N₂ buffer flows decrease from 175 sccm to 125 sccm, maintaining the same overall gas flow in each process run.
Figure 4.13(a) describes the effects of oxide film etching rates with increasing carrier gas flows into the catalyst bubbler. It is clear that increasing process pressure from 8 Torr, used for etching to 180 nm of depth, to 11 Torr used to reach the 560 nm etching depth, increases the etching rate of the oxide films. As described in section 4.2.1, the automatic pressure controller (APC) adjusts its open position to maintain a fixed pressure value.

At both 8 Torr and 11 Torr, this effect in etching oxide films with the carrier gas flows are increased from 25 sccm to 75 sccm is observed. The effect is clearer at 11 Torr than 8 Torr, due to the increased process pressure, and as such the increased residence time of the reactant gasses, enhancing the etch process. With a low carrier gas flow, the etching rate is expected to be lower as there is a reduced catalyst level available for the dissociation of HF molecules, while the process using 75 sccm of carrier gas flow would be expected to generate the faster of the processes. The effect is repeated at both 8 Torr and 11 Torr, suggesting that this is not measurement error or random effect at one data point, but repeated process behaviour. With higher carrier flows as described in Table 4.1, the concentration of catalyst has increased overall within the process chamber thus increasing the rate of HF dissociation. The increased catalyst levels leads to a regime where HF$_2^-$ molecules are more readily formed, which in turn enhances oxide etching, there is also an increase in reaction by-product formed in both H$_2$O and SiF$_4$.

With increased carrier gas flows, the APC adjusts itself to compensate for the increased pressure generated in the chamber due to the reaction by-products being created in a higher-pressure regime. The APC control valve will ultimately result in being opened further than with lower carrier gas flows in order to maintain the same fixed pressure within the chamber environment. However, the initial opening of the valve is sufficient to remove an amount of the chamber environment, including both supplied and reaction generated catalyst. Leading to the decrease in etching rate of oxide films at 75 sccm as the additional catalyst that would typically enhance the oxide etching rate is removed from the process chamber. This indicates that the amount of available catalyst is insufficient to maintain the process behaviours when the APC opens to negate the increase in process pressure. If the catalyst level was sufficient, a change in APC open position would not affect the process as shown in Fig. 4.13(a). The results here suggest that the etching rates observed could further be improved upon with increasing carrier
gas flows, leading to increased catalyst availability within the chamber. If there were sufficient catalyst to sustain the reaction when the APC corrects itself due to a change in the pressure within the process chamber then there would not be an observed decrease shown here.

The silicon nitride etching behaviour shown in Fig. 4.13(b) trends towards both the increase in carrier gas flow and increasing pressure similar to the oxide films. It is clear that the pressure also has a strong impact in the case of nitride. At the pressure of 8 Torr, the etch rate of oxide is less than the etch rate at the pressure of 11 Torr seen in Fig. 4.14(a). Silicon nitride in the same etch process, sees a less substantial decrease in etch rate at lower pressures in Fig. 4.13(b).

The selectivity shown in Fig. 4.12 is the key indicator under investigation and is a simple ratio of the oxide etch rate to nitride etch rate. The nitride etching rates are lower than those of silicon dioxide films and as such can indicate regimes where oxide films are capable of etching faster as the most suitable means of increasing the selectivity between the two films. This indicates where the selectivity towards nitride films may be improved: where the oxide etching rates increase faster than those of nitride films or by developing a more robust silicon nitride film as will be described in Chapter 5.

Figure 4.15 describes the etch selectivity values between oxide and nitride films at 5°C based on the information in Fig. 4.14. Figure 4.6 describes the etching behaviours of oxide and nitride films at a temperature of 5°C. Etching times are again 3 minutes. Process pressures have been reduced such that the target etching depths can be met in the same process times: 3.5 Torr for 180 nm and 4.5 Torr for 560 nm.
Figure 4.14 Silicon dioxide (a) and nitride (b) etch rate with increasing pressure and carrier gas flow at 5°C with an H₂O catalyst.
Processing at 5°C was performed to further increase the levels of available water catalyst to initiate and sustain etching at the oxide interface during the etch process. At 5°C, there is a greater level of water available to act as a catalyst than at 21°C. This leads to faster etch initiation. To ensure there is not an excess of water, which would lead to an uncontrolled etching process, the pressures are reduced accordingly to meet the same etch depths of 180 nm and 560 nm in the same etching time of 3 minutes. Additionally, at the temperature of 5°C, the catalyst supplied is more readily able to accumulate at the oxide interface, increasing the speed of etch initiation with HF. As described in section 4.4.2.3, the process pressure was decreased to 3.5 Torr from 8 Torr of pressure for 3 minutes of etching to reach 180 nm, while the pressure of 11 Torr was decreased to 4.5 Torr to etch the sample to the target depth of 560 nm after 3 minutes of etching at 5°C. The pressures were reduced to accommodate the increased level of catalyst that would be present in the process chamber from the samples themselves due to the decrease in process temperature.

Figure 4.14(a) shows etching rates for oxide films in the low temperature processes. Comparing the 8 Torr process at 21°C to the 3.5 Torr process at 5°C, the etch rates have increased as the temperature decreases due to the additional water available as previously described. The trend with the lower temperature also shows a more linear behaviour with the etching rates increasing as catalyst output from the bubbler increases with the carrier gas flow. At 21°C and 50 sccm of catalyst carrier gas flow, the etching rate was 60 nm/min, under the same gas flow at 5°C, the etching rate slightly increased.
to 65 nm/min. The trend with carrier flow at 5°C indicates improvement over the results achieved at 21°C. While with 75 sccm of catalyst carrier gas flow at 21°C appeared to show a decrease in etching rate due to the APC control compensating for an increase in chamber pressure. At 5°C the same conditions did not show the same reduction in etching behaviour. At low temperature as described, there is a greater level of available water vapour at the surface of the oxide samples, leading to a more sustained etching process where the change in APC position does not affect the etching behaviour in the same way, thus not showing the same trend.

Comparing Figs 4.13(b) and 4.14(b) with respect to nitride etching rates in these two temperature regimes, the etching rate of nitride is reduced in the region of 50% in processes at 5°C than those at 21°C, where etching rates have been reduced from 13 nm/min to 6 nm/min. The increase in catalyst availability leads to a regime where the HF$_2^-$ molecule is more readily formed as described in literature [96, 100]. As described it is common for this formation to reduce the available F$, which is accepted as the source of Si-N bond breaking. The etching rates for oxide films are increased in this regime by comparing Fig. 4.13(a) and Fig. 4.14(a) and as the oxide etch rates are enhanced, the nitride etching rates show a decrease at the same time, leading to the selectivity values observed in Fig 4.15 of 26:1, a substantial improvement over existing selectivity of PECVD oxide to PECVD nitride films of 7.4:1 [29].

At both 5°C and 21°C with an H$_2$O catalyst, high-pressure regimes indicate an increase in selectivity towards oxide films. The highest selectivity is observed to be 26:1 for PECVD oxide films to PECVD nitride films in the high-pressure regime at 5°C. A decrease from 21°C to 5°C lowered nitride etching rates from 13 nm/min to 6 nm/min. This supports the idea of improving selectivity by increasing the oxide film etch rate that leads to a reduction of the etching rate for silicon nitride films at the same time. The inherent water incorporated into the film is utilised in the low temperature regime to more readily initiate and sustain the etching of oxide films with vapour HF. These results show that while historically, many literature studies describe moisture as a problem for the etching of oxide films using HF vapour and to avoid its presence where possible, it can in fact be utilised to improve selectivity towards nitride and increase etching rates for oxide films without any apparent negative impact to the etching process.
Figures 4.16 to 4.18 show the comparison of oxide etching rates at both 5°C and 21°C in both low and high-pressure regimes. In Fig. 4.16, it is clear that high-pressure regimes, regardless of temperature, result in faster oxide etching, while Fig. 4.17 shows an increase in nitride etching rates at 21°C. In the case of nitride etching, these films are also etched faster in high-pressure regimes. What can be seen within these figures however is that the oxide etching rate is increased at a greater rate than the nitride films as temperatures are decreased, leading to the higher selectivities at both temperatures.

Figure 4.18 specifically looks at the difference in selectivity in the high-pressure regime at each of these temperatures. High-pressure regimes at both temperatures result in the highest selectivities of oxide towards nitride and the low temperature process generates the highest reported PECVD oxide to PECVD nitride selectivity to date of 26:1, which is a substantial improvement over the previously reported 7.4:1 [29].

![Figure 4.16 Comparison of oxide etching rates at 5°C and 21°C at both low and high process pressure conditions with water catalyst](image)
4.4.4 Ethanol as the Catalyst

The bubbler as described in Fig 4.3 containing water was emptied and re-filled with 100 ml of ethanol to act as the process catalyst. Much of the literature for HF acid and vapour phase HF processing discusses the use of alcohols primarily as a means for harvesting and removing excess water from structures and reducing the risk of stiction in the devices. In wet processing, additional alcohol rinse stages are used as a means of absorbing and removing water from the etch-front to control the process as a whole. As a comparison to the water processes described in section 4.4.3, all process parameters
were used with an ethanol catalyst instead. This allows investigation of catalyst behaviours by comparing both oxide and nitride etching rates. While the reaction mechanism by which silicon dioxide etches remains the same regardless of the choice of catalyst in use, the behaviours of the initiation and continuation of the etch will be affected by the choice of catalyst.

### 4.4.4.1 Direct Comparison with the Water Based Process

Figure 4.19 shows the selectivity values corresponding to the etching rates in Fig. 4.20. Figure 4.20 shows the etching rates of oxide and nitride films under the same conditions for direct comparison with the results in Fig. 4.13. The process time was 3 minutes, HF flow 150 sccm with increasing carrier gas flow and decreasing N₂ buffer flow. As this was a direct comparison of the process the same pressures were used, but not to target a specific etch depth, rather only to compare the effect of etching rates for both film types.

![Figure 4.19 Selectivity of oxide to nitride with an ethanol catalyst using the same process conditions as the water catalyst at 8 and 11 Torr and 21°C.](image-url)
Figure 4.20 Silicon dioxide (a) and nitride (b) etching rates with an ethanol catalyst using the same process conditions as the H$_2$O catalys process at 21°C.

A direct comparison with the described water process as described in section 4.4.3 was conducted. The difference in etching rates for both silicon dioxide and silicon nitride films are shown in Fig. 4.20. The measured etch rates of silicon dioxide films were obtained under the same conditions as described in Table 4.2. Using water as the process catalyst, silicon dioxide etch rates were measured at 60 nm/min with a catalyst carrier gas flow of 50 sccm at a pressure of 8 Torr. A direct comparison of this process with ethanol as the catalyst shows an oxide etch rate of 17 nm/min. For the same process parameters, the nitride etch rate with the water catalyst was 13 nm/min,
however with the ethanol catalyst, the etching rate of nitride was reduced to 7.3 nm/min. This shows selectivity of 4.5:1 for the water catalyst and 2.4:1 using the alcohol catalyst at 21°C. This result is primarily due to the large decrease in HF etching rate of oxide films, as the alcohol catalyst is not able to dissociate the HF molecule as efficiently as H₂O, leading to a slow initiation of the HF etching process.

While there was variation seen in Fig. 4.13(a) regarding oxide etching rates with the water catalyst at high carrier gas flows, a reduction in oxide etching rates with the ethanol catalyst is observed at 21°C, however the effect is less pronounced. This can be attributed to an insufficient level of catalyst present to sufficiently initiate the etching of the oxide film. Silicon nitride in this regime however appears to show this behaviour more clearly than the oxide. In regimes where less water is available, the formation of F⁻ becomes the strongest reaction by-product. When the APC adjusts itself based on the chamber pressure control, F⁻ is removed from the environment thus a reduction in nitride etching is observed as the carrier flow is increased from 25 sccm to 75 sccm.

While the greatest selectivity of oxide to nitride at 21°C and 8 Torr with a water catalyst was 4.5:1, the best observed in a direct process comparison with an alcohol catalyst is 2.4:1. Under the same gas flow conditions, at a process pressure of 11 Torr, oxide etching with a water catalyst shows an etch rate of 193 nm/min while using an ethanol catalyst, the etching rate of oxide is 8 nm/min. The trend observed in Fig. 4.13(a) with increasing gas flows is less prominent in Fig. 4.20(a), however, as there appears to be an inconsistent etch initiation with the oxide films using the ethanol catalyst the etching rates may be such that the APC adjustment does not affect the as is observed using the water catalyst in Fig. 4.13(a). The full effects of selectivity in direct comparison at both 8 Torr and 11 Torr at 21°C can be seen in Figs. 4.12 and 4.19. This comparison of the overall etch depths could not be seen as a fair and representative test, as a direct comparison does not give the etch process using an alcohol based catalyst a suitable period of time to initiate and maintain etching of oxide to the target etch depths. While the process catalyst may be different, the etching of oxide films will require an initiation condition and as alcohols are known to absorb water from the interaction, this appears to delay the initiation of etching oxide films. As such, the direct comparison is not a good example since the differing catalyst behaviours were not considered.
Figure 4.21 shows the etching rates of oxide and nitride films etched at 5°C. The low temperature conditions described in Table 4.2 for an H$_2$O catalyst process were replicated using an ethanol catalyst. Figure 4.22 describes the selectivity values achieved for oxide to nitride films at this lower temperature with an ethanol catalyst.

(a)

(b)

Figure 4.21 Silicon dioxide (a) and nitride (b) etching rates with an ethanol catalyst under the same process conditions used by an H$_2$O catalyst at 5°C.
Figure 4.22 Selectivity of oxide to nitride at 5°C using an ethanol catalyst under the same conditions as an H₂O catalyst.

The analysis of etching rates at the lower process temperature of 5°C is also directly compared with the ethanol process catalyst. While the highest oxide etch rate was 65 nm/min using the water catalyst, with ethanol, the rate was measured to be 22 nm/min. This is higher than the rate observed at 21°C however of 17 nm/min as was observed by comparing Figs. 4.13(a) and 4.14(a) which relate to a water catalyst process. As seen in Figs. 4.21(a) and 4.21(b), the etching rates of both the oxide and nitride films in Figs. 4.14(a) and 4.14(b) show the different behaviours based on the more prominent etch molecule available of either HF₂⁻ where an excess of water is available, or F⁻ when alcohol processing takes place at a temperature of 5°C.

Figures 4.23 to 4.25 show the comparison of these etching and selectivity rates at low temperatures. Figure 4.23 shows the clear difference that direct comparison of process catalysts has on oxide etching rates, while Fig. 4.24 shows the effects on a nitride film. As is highlighted in these figures, the nitride etching rates are comparable regardless of catalyst choice, while the oxide etching rates are substantially improved when using a water based catalyst. This leads to the selectivity comparison shown in Fig. 4.25 at 5°C and a high process pressure, where the water catalyst generated the highest selectivities.
Figure 4.23 Comparison of water and alcohol catalysts on oxide etching rates at 5°C under the same etch conditions.

Figure 4.24 Comparison of water and alcohol catalysts on nitride etching rates at 5°C under the same etch conditions.
Figure 4.25 Comparing the selectivity of oxide to nitride with both water and alcohol catalyst at 5°C in a high-pressure regime.

4.4.4.2 Comparison of Ethanol Etching Behaviours to Water Catalyst with Extended Process Times

Further to the work described in section 4.4.4.1, it is more appropriate to investigate process etch behaviours when targeting the same etch depths. As stated previously, two methods are available: increasing process time and increasing process pressure. The etching time was increased to etch to the target depths of 180 nm and 560 nm at the low and high pressures used in the process previously described at both 5 and 21°C. The resultant etching times are given in Table 4.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process Time at 21°C 8 Torr</td>
<td>40</td>
</tr>
<tr>
<td>Process Time at 21°C 11 Torr</td>
<td>40</td>
</tr>
<tr>
<td>Process Time at 5°C 3.5 Torr</td>
<td>120</td>
</tr>
<tr>
<td>Process Time at 5°C 4.5 Torr</td>
<td>145</td>
</tr>
</tbody>
</table>

Table 4.3 Modified process parameters required for matching etch depths with different pressure and temperature configurations.
Figure 4.26 Selectivity of oxide to nitride with an ethanol catalyst under increased process times at 21°C.

Figure 4.26 shows the respective selectivity between the two films in Fig. 4.27.

Figure 4.27 shows the results of etching oxide and nitride films. The 180 nm etch depth for oxide required 40 minutes at 8 Torr of pressure at 21°C while a 560 nm etch depth required 40 minutes at 11 Torr and 21°C.
To further understand the behaviours using the alcohol catalyst, the process times were increased to meet the target etching depths. Increased process times, which allow a more sustained etching process to develop, can show a clearer behaviour trend when compared to the direct comparison of oxide films at 21°C described in section 4.4.4.1. The results appear improved from those shown in Fig. 4.21(a), showing silicon dioxide films etching at a higher rate when in a high-pressure regime in Fig. 4.27(a). While the results regarding low temperature processing with a H₂O catalyst suggest that there is more water vapour, largely due to the incorporated moisture of the film, a high process
temperature inhibits the formation of the initiation layer on the surface of the interface of the oxide layer as described in numerous reports [22, 23, 31]. To match the etching depths as with the water catalyst process, etch times greater than those of the water catalyst process are required. Where the oxide films at 21°C reached 180 nm of depth with an etch rate of 60 nm/min using the water catalyst, the etching rate of oxide films with the extended process time was 9 nm/min for the alcohol catalyst. Increasing process pressure shows an improvement in the etching rate of oxide films by a factor of 3 over the rates measured in a low-pressure regime with the ethanol catalyst.

Silicon nitride films in this process regime behaved differently to the results observed in both Fig. 4.13(b) with water, Fig. 4.20(b) when compared to Fig. 4.27(b). While the water catalyst shows that both oxide and nitride films have an increased etching rate with the increased pressure, Fig. 4.27(b) at 21°C shows faster nitride etching in this series of tests in the low-pressure regime at 8 Torr than 11 Torr. All measurements of the film thickness were taken nine times and the series of tests was repeated to ensure this was not one series of erroneous results, but a repeatable behaviour. In relative terms however, the variance between these two sets of results was 1-2 nm/min. This small variance in etching rates between the nitride films in this regime however affects the selectivities described in Fig. 4.26. In the 21°C, low-pressure water process, the nitride films were measured etching at 13.33 nm/min, the nitride films with the ethanol catalyst show an etch rate of up to 3.55 nm/min for the same process gas flow. This indicates that the water catalyst based processes appear to etch nitride films at a greater rate than the alcohol catalyst, which shows the potential for the alcohol catalyst to provide high selectivities over the water catalyst. The results have shown that although the nitride films do etch more in the water catalyst regime, the etching rate of the oxide films is substantially greater, resulting in increased selectivities than those observed in this regime due to the lower etching rate of oxide films using the ethanol catalyst.

While the direct comparison process was too short in terms of etch time to discern the true etching results for the process, the longer process times have given a more realistic etching rate. The results do show a decrease in the overall etching rates of oxide films in contrast to the previous ethanol tests. Nitride etching rates in contrast to the direct comparison process are measured to have a much lower etch rate per minute. However, the relative rate of oxide etching has decreased at a greater rate than the nitride, which has an overall effect on selectivity leading to the observed results in Fig. 4.26 showing
there has been no improvement in selectivity when comparing this to a regime with water as the catalyst as the highest measured selectivity with the extended process times was 13:1 at 5°C and 4.5 Torr of pressure.

Figure 4.28 shows the etch behaviours of oxide and nitride films etching at 5°C. Etching to 180 nm at 3.5 Torr of pressure required 120 minutes while for 560 nm 145 minutes was required at 4.5 Torr. Figure 4.29 describes the selectivity results between the oxide and nitride films.

Figure 4.28 Silicon dioxide (a) and nitride (b) etching rates with an ethanol catalyst under increased process times at 5°C.
Figure 4.29 Selectivity of oxide to nitride with an ethanol catalyst under increased process times at 5°C.

For oxide films, the results from the higher pressure processes have shown to generate the highest etching rates due in part to the increase in the residence time of the etchant gasses comparing to their respective low-pressure counterparts. This can in the case of the ethanol catalyst, explain a lower etch rate being observed as the reactant gasses are removed more readily at low pressure. With the water catalyst the effects are further enhanced, the additional water supplied can cause a sufficient initiation layer across the oxide surface in a shorter time period. With ethanol, the results show that the initiation of the etch step is slower despite higher levels of catalyst being supplied with the high carrier gas flows. Overall, this leads to an improvement in selectivity results when increasing process times with the alcohol catalyst in contrast to the direct comparison process in section 4.4.4.1. The highest selectivity observed with increased process times at 21°C, was found in high-pressure conditions of 11 Torr. At 5°C, the selectivity is also improved in high-pressure regimes, but this result is not an improvement over results at 21°C. The highest selectivities at 21°C with high-pressure, were measured to be 13:1, an improvement over existing literature regarding these oxide and nitride films [29], but these results are only half of those achieved with the H₂O catalyst.

Figures 4.30 to 4.32 again compare the effects of the direct comparison process in section 4.4.4.1 with the extended process times from this range of experiments. As described in the previous section, the etch behaviours are not truly representative of the process due to the small etch depth reached in 3 minutes of etching time. In the following figures, the extended process times are compared to show the more realistic
nature of the alcohol etch process, including in Fig. 4.32, the highest reported selectivity of PECVD oxide to PECVD nitride using an alcohol catalyst in HF vapour etching at 12.7:1. Figure 4.30 shows the clearer oxide etching trends that extended process times are capable of when etching to a practical etching depth, where the three minute etch time process did not etch to a sufficient etch depth. Figure 4.31 shows similar consistency that was not possible in a very short process time. By allowing the process to develop with a longer process time, the true oxide and nitride etching behaviours as well as the selectivity values in Fig. 4.32 could be determined.

![Figure 4.30 Comparison of oxide etching rates with alcohol catalysts at 5°C and 21°C in high-pressure regimes with short and extended process times.](image1)

![Figure 4.31 Comparison of nitride etching rates with alcohol catalysts at 5°C and 21°C in high-pressure regimes with short and extended process times.](image2)
Figure 4.32 Comparing selectivity of oxide to nitride with alcohol catalyst at 5°C and 21°C in high-pressure regimes and with short and extended process times.

4.4.4.3 Comparison of Ethanol Catalyst to Water Catalyst with Increased Process Pressure

The final means of process comparison was to increase process pressure such that the target etching depths are met in the same process time as for the water catalyst based work. As it is apparent with the results so far, an increase in process pressure leads to an increase in etching rates for both oxide and nitride films. This has already been described as related to the residence time of the reactant gasses in the process module. In the following processes, the required pressure to meet the targets of etch depth in the same time were substantially higher than required using water which will lead to a further increase in the residence time of the reactant gasses. This will provide another perspective to the etching process with the ethanol catalyst.

Table 4.4 shows the increase in pressure required from the starting process in Table 4.2 to meet the target etch depths within the same process time as used with the water catalyst.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pressure (Torr)</th>
</tr>
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<tbody>
<tr>
<td>Low Pressure at 21°C</td>
<td>24</td>
</tr>
<tr>
<td>High Pressure at 21°C</td>
<td>35</td>
</tr>
<tr>
<td>Low Pressure at 5°C</td>
<td>12</td>
</tr>
<tr>
<td>High Pressure at 5°C</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 4.4 Increased pressure values for etch depth matching with use of ethanol catalyst.

Figure 4.33 shows the results of selectivity between the films. Figure 4.34 describes the etching rates of oxide and nitride films under increased process pressure conditions at 21°C. The etching time was 3 minutes. The process pressure was 24 Torr for 180 nm of etching depth in the oxide film and for 560 nm the required pressure was 35 Torr.

![Graph](image)

Figure 4.33 Selectivity of oxide to nitride with an ethanol catalyst with increased process pressures at 21°C.
Figure 4.34 Silicon dioxide (a) and nitride (b) etching rates with an ethanol catalyst with increased process pressure at 21°C.

Oxide etching in regimes with a significant increase in the process pressure shows an improvement in the silicon dioxide etching rates at 21°C in Fig. 4.34, in contrast to both the direct ethanol process and the increased process time regimes in sections 4.4.4.1 and 4.4.4.2. Of all three of the studied: direct comparison, extended process time and increased process pressure, this is the first regime where silicon nitride etching has been comparable or greater than the rates observed in the H$_2$O based process. The nitride etch rates in a low pressure regime are approximately 2 nm/min greater than those in a water based process and at 35 Torr, the etching rates of silicon nitride films are greater than those etched in a water based process by 11 nm/min as carrier gas flows increase. These
results show that comparable etching rates for oxide film using water or alcohol catalyst can lead to higher nitride etching rates. However, the oxide etching rates are such that even with the increased nitride etching rates in these regimes, the selectivity can be maintained at a good standard.

The process selectivity observed in the 21°C regime however has also produced the comparable selectivities described in literature [29]. This increases the etching rate of silicon nitride films to the region of those under the water-based conditions. The greatest selectivities, similar to all other results thus far, show the best results are achieved in higher process pressure regimes. Interestingly, the selectivity decreases as catalyst carrier gas flows are increased at these pressures. In lower pressure configurations, as the oxide etching rate is more affected by the catalyst flows, the selectivity appears to increase as the relative rate of increase in the oxide films is greater than the nitride films. Contrasting the selectivity of 6.4:1 with the alcohol catalyst in Fig 4.24, for the same process conditions, the selectivity with the water catalyst was measured at 10:1 in Fig. 4.12. This shows that while both regimes are capable of fast etching rates for oxide films, water appears to be the better of the two choices for maintaining a high selectivity of oxide to nitride. The use of alcohol as the catalyst in these results show that while there is an increase in etching for both films, the alcohol is still attempting to remove excess water from the environment, thus reducing the formation of HF\(_2\), which is necessary for increased oxide etching rates. As this happens, higher levels of F\(^-\) are available which is the key molecule required for nitride etching and so the increased process pressure allows for an increased etching rate due to the increased residence time of both the reactant gasses and the reaction by-products. The alcohol appears to always influence the reaction in such a way as to result in more of the molecules that would aid in nitride etching as compared to the regime using only water as the process catalyst.

Figure 4.35 shows the etching rates of oxide and nitride films under increased process pressure conditions at 5°C. The etching time was 3 minutes. For 180 nm of etch depth, the required pressure was 12 Torr and for 560 nm it was 28 Torr. Figure 4.36 shows the results of selectivity between the films.
Figure 4.35 Silicon dioxide (a) and nitride (b) etching rates with an ethanol catalyst with increased process pressures at 5°C.
Figure 4.36 Selectivity of oxide to nitride with an ethanol catalyst with increased process pressures at 5°C.

As with the 21°C processes, the 5°C processes were developed such that the increased process pressures would match the 180 nm and 560 nm target etch depths. In both cases, as can be seen in Table 4.4, the pressures required were higher than those of the H₂O process in Table 4.2. Again, the oxide film etching rates were comparable to those of the H₂O process results observed previously and shown in Fig. 4.35(a). It appears that the high-pressure oxide etching rates have plateaued for this configuration, as increasing carrier gas flows through the catalyst yielded no significant increase in the etching rate. This also appeared to be the case with the lower pressure etch set-up although a slight increase could still be measured as the catalyst flows were increased, suggesting that HF dissociation for the pressure and gas flow configuration meant that there was a limitation on the amount of reactive species formed that could react with the oxide and nitride films. This ultimately implies that if the system could supply a greater level of catalyst than it does currently then the etch rates would increase further as the bottleneck is the speed of HF dissociation rather than the oxide film etch rate itself.

As with the processes at 21°C, the silicon nitride results would be the key factor in whether high process selectivities can be attained. The results in Fig. 4.35(b) show that silicon nitride film etching in this increased pressure regime is higher than under similar water catalyst conditions. While at low pressure, the water based processes produced nitride film etching in the region of 5 nm/min, with the alcohol catalyst for the same process regime, this increased to 7 nm/min. At higher pressures, the increase in etch rate
was further enhanced. While the water based processes showed around 8-9 nm/min, the alcohol processes produced etching rates at 30 nm/min, a 300% increase in comparison to the water processes. This leads to a similar situation as seen at 21°C: while the etching rates of the oxides are the same, the etch rates of the nitride films are larger than those measured in the water based process. This has a negative effect on the selectivities shown in Fig. 4.36. Lower pressure experimentation generates a higher selectivity value of 7:1 compared to the high-pressure regimes due to the larger increase in etching rates for nitride films in the latter case.

To achieve a high selectivity with either catalyst, high process pressures appear to be a key requirement of the experimentation set-up described. The highest selectivities with alcohol were 13:1 and achieved at 21°C with an extended process time at 11 Torr of pressure. The catalyst carrier gas flow appeared to make little difference as it increase from 25 sccm to 75 sccm at this pressure, with selectivities of 11:1, 12:1 and 13:1 respectively. These results however are still less than those gained from the work performed utilising an H₂O catalyst. As it is shown, the best results in that case required a low process temperature and a high process pressure to achieve selectivities of up to 26:1.

In these high process pressure regimes with an ethanol catalyst, one aspect of the etch behaviour that is difficult to quantify is how representative the ethanol process catalyst is in relation to the improved results in selectivity observed in Figs. 4.33 and 4.36. While the aim of the investigations is to assess the influence of increased pressures using ethanol as the process catalyst, one cannot ignore the effects of the water by-product generated from the oxide etch reaction with HF. A high-pressure regime will increase the residence time of the process and the reactant gasses. This will generate increased etching rates for oxide films and in turn, nitride films. It is also a means of retaining a greater level of the generated by-product H₂O that will enhance the etch process with additional catalyst. The use of the alcohol catalyst is for both removing and controlling excessive levels of H₂O formation as well as acting as the catalyst in the reaction of HF with the oxide films. The rapid formation and retention within the process environment of water would appear to largely overcome the effects of the alcohol in high-pressure regimes. Hence, one reason why the results from the high-pressure studies using the alcohol catalyst begin to show similar etching rates for both oxide and nitride films as well as the selectivity trends to be comparable to the H₂O
processes is due to the dual-catalyst effect. With the process pressures being over three times greater in both cases: the 8 Torr H₂O process against the 24 Torr with ethanol and the 11 Torr H₂O process against the 35 Torr pressure with ethanol, it is clear that without the substantial increase in pressure, the etching rates of oxide films in the ethanol based process would remain much lower than those using H₂O as the catalyst.

In the following figures, 4.37 to 4.42, comparisons at 21°C and 5°C between oxide and nitride etch rates as well as selectivites are shown under the high pressure options for each regime and clarified in each figure. Figure 4.37 describes the oxide etching between the water based catalyst, the extended process time results of section 4.4.4.2 and the extended process pressure results from above at 21°C. It is clear that the oxide etching favours the water based process as well as the alcohol process utilising increased process pressure. The nitride etching described in Fig. 4.38 shows this trend too, however the nitride etching at this temperature also shows that a high process pressure enhances the nitride etch faster than when compared to the water based process. In both cases, the extended process time shows substantially reduced etching rates of oxide and nitride films. In fact, from Fig. 4.39 the selectivity in this extended process time results in the greatest selectivity between PECVD oxide and PECVD nitride films reported using an alcohol catalyst under vapour phase conditions at 12.7:1. The increased nitride etching rates of both the water and high-pressure alcohol process lead to much reduced selectivites.

![Figure 4.37 Comparison of oxide etching rates at 21°C comparing the water based process, extended process time with alcohol and high pressure with alcohol regimes.](image-url)
Figure 4.38 Comparison of nitride etching rates at 21°C comparing the water based process, extended process time with alcohol and high pressure with alcohol regimes.

Figure 4.39 Comparing the selectivity of oxide to nitride at 21°C with a water based process, extended process time with alcohol and high pressure with alcohol regimes.

In figures 4.40 to 4.42, the high pressure and low temperature results for oxide and nitride films under the same process conditions are considered. Figure 4.40 shows the oxide etching rates at 5°C. Much like the behaviours at 21°C, the extended process times show substantially lower oxide etching rates than either the water or increased pressure regimes. However, the nitride etching rates in the water based process are similar to the extended process time results with alcohols, which is unlike the increased process pressure regime that continues to result in a high nitride etch rate. The selectivity trends in Fig. 4.42 show the highest reported PECVD oxide to PECVD
nitride selectivity reported anywhere at this time in literature using a water based catalyst process at 26:1.

Figure 4.40 Comparison of oxide etching rates at 5°C comparing the water based process, extended process time with alcohol and high pressure with alcohol regimes.

Figure 4.41 Comparison of nitride etching rates at 5°C comparing the water based process, extended process time with alcohol and high pressure with alcohol regimes.
These results further suggest that while a high pressure enhances the oxide etching rate, when using a high process pressure, taking into account the effects of the chamber conditions when the APC controls the chamber environment in fact leads to effects such as largely increased nitride etching results which results in the loss of selectivity between oxide and nitride films. These high-pressure regimes using alcohols as previously described, lead to regimes where a high amount of catalyst and reaction by-product $H_2O$ remains. These work in tandem to increase the oxide etching rate as can be seen, but the conditions also result in the nitride etch results, further highlighting the dynamic behaviour of the HF vapour phase etching when investigating the range of process controls available.

**4.4.4.4 Effects of Increased Process Temperature on Selectivity**

As stated in Chapter 2, the alcohol based HF etching processes are typically carried out at high process temperature. To understand high process temperature behaviours in this etch system, a fixed process pressure of 24 Torr was used while the temperature was increased from $21^\circ$ to $40^\circ$C. This temperature was near to the highest operational temperature of $50^\circ$C on the memsstar system. Other commercially available HF vapour systems operate at temperatures over $100^\circ$C to ensure water vapour is removed from the reaction environment prior to etching and produce acceptable selectivities towards silicon nitride films under these conditions. Table 4.5 shows the process times required to etch to 180 nm at the selected temperatures.
Table 4.5 Process times for a 180 nm target etch depth with increasing process temperature.

Figure 4.43 shows the effects of selectivity between oxide and nitride films with increasing temperature. There is a clear trend showing a reduction in selectivity as temperatures increases. Figs 4.44 and 4.45 show the related etching rates of oxide and nitride films that provide the results in Fig. 4.43.

Figure 4.43 Selectivity of oxide to nitride with an ethanol catalyst under increasing process temperatures.
Figure 4.44 Effects of silicon dioxide etch rates with an ethanol catalyst and increasing process temperatures.

Figure 4.45 Effects of silicon nitride etch rates with an ethanol catalyst and increasing process temperatures.

Figure 4.43 shows the selectivity of oxide to nitride films with increasing carrier gas flows at temperatures of 21°C to 40°C. The results clearly show that for the process regime used on the memsstar system, increasing process temperatures negatively impacts the selectivity towards silicon nitride films. At 40°C, selectivities below 1:1 are measured. In these cases, nitride films are now etching faster than the oxide films.

The effect of nitride film etching rates in relation to selectivity can be more clearly understood by examining the etch rates of both oxide and nitride films. Figs. 4.44 and 4.45 show the progression of oxide and nitride etching rates with process temperatures.
respectively for a process at 24 Torr, 150 sccm of HF flow, 150 sccm of N\textsubscript{2} buffer gas flow and 50 sccm of catalyst carrier gas flow. The oxide etching rate decreases from 60 nm/min at 21°C to 14 nm/min at 40°C. This result, due to the increasing temperature and slowing the etch initiation at the sample surface, shows that the dependence of the HF reaction with oxide in the presence of the catalyst at the etch interface is for etching to be initiated on an oxide film. Interestingly, silicon nitride etching undergoes a strong change when moving from 21°C to 30°C. In the 21°C process, the silicon nitride film was etched at 15 nm/min. At 30°C, the etching rate of the nitride films drops to 9 nm/min and increases back to 15 nm/min at 40°C. The change in the etch behaviour can be viewed in part by the change of the surface properties of the film and the environment within the process chamber.

At 21°C, the lower process temperatures do not drive either the initiation layer or the additional process catalyst supplied to the environment away from the sample interface as readily as at the increased temperatures and as such, there is a large amount of dissociation of HF with more readily available catalysts, both the supplied alcohol catalyst and reaction by-product H\textsubscript{2}O. This allows for a reasonable etching rate of both oxide films and nitride in such a way that generates the highest selectivities as shown in Fig. 4.43. As the temperatures increases, the availability of the reactant H\textsubscript{2}O is reduced, pushing the etching rates substantially down as shown in Fig. 4.44. In this regime, the dissociation taking place will lead to higher levels of H\textsuperscript{+} and F\textsuperscript{-} ions being formed than the HF\textsubscript{2} that is preferred, leading to regimes where the nitride films can begin to etch at comparable rates as shown in Fig. 4.45, and as seen at 40°C, it begins to etch faster than the oxide counterparts.

**4.4.5 Discussion of Results with Current Literature**

In Chapter 2, the etching rates for different types of oxide film and etch conditions were highlighted in Tables 2.3 and 2.4, describing some of the highest reported etching rates of silicon dioxide and silicon nitride films prior to this work in liquid and vapour phase processes. In many reports, the etching rates were given in angstroms per second due to the low etching rates observed. The greatest reported thermal oxide etch rate was seen at 116Å/s, or 690 nm/min [27]. In the alcohol catalyst vapour phase processes, little information regarding PECVD based films was reported. However, PECVD oxide etching rates were reported at 38Å/s, or 230 nm/min when water was used as the process catalyst [29]. It was also found that etching rates for oxide films varied based on
the type of oxide being etched. This primarily stems from the variation in process pressures utilised, as well as the process temperatures. This study is the first time that both catalysts have been used in the same hardware configurations under comparable process conditions.

Table 2.5 describes the reported etch rates of silicon nitride films. Of most interest is the comparative etch rates of PECVD silicon nitride and silicon dioxide films from Table 2.4. An apparent selectivity of 7.4:1 in favour of silicon dioxide etching has been reported previously [29]. These films were not etched at the same time in the same process however, so it is unclear if this result would be true if both samples are etched at the same time. In both PECVD and LPCVD types of nitride films however, it can be seen that the etch rates are lower than their wet-etch equivalent results. This is to be expected, as the vapour-phase processes are more restrictive in terms of gas flows reducing the capability for the etch processes to develop. It is this reduction in the etching rates in contrast to wet processing that reduces the likelihood of the stiction effect. In a high-pressure water catalyst reaction, the PECVD films can be etched as fast as 0.23 µm/min.

The etching mechanisms of silicon dioxide and silicon nitride films in vapour phase HF etching have been described previously [33, 34, 97, 98]. The behaviours of vapour phase etching using water catalyst processing have also been discussed [24, 25, 27, 95, 99]. In the results of section 4.4.3 and 4.4.4, oxide etch rates have been seen as high as 194 nm/min in both regimes utilising water and alcohol catalysts where the process conditions have been adjusted to generate these etching results. For processes under a greater level of vacuum than previously reported, [29], the similar etching rates of the same films are significant results, highlighting that the process can in fact be controlled to provide high etching rates regardless of the catalyst. Throughout this work, a large emphasis has been placed on creating regimes where oxide film etching is enhanced in a controlled manner. In terms of the etch mechanism outlined above, etch systems where HF$_2^-$ formation is more readily generated are critical. Throughout the results at the lower processing temperatures and also in higher process pressure regimes, there is a clear upward trend in etching rates for oxide films when the level of the carrier gas flow is increased. As seen in Figs. 4.9, 4.10 and 4.11 however, as the N$_2$ carrier flow is increased, the actual concentration of the catalyst reduces. This leads to an overall reduction in the concentration of the catalyst, and subsequently would lead to a decrease
in the concentration of catalysts available for the dissociation of HF, i.e. an H⁺ concentration reduction. This pushes the etching regime into a situation where higher pH values can be generated. As previously reported, in regimes where there is a reduced H⁺ concentration, the HF₂⁻ molecules are expected to more readily be created within the etch environment [100]. The variability observed in the oxide etching rates, especially within the ethanol direct comparison processes, stem from an inability to generate even and consistently formed initiation surface layers as previously described.

In terms of silicon nitride etching, a high process pressure regime appears to enhance the etching of silicon nitride films more with an ethanol catalyst than in processes where water is the primary catalyst used. As previously reported [41], higher temperatures have continually been found to reduce the etching rate of oxide and nitride films, however the rate of decrease was found to be more significant with oxide films than nitride leading in this case to the regimes where nitride films etched faster than oxide films. This trend towards high silicon nitride etching with high process temperatures is confirmed in literature [42]. The etching process temperature was 100°C, which was not possible on the system in this study, but this trend was studied to some degree by increasing the temperature to 40°C as shown in Fig. 4.43.

One of the earliest models defining HF etching of oxides would suggest that the regimes enhancing the formation of the HF₂⁻ molecule would increase the etching rates of oxide films substantially over simple free fluorine F⁻ [95]. From the results achieved and as already stated in other literature [100], regimes in which the HF₂⁻ molecule formation is enhanced such as a regime with higher levels of water that become H₃O⁺ during the reaction, can enhance oxide film etching. This can be seen not only in the experiments where water is the primary catalyst in section 4.4.3, but also in regimes where a higher process pressure is utilised.

In the regime using higher process pressures to increase the residence time of the process gasses, the chamber environment is less readily pumped away to maintain higher pressures. This in turn increases not only the effect of the reactant gasses, but also the reaction by-products that form from the reaction in etching of oxide films. This includes the increased residence time of H₂O reaction by-product, which acts as a second catalyst in the case of processes where ethanol has been the primary catalyst and acts as an additional source of catalyst. This agrees with results in section 4.4.3 and
section 4.4.4.2. In this case, the mechanism described in [95] and further discussed in [100] holds in the experiments described. A model that describes etching as a combination of multiple etching stages has also been assessed [99]. This was developed as in [100], with reactions concerning etching in solutions of HF rather than the vapour phase. The experimental work conducted as part of an in-depth investigation into the effects of water on the initiation of etching for oxide films [99], suggests that the etching of oxide itself influences the generation of additional and excess levels of H$_2$O catalyst.

The hardware system in the previous work used an in-situ Fourier transform infrared (FTIR) spectroscopy system directed across the sample under etching conditions [99]. FTIR analysis is further described in Chapter 5 however, in simple terms, the FTIR analysis allows for analysis of chemical bonds on a target sample. This allows for the analysis of H$_2$O formation to be tracked during the etching process. The results showed that at low etching rates, there was no substantial formation of H$_2$O on the surface with HF dissociation occurring in the gas phase above the surface of the sample rather than explicitly needing a thin film of H$_2$O on the surface prior to any etch taking place. In regimes where faster etching rates were seen however, there was a clear H$_2$O layer, composed of vapour and liquid, on the surface of the sample, enhancing the dissociation of the HF molecule to allow for the subsequent etching of silicon dioxide films. Interestingly, if this H$_2$O layer appeared to get thicker, the etching rate would slow.

The authors suggest that in fact this can slow the dissociated material reaching the oxide interface in a timely manner, thus slowing the etching rate observed across the device and summarising the results by suggesting that control of this initiation and the subsequent etching utilising the H$_2$O layer is not only important for initiation, but further control is also required to stop slowing of the etch rate by generation of excess catalyst from the reaction of HF and oxide layers. This effect is more pronounced in alcohol-based etching. The alcohol is acting as a catalyst to dissociate the HF, however it is also trying to absorb water where possible, which leads to a significantly reduced rate of HF dissociation and increased etch initiation time. The results also show that the effect can, in part, be overcome in regimes where additional H$_2$O is formed in configurations that enhance H$_2$O formation. The results of the alcohol processes at higher pressures increase residence times of reactant gasses and as such, allows for a longer residence time of by-product H$_2$O. In these results, the etching rates could be
seen as comparable to the regimes where H₂O was the primary and only catalyst. Overall, these high-pressure alcohol regimes still suffered from the reduced selectivities in comparison to the water only regimes.

The most recent example of an etch model being applied to the wet etch process discussed a range of common MEMS and CMOS films and the means to define the general behaviour of an etching process [102, 103]. In this work, a model for wet etching of PECVD and HDP (high density plasma) oxide films as well as PECVD silicon nitride films. The proposed model has three distinct etching regions: initiation, steady state and rinse stages. The initiation stage has also previously been described in other literature describing the effects of initiation time [99]. The model shows that the initiation stage increased until the etch rate acceleration speed becomes a steady rate. The reason for developing this model for wet etching processes was to better understand the effects on the etching rates. While commonly, etch rates are given as a simple rate based on the total amount of material removed in a defined etch period, an attempt was made to clarify the pre and post steady state etching effects to give a more accurate value. The experimental method also defined the effect the rinse step has after the main etching step. It was found that in this regime, the rinse step could in some configurations, enhance the etching rate. Certainly, it would appear that building a means of measuring the change of film thickness into the memsstar etch chamber would help in understanding the effects of not only the etch initiation, but also the subsequent etch stabilisation and the chamber purge steps.

Some previous research also used a quartz crystal microbalance as a means of assessing film change in-situ which is not currently possible in the etch system used in this work. The model provides a close correlation to the etching experiments in both HF/H₂O and HF/IPA (isopropyl alcohol) baths. It was found, as described throughout this chapter, that etch regimes utilising water, or regimes in which there is a higher level of water available due to process conditions, generate faster etching results than those that solely utilise the alcohol based catalyst. It has typically been the case that wet etching processes are faster than vapour phase processes for oxide film etch rates and with that, in simple structures, afforded a relatively useful selectivity towards the nitride films. In the case of the etch results within this study, selectivity of HDP oxide to PECVD nitride films is reported at an apparent 24:1 based on the results of two blanket films etched in separate tests and 84:1 for PECVD oxide to PECVD nitride films [104]. These
selectivities are certainly the highest selectivities seen in any wet etch process reported and greater than the results of the vapour phase etching results generated in this chapter. While this would obviously suggest that designers and users should continue using wet processing, the issue of stiction will force a move to the vapour phase release process for nearly all major functional MEMS devices in the very near future.

As previously stated, these selectivities are ideal in devices that are physically capable of withstanding the effects of a wet etch process, but for future MEMS designs, the wet process cannot be used to produce good final results. There was also an interesting result that the nitride film etch rates are less in the presence of the oxide films than without, suggesting an interplay between these films when present thus showing that the standard perceptions regarding selectivity may not be suitable. The real method to understand film etch rates and selectivities as stated “cannot be characterised accurately by experiments on single films only” [103], showing that the films under investigation must be present in the same process to show the accurate results. This study into the selectivity of these PECVD films may also be the only reported results to describe the etching of these materials in a single etch process rather than in sequential processes. Overall, the etching results throughout section 4.4 do not conflict with the reported work in literature on the existing etching processes. The results do however show the differences between the choices of process catalyst. The use of either water or alcohol will define the process capabilities of the system and the level of control that is possible based on the designs of the semiconductor or MEMS devices for manufacturing.

4.5 Conclusion
A comparison of water and ethanol as process catalysts in vapour phase HF etching of silicon dioxide and nitride films has been described. In direct comparison of the same process, the etching rates of oxide films showed a large difference: etching rates greater than 200 nm/min using water as the catalyst were measured in contrast to 20 nm/min with the ethanol catalyst. The proposed comparative mechanisms of the two catalysts suggest that the utilisation of water as the process catalyst enhances the formation of the HF$_2$ moieties, which allows a faster reaction with oxide films while slowing the rate at which nitride films are etched at the same time.

This behaviour also affects the selectivity of oxide to nitride films, where the highest selectivities towards nitride were measured at 26:1. This is the highest selectivity of
PECVD oxide to PECVD nitride film under water based process conditions currently to have been reported. This is due to the overall increased oxide etching rate in contrast to nitride films with the water catalyst, while a selectivity of 13:1 is achieved using the ethanol based catalyst. The highest results of 13:1 observed using the alcohol-based processes disguise the effects of the reaction by-product H₂O. This regime allowed for the subsequent interaction of H₂O to additionally supplement the etch rate already initiated by ethanol. In fact, the results suggest that the increase in process pressure which would enhance an increase in reaction by-product in the process environment including H₂O, creates the regimes in which a higher selectivity can be achieved using an initial alcohol based catalyst. A series of tests conducted at high process temperatures up to 40°C showed the selectivity of oxide to nitride decreasing to 0.9:1, where nitride etching rates become higher than the oxide films. This effect was also observed in the previous literature. The results revealed that at high temperatures using alcohol as the catalyst, the selectivity could move in favour of nitride films etching faster than oxide leading to some interesting future possible design projects.

While using alcohol as the primary catalyst has been shown to result in slower etch rates, the effect can be of benefit in allowing finer control of the etch depth than the water catalyst based approach when the dimensions are critical in devices. However, the increased etching speed and greater level of selectivity towards nitride films with the water based process in the case of this study, would be the more beneficial route for process catalyst choice.
Chapter 5 Effects of Silicon Nitride Deposition and Process Conditions on HF Vapour Phase Etching Behaviours

5.1 Introduction

In Chapter 4, the effects of process catalysts used in vapour phase HF etching of SiO₂ and Si₃N₄ films were studied. Results show etching behaviours for silicon dioxide and nitride films as well as their selectivity values due to the choice of catalyst used in the process. In Chapter 4, one key mechanism regarding silicon nitride film etching as described in literature [96, 99] describes the substitution of fluorine to break Si-N bonds while forming Si-F bonds leading to the SiF₄ reaction by-product being formed. In a standard manufacturing process, PECVD films are deposited at temperatures below 400°C to avoid alloying of aluminium films with other CMOS films leading to a change in electrical properties of the deposited films. It has long been the aim in manufacturing groups, to replicate the properties of higher quality LPCVD films while depositing these films at a low temperature [111]. Various possible compositional changes can occur to the films that can provide improvement in etch performances: chemical composition being the primary change. This ultimately affects parameters such as refractive index (RI). Being an indicator of the properties of a material determining the composition and the arrangement of atoms, RI is considered in the semiconductor industry, to be a guiding indicator in the general behaviour of materials.

This however, is not necessarily the best indicator to monitor when assessing etch selectivities in films. A typical PECVD silicon nitride can have an RI value of 2.0. A standard LPCVD silicon nitride film can also have an RI value of 2.0. These films behave very differently in the HF etch process, and yet, one of the main values used as a guide for materials is the same. Chemical composition and its role in how robust a film will be in an HF etch step is critical. Investigation into whether a film can be modified by deposition processes and further post processing steps to increase the robustness can be performed. The analysis of various process conditions allows insight into possible material and process combinations that enhance silicon nitride robustness, leading to an improvement in etch selectivity towards oxide films.

When investigating silicon nitride film deposition techniques in literature, primary research focus has tended towards electrical characterisation from the perspective of
solar cell applications [110, 112]. In fact, there have been substantial studies into different deposition techniques and post processing techniques to control the properties for nitride films. Modification of the hydrogen content [109, 111, 113], deposition feed gas using dichlorosilane (DCS) [105, 107] and trichlorosilane (TCS) [105] as well as physical changes to the deposition systems [106, 108], and post process annealing [115, 116] of nitride films have all previously been described. Although wet etching of modified silicon nitride films has been reported [117], there is no study of the effects on film deposition conditions and annealing in the vapour phase etching of the films.

Throughout these reports, a number of trends have been reported from various authors. Many studies focus on the ratio of the feed gasses. In this research and in others, this refers to the gas mix of two key process gasses: silane (SiH₄) and ammonia (NH₃). With silane being the obvious source for silicon and ammonia, the source of nitrogen. Ammonia is preferentially used over diatomic nitrogen, N₂, as it is easier to break down ammonia under plasma conditions than N₂, which leads to faster deposition rates of nitride films. The ratio of the gas mix influences the overall gas composition: the relative change in silicon, nitrogen and hydrogen within a deposited film. This subsequently changes the material behaviours from etching rate and refractive index to electrical characteristics. The relative change in the etching behaviour due to deposition conditions is the main investigation points of this chapter. Previous work indicates that with increasing silane to ammonia ratio, silicon and hydrogen contents increase within the film while nitrogen content decreases [106, 109, 110, 112]. Using measurement methods that can detect these compositional changes and understand the behaviour of silicon nitride film etching, can lead to the development of robust silicon nitride films capable of improving the etching selectivities of oxide films towards nitride films. This chapter aims to investigate a means of improving silicon nitride selectivities for PECVD films and improving selectivity results in vapour phase HF etching process as a whole.

5.2 Hardware overview
The memsstar Xeric Oxide etch system as described in Chapter 4 is used to conduct the HF vapour phase etching experiments for silicon nitride films. A vaporiser system is now used to improve the stability of the source water catalyst introduced into the system. This change, while improving the overall consistency of the system, does not change the overall performance of the etching behaviours from those previously described in Chapter 4.
The vaporiser unit, manufactured by Horiba, consists of two main components: a liquid flow meter (LFM) and a vaporiser control unit that has a 2-stage heating system inside. The implementation of this is shown in Fig. 5.1. Process N₂ is supplied to the vapouriser and water is supplied to the LFM inlet. The liquid water is first heated to 120°C to become a vapour, which then goes in to the main vapouriser section of the unit. The vaporiser unit is heated to a constant 200°C to ensure the controlled vapourisation of the liquid as it exits the unit and is then delivered to the process chamber where it is subsequently mixed with HF, similar to the method with liquid bubblers.

![Figure 5.1 Schematic of the vaporiser configuration for water catalyst.](image)

### 5.3 Film Deposition and Sample Preparation

Silicon nitride films were deposited by PECVD deposition on the STS multiplex CVD system. As described in Chapter 4, this is a PECVD deposition system able to deposit films under different conditions. While in Chapter 4, the study of selectivity was related to the standard silicon nitride film, this chapter looks to further develop this film and improve processing capabilities.

In the PECVD system, a number of process parameters can be modified: deposition temperature, SiH₄ flow, buffer nitrogen flow and NH₃ flow. This allows for a multitude of modifications to the process in which the films are deposited, which can then highlight the effects of the process parameters on silicon nitride robustness under etch conditions in the vapour phase HF system. These PECVD films were deposited onto 100 mm diameter <100> silicon wafers.
A screening experiment was designed to assess the effects of the deposition gas flows in the first instance. The standard silicon nitride deposition process was described in Chapter 4. The standard deposition process as used within the SMC, consists of 40 sccm of SiH\textsubscript{4}, 20 sccm NH\textsubscript{3} and 1960 sccm of N\textsubscript{2} which is a gas ratio of 2:1 of silane to ammonia. Using this process as a standard reference, investigations into the ratio between the silane and ammonia flows were conducted. The N\textsubscript{2} flow of 1960 sccm remained constant throughout all deposition processes. Processes investigating gas ratios of 1:1, 1.5:1, 2.5:1 and 3:1 between the SiH\textsubscript{4} and NH\textsubscript{3} were also used as part of this work.

Two additional deposition processes were used in the analysis. One of these was loosely based on process trends from the Applied Materials (AMAT) P5000 PECVD system and from literature describing a modified nitride film suitable for high UV transmittance in flash devices \cite{125}. This uses a ratio with a higher flow of ammonia (25 sccm) to silane (20 sccm). The other film, referred to as SiH nitride, uses 40 sccm of SiH\textsubscript{4} and removes all NH\textsubscript{3} from the deposition process. Both processes also utilised the 1960 sccm of N\textsubscript{2} flow. From these process descriptions, the results allowed for behaviours shown later in this chapter. The gas flows for each nitride film are shown in Table 5.1.

As part of the film analysis, a number of the different film types were deposited. Samples were deposited in the PECVD system at 300°C, additionally, samples from each gas ratio were annealed at increased temperatures in an oxidation furnace at atmospheric conditions as described in Chapter 3. The samples were further annealed at 400°C, 500°C and 600°C for 1 hour each within an oxidation tube furnace as described in Chapter 3. The furnace temperature was ramped up at 5°C per minute to the target temperature from the starting temperature of 250°C, then remained at the target temperature for 1 hour and returned to 250°C before the samples were removed from the furnace. Samples annealed above 600°C were not possible as the films would crack due to apparent stress in the film. Analysis by EDX, FTIR, ellipsometry and stress calculations will further identify important film parameters that affect the etching robustness of the nitride films.

The tests were used to assess the relative selectivity towards silicon dioxide films. Having established the most robust films, assessing selectivity as a process parameter is critical. PECVD silicon dioxide films as described in Chapter 4, were deposited onto
100mm <100> wafers as the silicon nitride films and etched under the same process conditions.

<table>
<thead>
<tr>
<th>Silane Flow (sccm)</th>
<th>Ammonia Flow (sccm)</th>
<th>Gas Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>20</td>
<td>1:1</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
<td>1.5:1</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>2:1</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td>2.5:1</td>
</tr>
<tr>
<td>60</td>
<td>20</td>
<td>3:1</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
<td>UV</td>
</tr>
<tr>
<td>40</td>
<td>0</td>
<td>SiH</td>
</tr>
</tbody>
</table>

Table 5.1 Gas flow parameters for deposition of Si$_3$N$_4$ films.

The PECVD deposition process was carried out at the pedestal temperature of 300°C and a plasma power of 60 W. The RF frequency was set at 13.56 MHz as it is the standard setting for RF generated plasma systems.

5.4 Characterisation Techniques for Nitride Films

5.4.1 Ellipsometry

Film analysis requires a number of methods for a full understanding: optical measurement of film thicknesses, ellipsometry for film thickness confirmation and values for refractive index, and FTIR and EDX analysis to understand the chemical change in the films based on the results of chemical composition.

Ellipsometry is an optical analysis method used for understanding the fundamental properties of a thin film. It works on the principle of light polarisation and the change that occurs through a film. It is sensitive enough to distinguish a large range of key film properties along with thickness, such as crystallinity, roughness and dopant levels with the application of the right model.

The light source and detector can either be at a fixed angle of incidence (\(\Phi\)), an angle of 70° is typical, or can have variable measurement angles for multiple measurement capabilities.
Light from the source passes through a polariser, shown in Fig. 5.2, and is then reflected from the surface of the sample. The reflected light then continues through an analyser to reach the detector. The detector system calculates the change in polarisation of the light reaching the detector. By applying the results of this into a defined model for the material under investigation, the key parameter \( n \), the refractive index, can be determined as well as the thickness of the film. The system used for this analysis is shown in Fig. 5.3.

5.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) analysis is a means for assessing the chemical composition of materials by analysing the absorption peaks corresponding to specific chemical bonds. This means that the levels of specific bonds can be assessed
associated with the film deposition processes. As the process for film deposition is modified, the varying levels of relative chemical compositions will change, for example: silicon nitride films will contain varying concentrations of Si-N, Si-H and N-H bonds. By changing the deposition process parameters, the expectation was to see bond absorption peaks change. The FTIR analysis helps understand the changes in the chemistry of the film and better understand what changes have significant effects on the etch behaviours of the specific films. In Figs. 5.4 and 5.5, a basic diagram of the principle of operation and the FTIR system are shown. A beam splitter was used to divide the beam into two beams, one reaching a fixed mirror and the other reaching a moving mirror. The reflected beams are recombined and then pass through the sample before reaching the detector. The results of interference between the two beams undergo Fourier transform to produce results in the frequency domain, which indicate the composition of the film.

![Figure 5.4 Standard FTIR configuration [129].](image)

As described in Chapter 3, a PECVD deposition system typically consists of two parallel plates, one acting as a cathode, the other as the anode. An argon-based plasma is generated between these plates when the feed gas is supplied to the chamber. This gas is ionised by the plasma and the ions are accelerated towards the plate due to a bias between the charged upper plate of the chamber and the grounded pedestal containing the sample to be deposited. The wafer is placed on the sample holder so that the ionised gasses begin to form specific material layers on the surface.
5.4.3 Energy Dispersive X-Ray spectroscopy (EDX)

Energy Dispersive X-Ray spectroscopy (EDX) and to a lesser degree, Secondary Ion Mass Spectroscopy (SIMS), were used as the means for understanding the film composition. EDX is an analysis tool that utilises the energy change in a film by analysis of the X-ray spectrum. High-energy beams of particles are focused onto the sample being studied. The incident beam may excite an electron in an inner shell of a molecule, which causes its ejection from the molecule. This ejection from the shell creates a vacancy or hole where the electron was previously. An electron from an outer, higher-energy shell fills the hole, and the difference in energy between the two shells may be released in the form of an emitted X-ray photon. The number and energy of the X-ray photons emitted from a specimen can be measured by an energy-dispersive spectrometer. The X-ray energies are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted; this allows the elemental composition of the specimen to be measured.

The results from EDX analysis are highly accurate, to within a measurement accuracy of ± 2%, but are only as accurate as the user performing the analysis. The standard software allows the users to specify the materials under investigation for fast analysis, but not including elements, which can lead to key information being omitted. The elemental concentrations are relative to the film under investigation, which will give a result based on the films rather than an explicit value for a chose element. The biggest limitation of the EDX analysis is its inability to measure hydrogen. As there is only one electron shell, there will be no energy difference between the implanted and ejected
shell and so its presence cannot be measured. The system used for this analysis is shown in Fig. 5.6.

![EDX system at Heriot-Watt University.](image)

Figure 5.6 EDX system at Heriot-Watt University.

SIMS, like EDX, is a powerful means of measuring energy changes in materials by the interaction of focused ion beams. Secondary ions are ejected from the material under investigation and the energies and structures are further analysed by a mass spectrometer. SIMS, unlike EDX, is able to detect hydrogen in the samples. SIMS requires a thin conductive layer to be sputtered onto the samples under investigation.

### 5.4.4 Stress Measurement Method

Film stress measurements were performed on each sample to assess how the stress induced by varying the deposition conditions is affected. This was conducted on both a FSM 500TC stress measurement system and a Dektak surface profilometer system within the SMC, both of which are shown in Fig. 5.7.
The FSM system measures wafer curvature by reflection of laser light incident on the surface of the sample over two measurements, the sample wafer without film and the sample wafer with film under measurement. From this, the stress induced on the wafer from the film can be determined. The information indicates the film properties and their influence on the etching rates of the films.

The Dektak system is a surface profilometer that measures the physical curvature of samples using a tip, which scans across the length of the wafer. By measuring the curvatures of the wafer before and after deposition of the nitride film, it is possible to calculate the stress across the sample wafer. In both measurement systems, the scan length is 80 mm across the wafers.

5.5 Experimental process
The etch process was the same for all of the HF etching processes performed on the tool as shown in Table 5.2. In maintaining a fixed etch process, the effects of the silicon nitride etching can be analysed.
Parameter & Value
---
HF Flow (sccm) & 150
N₂ Vaporiser Flow (sccm) & 100
LFM set-point (mg/min) & 10
Process Temperature (°C) & 5
Process Pressure (Torr) & 7.5

Table 5.2 Vapour phase HF etch process parameters.

From Chapter 4, it was observed that while oxide films and selectivities were much higher in this regime, nitride films showed an increased etching rate at the same time. Therefore, utilising a regime where nitride films are shown to etch faster will more clearly show the differences in etching rate.

The process conditions are set such that in 3 minutes of etching, an etch depth of 0.5 µm of PECVD silicon dioxide is achieved, an equivalent of 167 nm/min, similar to the rates achieved in Chapter 4 with a water bubbler unit. This process will compare an initial etch selectivity towards PECVD nitride films and subsequent process times will increase to 30 minutes due to the slow etching rates of nitride in contrast to oxide. The increase to 30 minutes of etching will allow the film to etch to a greater depth to improve measurement accuracy.

5.6 Results
5.6.1 Initial Screening Results
The first tests were used to investigate the etching of gas ratios of silane in relation to the gas flow of ammonia. Table 5.3 shows the etching rate results of these samples. A sample of the standard PECVD silicon dioxide was also included in this test as a reference for oxide film etching rates in the same process. This can be used to assess the selectivity values based on the etching rates of all the films under investigation in the same etch regime. The oxide film was deposited using the process described in Chapter 3 to a thickness of 1 µm. The wafers were diced into 2 cm x 2 cm chips and etched for 3 minutes at the same time as the nitride samples. The oxide chips were not included in the 30 minute etch process as it is not possible to deposit a thick enough film to last for the 30 minutes in the etch process. Table 5.4 shows the basic material composition and optical property based on the EDX, SIMS and ellipsometry analysis for the silicon and
nitrogen content (EDX), and from separate analysis methods, the hydrogen content (SIMS) and refractive index (ellipsometry).

<table>
<thead>
<tr>
<th>Film Description</th>
<th>Etch Depth at Time 3 minutes (nm)</th>
<th>Etch Depth at Time 30 minutes (nm)</th>
<th>Selectivity at 3 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard PECVD Oxide</td>
<td>500</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>UV Nitride</td>
<td>30.1</td>
<td>301.5</td>
<td>16.5:1</td>
</tr>
<tr>
<td>2:1 Silane Ammonia Ratio</td>
<td>22.2</td>
<td>236.3</td>
<td>21.4:1</td>
</tr>
<tr>
<td>Silane Nitride</td>
<td>5.5</td>
<td>70.8</td>
<td>69.6:1</td>
</tr>
</tbody>
</table>

Table 5.3 Results of initial test etching based on gas ratio changes.

<table>
<thead>
<tr>
<th>Analysis Method</th>
<th>EDX</th>
<th>SIMS</th>
<th>Ellipsometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film</td>
<td>Silicon Content %</td>
<td>Nitrogen Content %</td>
<td>Hydrogen Content %</td>
</tr>
<tr>
<td>UV Nitride</td>
<td>32.92 ± 2%</td>
<td>67.08 ± 2%</td>
<td>19 ± 5%</td>
</tr>
<tr>
<td>2:1 Ratio</td>
<td>37.04 ± 2%</td>
<td>62.96 ± 2%</td>
<td>14 ± 5%</td>
</tr>
<tr>
<td>Silane Nitride</td>
<td>44.18 ± 2%</td>
<td>55.82 ± 2%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 5.4 Silicon nitride properties from EDX, SIMS and Ellipsometry analysis.

5.6.2 Nitride Etching Behaviours with Metrology Techniques
As described in section 5.3, various silane and ammonia gas flows were utilised in preparation of nitride films with different material compositions. Section 5.4 described the main analysis methods that would be used to understand these compositional changes. In total, 7 different types of silicon nitride films were deposited as part of this analysis, as shown in Table 5.2. Each series had 4 subsequent variations: as deposited nitride at 300°C and samples annealed at 400°C, 500°C and 600°C respectively.

Figure 5.8 shows the effect of changing the silane/ammonia gas ratio on etch depth for the samples deposited at 300°C after annealing and after etching for 30 minutes. The
results show a decrease in etching rate as gas ratio increases in favour of silane gas flow. This is also shown for each gas series in Fig. 5.9. The etch depths also decrease after each anneal stage. The samples annealed at 500°C and 600°C show a close behaviour in terms of the overall etching rate, suggesting that above temperatures of 500°C, there is little change to the nitride that would further decrease nitride etching rates. The measurement error of the Nanospec300 system of ± 5 nm is included on the 300°C series, however the error is small in relation to the etch depths measured.

Figure 5.8 Etch depth nitride films deposited at all anneal temperatures as a function of increasing gas ratio mixtures.

Figure 5.9 Etch depth values as a function of the anneal temperature for different ratios of SiH₄:NH₃ gas ratio.
5.6.2.1 Results of Nitride Etching and Refractive Index

Ellipsometry was used to obtain the refractive index of the nitride films that were deposited and annealed in preparation for etching. The real $n$ values of refractive index were measured at the wavelength of 650 nm. Fig. 5.10 shows the RI values as a function of the gas ratio.

![Graph showing refractive index as a function of silane and ammonia flows at all anneal temperatures.](image)

Figure 5.10 Refractive Index as a function of silane and ammonia flows at all anneal temperatures.

Figure 5.11 shows the effect of the etching depth with relation to refractive index at all anneal temperatures. The film thickness measurement error of the Nanospec3000 system is also shown in the error bars. The refractive index as already discussed, is considered as a key identifier of the material robustness, such that industrial designs will specify RI values for nitride films at the design stage. The samples with similar RI after an anneal process are shown to have decreasing etching rates as shown in Fig. 5.11. Figure 5.12 shows the effect of increasing anneal temperatures for each gas ratio on the RI values of the samples.
5.6.2.2 Results of Nitride Etching and FTIR measurements

FTIR analysis provides information on relative changes in absorbance in the film under investigation. The FTIR analysis can distinguish relative changes in specific wavenumber values that relate to specific chemical bonds. The results of the Si-H bond at 2300 cm\(^{-1}\) and N-H bond at 3700 cm\(^{-1}\) in Figs. 5.13 to 5.16 show distinct changes across the temperature range. This change in absorption at these key peaks with increasing anneal temperatures is shown in Figs. 5.17 and 5.18.
Figure 5.13 FTIR trace comparison of all gas ratios deposited at 300°C.

Figure 5.14 FTIR trace comparison of all films at 400°C.
Figure 5.15 FTIR trace comparison of all films at 500°C.

Figure 5.16 FTIR trace comparison of all films at 600°C.
Figure 5.17 Relative change in absorption peak with increasing anneal temperature at the 2300 cm⁻¹ wavenumber for Si-H bonds.

Figure 5.18 Relative change in absorption peak with increasing anneal temperature at the 3700 cm⁻¹ wavenumber for N-H bonds.

5.6.2.3 Results of Nitride Etching and EDX measurements

EDX analysis provides relative compositional changes in the silicon nitride films deposited in this work. The EDX technique is unable to determine hydrogen as previously described, but is able to show the change in both silicon and nitrogen contents. These results, along with those in Fig. 5.19, show the effect of increasing silicon content from 35% to 47% on the etch depth obtained for the etch time of 30
minutes. Figure 5.20 shows the effect of annealing temperature on the silicon content of the nitride films. Figure 5.21 includes EDX measurement error indicators of ± 2 %.

Figure 5.19 Etch depth nitride films with increasing anneal temperature as a function of silicon content.

Figure 5.20 EDX analysis of silicon content with increasing anneal temperature.

Fig. 5.21 shows the same etching depth results as Fig. 5.19, but plotted as a function of the nitrogen content in the nitride films. Figure 5.22 shows the effect of nitrogen content for each gas ratio with increasing annealing temperatures.
Figure 5.21 Etch depth nitride films with increasing anneal temperature as a function of nitrogen content.

Figure 5.22 EDX analysis of nitrogen content with increasing anneal temperature.

Figure 5.23 shows the relationship between the RI from the ellipsometry analysis and the silicon/nitrogen ratio in the films from the EDX analysis. The refractive index increases as the silicon content increases.
5.6.2.4 Results of Nitride Etching and Film Stress Measurements

Figures 5.24 to 5.30 show the results of etching rate of nitride in relation to the stress of the film. The figures show the correlation between etching rates, increasing annealing temperature and the behaviour of stress for each nitride sample. It was found that etching rates decrease with increasing anneal temperature; the stress behaviours of the nitride films follows these trends very closely with each of the nitrides deposited. As temperatures rise above 500°C, stress in each sample is shown to increase. It was found the annealing at temperatures above 600°C was unsuitable, as the nitride films would crack under apparent stress in the film.

Figure 5.24 Comparing stress and nitride etching rates with increasing anneal temperatures with 0.8:1 gas ratio - UV nitride.
Figure 5.25 Comparing stress and nitride etching rates with increasing anneal temperatures with 1:1 gas ratio.

Figure 5.26 Comparing stress and nitride etching rates with increasing anneal temperatures with 1.5:1 gas ratio.
Figure 5.27 Comparing stress and nitride etching rates with increasing anneal temperatures with 2:1 gas ratio.

Figure 5.28 Comparing stress and nitride etching rates with increasing anneal temperatures with 2.5:1 gas ratio.
Figure 5.29 Comparing stress and nitride etching rates with increasing anneal temperatures with 3:1 gas ratio.

Figure 5.30 Comparing stress and nitride etching rates with increasing anneal temperatures with 4:0 gas ratio - SiH nitride.

5.7 Discussion of Results
5.7.1 Analysis of the Initial Screening Results
Table 5.1 shows the gas flows used for film deposition. All films were deposited to an approximate thickness of 1 µm and the thickness values were obtained by Nanospec3000 measurements. As described in Chapter 3, the PECVD films were deposited on the STS PECVD system at the temperature of 300°C. In Table 5.3, the initial etching results of the three PECVD nitride films are provided along with the etching depth of a standard PECVD oxide film and the calculated results of selectivity. The differences in nitride material composition are described in Table 5.4. The results
show that in terms of the basic deposition gas ratio parameters, as the silane content increases in relation to the ammonia flow, the etching rate decreases. The etch rates are found to decrease from 10 nm/min to 2.4 nm/min under the same etch conditions as the gas ratio of silane to ammonia is increased from 0.8:1 to the SiH nitride respectively. This change in etching rate correlates with a number of compositional factors: an increase in silicon content and increased RI of the nitride films. The hydrogen content measured with SIMS analysis and shown in Table 5.4 agrees with those previously reported in literature [110]. The hydrogen content was measured in the region of 15% at the gas mix ratio of 0.92 and 13% at the SiH₄/NH₃ ratio of 1.5. In addition to the UV nitride film, information provided in an Applied Materials PECVD training manual [126], states that the hydrogen content of UV nitride is typically in the region of 20%, further agreeing with SIMS analysis.

The PECVD oxide film, which was etched for three minutes alongside each of the nitride samples, provided a reference value for defining the selectivity of the PECVD oxide against PECVD nitride films. As the silicon content within the nitride increases, etch rate for this film decreases leading to an increased selectivity of oxide to nitride from 16:1 to 65:1, a clear improvement to the results obtained in Chapter 4 and also a substantial improvement over the highest reported selectivities of 7.4:1 in existing literature [99].

The etching mechanism of silicon nitride in HF etching has been described previously in Chapter 4. The HF process conditions used in these experiments show similar etching rate behaviours for the oxide films at 167 nm/min and the same nitride films at 7.3 nm/min as those reported under similar process conditions in the work of Chapter 4. From Table 5.4, it is clear that the deposition processes using higher silane to ammonia ratios lead to nitride films that incorporate greater levels of silicon. This increase in silicon content and conversely, a reduction in nitrogen content, leads to a reduction in the density of Si-N bonds within the nitride film, leading to a reduction in the speed at which the Si-N bonds interact with the HF molecules, thus a reduction in the overall etching rate of the nitride films.

5.7.2 Analysis of Nitride Etching Rates with Metrology Techniques

Figure 5.8 shows the change in etching behaviour of the nitride films as the gas ratio is increased towards a greater level of silane over ammonia. It is clear that as anneal
temperature is increased, etching depths decrease. This trend continues at anneal temperatures up to 500°C, but do not substantially change at the highest temperatures of 600°C. This would appear to show a plateau in etching rates with annealing. As samples were not annealed at temperatures above this, it is unclear if etching rates would continue to remain constant with those at 500°C and 600°C, or whether the rates would decrease further as samples were annealed at higher temperatures. When assessing the behaviour by gas ratio in Fig. 5.9, this plateau effect is again clear at 500°C and 600°C.

5.7.2.1 Analysis of Nitride Etching by Ellipsometry

From ellipsometry measurements, the refractive index (RI) was calculated. The ellipsometer is capable of providing a correlation of experimental data to the defined model that a user creates within the analysis software. This includes defining the seed layer and the nitride film thickness, which are all known prior to analysis. Ensuring the data accuracy allows the accuracy of the model for the calculation of the RI and the extinction coefficient. The extinction coefficient is defined as the imaginary component of the complex index of refraction as defined in equation (5.1) [127],

$$\bar{n} = n + ik$$

(5.1)

Where $\bar{n}$ is the complex refractive index, and $n$ and $k$ are the refractive index and extinction coefficient respectively. The ellipsometry data generated shows good correlation between the experimental information and the model as collated within the analysis software over three measurement passes between 65° - 75°, at 5° increments. An example of the output is given in Fig. 5.31. This confirms the data provided to the software such as the substrate wafer thickness and nitride thickness are correct since the red model fit and green results obtained with three experimental passes closely match. This confirmation is to ensure the RI values calculated are accurate. If the model fit is wrong due to incorrect film data, the subsequent analysis cannot be considered accurate.
The standard refractive indices within the semiconductor industry and by extension, the MEMS industry, take the values of a material at the wavelength of 650 nm, which is where RI values were taken from for this study. The system also shows the calculated n and k values for each film, with an example of this shown in Fig. 5.32.

Figure 5.31 Ellipsometry confirmation of material properties by experimental analysis against model at 3 measurement angles.

Figure 5.32 Ellipsometry optical constant output of refractive index “n” and extinction coefficient “k” values.
Prior to 9-point measurement of the films in the Nanospec3000 system at the completion of the 30 minute etching process, each sample was placed on a hotplate at 200°C for 30 seconds in an extracted environment. The extract is required as the NH₄F residue decomposes into ammonia gas and HF vapour. The mechanism has been described as occurring when the reactant fluorine generated by dissociated HF reacts with nitrogen and hydrogen in the silane based PECVD nitride films, which has been previously reported [21, 29]. This residue was reported to be an ammonium fluoride based by-product that is formed on the surface of the nitride. Under measurement, this residue impedes the accuracy of the optical measurement of the film. By removing this film from the sample prior to measurement, the fit of the measurement is within expected regions, resulting in accurate film thickness data.

Figure 5.10 describes the correlation between increase in silane flow and RI. Figure 5.11, similar to Fig. 5.8, shows a decrease in etch depth with increasing RI, which from Fig. 5.10 correlates to an increase in silane flow. As has been shown, with an increase in the annealing temperature, the etching depth decreases until 500°C. At 300°C, the UV nitride is the largest etching depth of these films with a total etch depth of 285 nm in 30 minutes and the value is halved after annealing at both 500°C and 600°C. The silane nitride, with the highest silane flow used among all the samples, reached an etch depth of 76.5 nm, only 25% of the total etched depth of the UV nitride. Figure 5.12 shows the significant increase in RI values in the SiH nitride more clearly with a silicon content increase. The anneal temperature has a small effect on RI in each nitride, similar to the behaviours shown in Fig. 5.9.

5.7.2.2 Analysis of Nitride Etching by FTIR

The FTIR analysis can show absorption peaks at wavenumbers relating to specific chemical bonds and as such will indicate regions of increasing or decreasing chemical bond concentration. All samples across the annealing temperature range show peaks at the wavenumbers in the region of 3700 to 3300 cm⁻¹, 2400 to 2100 cm⁻¹, 750 cm⁻¹ and 500 cm⁻¹. These peaks correlate with the chemical bonds shown in Table 5.5.

From Fig. 5.13, the different deposition processes show similar chemical compositions, however the peak between 2400 and 2300 cm⁻¹, the Si-H peak, shows variation. In fact, this peak appears to be the most obvious change in the traces along with the peak at 3700 cm⁻¹.
After annealing the samples at 400°C, 500°C and 600°C, the samples were tested to measure the change in material composition. The FTIR results show the effects on the films with increasing anneal temperatures. Their respective trace outputs are shown in Figs. 5.14, 5.15 and 5.16. The results show a change in peak absorbance due to increasing annealing temperature. In fact, assessing the change in both of these major peaks across all anneal temperatures with the different gas ratios shows the major chemical modification to the films in terms of the FTIR analysis after the first anneal at 400°C. Subsequent anneals at 500°C and 600°C do not change the material absorption any further. This is highlighted in Figs. 5.17 and 5.18.

As the films show a large change between 300°C and 400°C, but very little further change after, this would suggest that an initial anneal causes this effect. While there may be a change in the hydrogen content that cannot be determined in this work, its lack of further change after initial annealing suggests it is not the cause for the continuing decrease in the etching rates observed in Figs. 5.8 and 5.11. The previous literature however, has described this phenomenon when performing a similar analysis on similar PECVD films under wet etching conditions [123, 124]. In both studies, anneal processes were carried out at temperatures greater than 650°C, however the results described in Figs. 5.17 and 5.18 suggest that the incorporated hydrogen within the PECVD nitride is released from the nitride at lower temperatures than previously reported. In both the work of this chapter and the literature however, it is clear that the

<table>
<thead>
<tr>
<th>Bond</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-N</td>
<td>490-430</td>
<td>[111]</td>
</tr>
<tr>
<td>Si-N</td>
<td>500-480</td>
<td>[106]</td>
</tr>
<tr>
<td>Si-N</td>
<td>870-720</td>
<td>[111]</td>
</tr>
<tr>
<td>Si-N</td>
<td>890-850</td>
<td>[106]</td>
</tr>
<tr>
<td>N-H/N-H₂</td>
<td>1150</td>
<td>[111]</td>
</tr>
<tr>
<td>N-H</td>
<td>1170</td>
<td>[106]</td>
</tr>
<tr>
<td>N-H₂</td>
<td>1550</td>
<td>[111]</td>
</tr>
<tr>
<td>Si-H</td>
<td>2140</td>
<td>[111]</td>
</tr>
<tr>
<td>N-H</td>
<td>3330</td>
<td>[111]</td>
</tr>
<tr>
<td>N-H</td>
<td>3346</td>
<td>[106]</td>
</tr>
</tbody>
</table>

Table 5.5 Wavenumbers describing FTIR bonds.
change is distinct and does not vary significantly once the initial hydrogen release occurs. The mechanism for the decreasing etching rates with increasing anneal temperatures however, cannot be fully explained by the reduction of the hydrogen content within the film either as the etch rate of all nitride gas mixtures continues to decrease at each of the three anneal temperatures. While the previous results show a correlation between the gas ratios and etch depth in each temperature range, the ellipsometry and FTIR analysis do not explain the fundamental change in the nitride films across the increased annealing temperatures that would explain the continued decrease in etching rate.

As the silane flows increase from the UV nitride to the SiH nitride films, the concentration of Si-N bonds decreases as the nitrogen concentration is reduced within the film, thus reducing the ease of nitride etching. This does not account for the change in etching rates with increasing anneal temperature however. While the FTIR analysis does suggest that there is a slight change in absorption with increasing anneal temperature, but higher temperatures did not change the material properties any further.

Assessment of etch depth based on the RI values in Fig. 5.10 and Fig. 5.11 includes the effects of the annealing temperatures between 400°C to 600°C. It is clear that approaching the higher temperatures, the etch rate and RI values again begin to reach a common behaviour trend above 500°C which would suggest there is a plateau effect on the material composition which was also shown in Figs. 5.17 and 5.18.

5.7.2.3 Analysis of Nitride Etching by EDX

EDX analysis is able to provide information regarding silicon, nitrogen, oxygen, carbon and fluorine content. In all results, carbon and fluorine values were below the detection level and as such, only information on silicon and nitrogen atoms in the films is reported. The samples were inspected by EDX analysis and the film properties are shown in Table 5.6. This analysis was able to clearly show the silicon and nitrogen contents of the various nitride films based on the different gas ratio mixtures. The ellipsometry work has previously shown the refractive index of the films with respect to gas ratio in Fig. 5.10. The addition of the EDX analysis further clarifies the composition in the films produced using these gas ratios.
<table>
<thead>
<tr>
<th>Gas Ratio</th>
<th>Relative Silicon Content (%)</th>
<th>Relative Nitrogen Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8-1 (UV)</td>
<td>34.93</td>
<td>65.07</td>
</tr>
<tr>
<td>1-1</td>
<td>37.86</td>
<td>62.14</td>
</tr>
<tr>
<td>1.5-1</td>
<td>38.93</td>
<td>61.07</td>
</tr>
<tr>
<td>2-1</td>
<td>41.24</td>
<td>58.76</td>
</tr>
<tr>
<td>2.5-1</td>
<td>40.96</td>
<td>59.04</td>
</tr>
<tr>
<td>3-1</td>
<td>41.27</td>
<td>58.73</td>
</tr>
<tr>
<td>4-0 (SiH)</td>
<td>47.32</td>
<td>52.68</td>
</tr>
</tbody>
</table>

Table 5.6 Silicon and Nitrogen from EDX analysis for the deposited gas ratios at 300°C.

From EDX analysis, a typical output trace is shown in Fig. 5.33. As can be expected from an analysis of silicon nitride films, large peaks of silicon and nitrogen are observed with negligible values of oxygen, fluorine and carbon, which are all below the detection limits. Table 5.6 shows the results for the various films deposited at 300°C.

As the gas ratio increases, the relative silicon content is increased from 35% to 47% by increasing the amount of silane used in the deposition process. The etching rates of the nitride films relating to the increasing silicon content with the nitride films are shown in Fig. 5.19 before and after annealing. The Si content however, appears largely unchanged while considering the EDX measurement error of ± 2%. As silane is the
primary silicon feed source for these films, an increase here would naturally lead to an increased Si content in the film which has been shown to increase RI values with increasing gas ratio. As can be shown, nitrogen content in the film decreases in relation to the increase in silicon. EDX analysis of silicon content for each film with increasing annealing temperature however, shows there are small incremental changes in the silicon content of the films with the exception of the silane nitride, which increases by over 6%. Figure 5.20 shows the change in Si content across each gas ratio with increasing anneal temperature. While it is clear that the increased ratio leads to an increase in Si content, subsequent anneals do not then further change these values. The inverse of silicon content in nitrogen is described in Figs. 5.21 and 5.22 where the inverse behaviours to those of silicon can be seen. In Fig. 5.10, the RI values were plotted against deposition gas ratio. By using the EDX results, the values of RI could be plotted as a function of the silicon to nitrogen ratio. The results show a very clear trend as the Si/N ratio increases but is consistent across all temperature ranges. Alongside the FTIR and ellipsometry results, EDX results cannot describe the change in the nitride films that leads to a continuing decrease in etching rate with increasing annealing temperature.

**5.7.2.4 Analysis of Nitride Etching by Film Stress**

The modification to material properties such as silicon and nitrogen content has been described in this work. The results from the EDX, ellipsometry and FTIR measurements have demonstrated the effects and the subsequent changes that occur to nitride films under varying deposition conditions. The results from all these techniques have shown the change in silicon content, nitrogen content, refractive index and the relative change in the incorporated Si-H and N-H bonds within the films due to the gas flow changes at deposition or post deposition anneals. It is clear that as silicon content increases due to the increasing silane flow, the RI increases and the etch robustness is improved. This is a commonly described behaviour in the literature [120, 121, 122, 123, 124], which clearly describes the observed etching behaviours. One effect unexplained by the analysis in this chapter or answered in the literature, is the decrease in etching rate when the annealing temperature is increased. While Figs. 5.17 and 5.18 have described the change in the hydrogen content within the film after annealing at 400°C and above, there is little change in the film from the FTIR analysis above 400°C that would explain the continuing trend in decreasing etch rate as anneal temperatures increase. The internal stresses of the samples measured in this study are assessed to understand if a
correlation exists between the etching behaviours and the increasing anneal temperatures. Figures 5.24 to 5.30 describe the change in stress in relation to the nitride etching rates across all anneal temperature and gas ratio mixtures.

The stress measurements of the films were performed on each wafer as described in section 5.4.4. The stress results are compared against the etching rates similar to the approaches in EDX, FTIR and ellipsometry analysis. The wafer bow was measured on each sample before and after deposition of the film to calculate the stress generated by the silicon nitride film. Both the FSM and Dektak systems were used to compare the wafer bow of the samples. The Dektak system is a physical measurement of the wafer using a mechanical probe, while the FSM uses reflected laser light to measure the curve of the sample. The measurements were compared to each other based on the maximum heights of the bow measured. A constant difference was found between the Dektak and FSM values. The Dektak measurements were a consistent 48% less than those measured by FSM, as shown in Table 5.7 and could be used to scale any results measured on either system. The designations a, b, c and d refer to anneal temperature of the sample: a - 300°C, b - 400°C, c - 500°C and d - 600°C.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Dektak Maximum Bow (µm)</th>
<th>FSM Maximum Bow (µm)</th>
<th>Dektak/FSM ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>66.7</td>
<td>126.43</td>
<td>0.53</td>
</tr>
<tr>
<td>11c</td>
<td>59.2</td>
<td>109.66</td>
<td>0.54</td>
</tr>
<tr>
<td>251d</td>
<td>59.7</td>
<td>114.25</td>
<td>0.52</td>
</tr>
<tr>
<td>SiHa</td>
<td>68.2</td>
<td>129.84</td>
<td>0.53</td>
</tr>
<tr>
<td>SiHc</td>
<td>30.5</td>
<td>61.5</td>
<td>0.50</td>
</tr>
<tr>
<td>UVb</td>
<td>58.1</td>
<td>109.37</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 5.7 Comparison of offset in bow measurement in Dektak and FSM measurement systems.

The offset was used to correlate samples that could not be measured on the FSM system. Due to its use of a laser as the means of measuring bow, if the sample was not reflective enough for the detector, the bow could not be measured. This ratio in the systems allows the FSM data to be aligned with the values found in the Dektak measurement. The wafer bow can be used to calculate the stress in the film based on the initial stress in the substrate and the substrate with a deposited film on its surface.
Figures 5.24 to 5.30 describe the trend of film stress with increasing anneal temperature against the etching rates of nitride films. In all examples, there is a clear trend that the stress in the film decreases from 300°C to 500°C. The literature work has shown that the stress in nitride films increases when silane flows are reduced or when ammonia is increased during deposition [122], the higher etch rate has been more closely linked to the gas flows and the stress reported as a secondary effect. The EDX analysis has shown that as anneal temperatures increase, the material composition of the film does not change significantly enough to relate to the change in etching rate. An increase in silicon or subsequent decrease in nitrogen content by increasing gas ratio does change the overall etching behaviour as observed in this work. The results in the literature do not show the nitride composition data from an EDX analysis to confirm the cause of the change in stress of the films. The work does confirm that reduced hydrogen content would lead to a decrease in etching rate as can be inferred from this study, but again, the change cannot be observed across all samples without full hydrogen analysis which could not be performed in this study. The results from Figs. 5.24 to 5.30 suggest however that increasing annealing temperatures lead to a further modification of the film. While this may not be a compositional change, as no change is found through material analysis by EDX or FTIR, it is believed that a subsequent change at the atomic level must occur, which can be identified by the change in the stress within the nitride films.

Table 5.8 shows the results of stress in each gas flow series with increasing anneal temperature. It can be seen in Table 5.8 and Figs. 5.24 to 5.30 that the stress in each series decreases on the whole from values at 300°C, there is a consistent increase in the stress again at 600°C. As described earlier, when performing annealing of the nitride samples in the oxidation furnace at temperatures above 600°C, the nitride would be found to be cracked and flaking from the silicon surface. It was believed that the temperature was sufficiently high enough to induce internal stress in the film to break the nitride film.

The results in Table 5.8 would suggest that the increase in stress again at 600°C may have reached a threshold point in the film. As the stress in the film is relaxed due to the increased annealing temperatures, the etching rates as shown in Table 5.9 decrease in line with this effect. However the nitride etch rate continues to reduce even at 600°C when the stress begins to increase again. If samples were to have survived an anneal at
700°C, one would expect the etch rate to remain low, while the stress would continue to rise again as the increased temperatures began to induce stress leading to the cracking observed in samples that were annealed but not used in this work at the 700°C temperature.

<table>
<thead>
<tr>
<th>Gas Ratio</th>
<th>Deposition Temperature 300°C</th>
<th>Anneal Temperature 400°C</th>
<th>Anneal Temperature 500°C</th>
<th>Anneal Temperature 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 (UV)</td>
<td>979</td>
<td>674</td>
<td>444</td>
<td>466</td>
</tr>
<tr>
<td>1</td>
<td>711</td>
<td>1190</td>
<td>458</td>
<td>704</td>
</tr>
<tr>
<td>1.5</td>
<td>574</td>
<td>469</td>
<td>211</td>
<td>678</td>
</tr>
<tr>
<td>2</td>
<td>1180</td>
<td>713</td>
<td>453</td>
<td>743</td>
</tr>
<tr>
<td>2.5</td>
<td>891</td>
<td>728</td>
<td>383</td>
<td>617</td>
</tr>
<tr>
<td>3</td>
<td>1010</td>
<td>773</td>
<td>603</td>
<td>694</td>
</tr>
<tr>
<td>4 (SiH)</td>
<td>904</td>
<td>700</td>
<td>402</td>
<td>769</td>
</tr>
</tbody>
</table>

Table 5.8 Nitride film Stress in mega Pascal (MPa) with respect to gas flow ratio and anneal temperature.

<table>
<thead>
<tr>
<th>Gas Ratio</th>
<th>Deposition Temperature 300°C</th>
<th>Anneal Temperature 400°C</th>
<th>Anneal Temperature 500°C</th>
<th>Anneal Temperature 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 (UV)</td>
<td>9.501</td>
<td>7.758</td>
<td>5.31</td>
<td>5.35</td>
</tr>
<tr>
<td>1</td>
<td>8.81</td>
<td>7.47</td>
<td>4.78</td>
<td>4.25</td>
</tr>
<tr>
<td>1.5</td>
<td>7.17</td>
<td>6.38</td>
<td>5.03</td>
<td>4.74</td>
</tr>
<tr>
<td>2</td>
<td>7.51</td>
<td>5.05</td>
<td>2.92</td>
<td>2.55</td>
</tr>
<tr>
<td>2.5</td>
<td>5.49</td>
<td>3.12</td>
<td>2.12</td>
<td>2.19</td>
</tr>
<tr>
<td>3</td>
<td>5.45</td>
<td>4.26</td>
<td>2.57</td>
<td>2.31</td>
</tr>
<tr>
<td>4 (SiH)</td>
<td>2.55</td>
<td>1.95</td>
<td>1.01</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table 5.9 Etch rate of silicon nitride films with respect to gas ratio and anneal temperature.

As the overall aim was to assess whether the subsequent post annealing could improve etch selectivity, the final assessment however is to observe the change in selectivity between two PECVD oxide and nitride films. From Table 5.3, the PECVD oxide film etch rate was approximately 167 nm/min. Using this value and the results of the etch
rates in nm/min from Table 5.9 for nitride etch rates observed, a final selectivity ratio can be calculated between PECVD oxide and nitride films.

<table>
<thead>
<tr>
<th>Gas Ratio</th>
<th>Deposition Temperature 300°C</th>
<th>Anneal Temperature 400°C</th>
<th>Anneal Temperature 500°C</th>
<th>Anneal Temperature 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8 (UV)</td>
<td>17.58</td>
<td>21.53</td>
<td>31.45</td>
<td>31.21</td>
</tr>
<tr>
<td>1</td>
<td>18.96</td>
<td>22.36</td>
<td>34.94</td>
<td>39.29</td>
</tr>
<tr>
<td>1.5</td>
<td>23.29</td>
<td>26.18</td>
<td>33.20</td>
<td>35.23</td>
</tr>
<tr>
<td>2</td>
<td>22.24</td>
<td>33.07</td>
<td>57.19</td>
<td>65.49</td>
</tr>
<tr>
<td>2.5</td>
<td>30.42</td>
<td>53.53</td>
<td>78.77</td>
<td>76.26</td>
</tr>
<tr>
<td>3</td>
<td>30.64</td>
<td>39.20</td>
<td>64.98</td>
<td>72.29</td>
</tr>
<tr>
<td>4 (SiH)</td>
<td>65.49</td>
<td>85.64</td>
<td>165.35</td>
<td>163.73</td>
</tr>
</tbody>
</table>

Table 5.10 Relative selectivity of PECVD oxide to nitride films with respect to gas ratio and anneal temperature.

In Chapter 4, the greatest selectivity between PECVD oxide and nitride films was 26.6:1. From Table 5.10, at 300°C, by increasing the gas ratio from 2:1 to a silane rich gas mixture that required no ammonia, the selectivity is increased to 65:1. Annealing the nitride increases selectivity further to 164:1 in the SiH film. This value would be ideally reached where the oxide film is deposited on top of the nitride film after having been annealed and is acting as an etch stop. However, if the nitride were to be annealed after deposition above the oxide layer, the oxide behaviours could also be affected by the anneal stage and the selectivity may also be affected. The results have shown throughout the metrology methods that high annealing temperatures can be utilised to reduce the etching rate of the nitride films. Above anneal temperatures of 500°C, there is no clear gain in etching behaviours as confirmed by both the etching rates in Table 5.9 and the selectivities in Table 5.10. It is clear that a reduction in the stress in the PECVD nitride films due to the anneal process causing a further compositional modification can reduce the etching rates. This was clearly demonstrated at each of the chosen gas ratios for nitride deposition.

5.8 Summary

This study focused on the deposition and post processing conditions applied to nitride films to increase the etch robustness under the same vapour phase HF etching.
conditions as described in Chapter 4. EDX, FTIR, ellipsometry and stress analyses were performed to understand the compositional changes in the film and the effects on etch robustness. The etching rates of nitride films have been shown to decrease from 9.5 nm/min to 2.5 nm/min with an increasing silane to ammonia gas flow ratio of 0.8:1 using 20 sccm of SiH$_4$ and 25 sccm of NH$_3$ to a silane only based nitride film using 40 sccm of SiH$_4$. Upon annealing at 500°C, these etch rates decreased to 5.3 nm/min and 1 nm/min respectively, thus showing not only a change in material properties with increased silane flows, but a structural change within the film in the annealing processes.

The EDX analysis could discern the change in silicon and nitrogen content within the nitride film as the ratio of silane to ammonia is increased in favour of the silane flow, however no change was found as the anneal temperature increased. Increasing silane flows led to higher levels of silicon from 35% to 47% with a 0.8 ratio to a SiH deposition. In these regimes, the refractive index was also observed to increase in line with silane flow from 1.91 to 2.23. The analysis after annealing the films show no significant impact in the respective silicon content, which is measured at 35.5% and 47% respectively. The FTIR analysis was able to observe a change at two distinct absorption peaks associated with Si-H and N-H, which agrees with the existing literature describing the modification of hydrogen content after annealing. This change was observed by annealing the samples at 400°C after deposition at 300°C, subsequent increases in anneal temperature to 500°C and 600°C do not show any further change in the material composition as expected.

The stress analysis for each gas ratio however, shows a correlation between etching rates and anneal temperatures that other analysis techniques do not. As the anneal temperature is increased, stress is shown to decrease. The decrease in stress relates to a similar decrease in etching rate. The role of stress in nitride films has been discussed in the previous literature however there has not been an outright correlation with stress in nitride films and etching rates in these films. In fact, there has been no reported link in literature explicitly made between the nitride film stress and its effect on the HF vapour phase etching rate. While some of these analysis techniques have been considered in the literature, a complete analysis has not been made. The annealing process appears to further change the property of the nitride film in a manner that can be indicated by the analysis of the stress in the film. This suggests that while the composition appears to be
unchanged, an atomic reorganisation of the atoms may be causing the change in the stress of the films.

The results have shown that selectivity of oxide films to nitride can be improved by modification of the standard nitride film: by changing the gas ratio to a regime where more silane is used and subsequent annealing can improve selectivity. This has led to PECVD oxide and nitride film selectivities from 17:1 to 31:1 for a 0.8 silane to ammonia gas ratio when increasing the temperature from 300°C to 600°C, while a silane only based nitride shows selectivities ranging from 65:1 to 164:1. A substantial improvement by a factor of 5 has been obtained over the values obtained in Chapter 4. Application of these techniques has the potential to allow devices using PECVD oxide and nitride films to realise critical designs where final dimensions must be more carefully controlled.
Chapter 6 Continuous Flow Vapour Phase XeF$_2$ Etching of Silicon and Related Films

6.1 Introduction

In Chapter 2, XeF$_2$ etching of silicon was reviewed. In the previous work, the hardware configurations were based on a pulsed-processing system. This design utilises the natural vapour pressure of XeF$_2$ at approximately 4 Torr. These systems use an expansion chamber as an intermediate stage between the solid XeF$_2$ source material and the etch chamber. The expansion chamber is filled with XeF$_2$ vapour slowly until the pressure reaches a pre-defined value. At this point the XeF$_2$ is introduced into the etch chamber and the silicon etching can be initiated. Users can allow etching until either the reactive gas is fully consumed, or evacuate the chamber after fixed time interval. The system can be operated with multiple cycles, or pulses - the number of time intervals being dependant on the etch requirement, hence the term pulsed processing.

Continuous flow processing, utilises a continuous supply of XeF$_2$ into the etch chamber. Whereas in the pulsed system, the XeF$_2$ is in a container with a single outlet allowing the natural vapour of XeF$_2$ to amass in the expansion chamber, the continuous flow XeF$_2$ processing method has the XeF$_2$ in a solid source “bubbler”. Unlike the liquid bubblers described in Chapter 4, in which nitrogen gas flows through a liquid, memsstar have designed a solid source “bubbler” which introduces a carrier gas into the bottom of the bubbler to evenly disperse the carrier gas allowing for a more even distribution over the solid source. This generates a higher saturation of the carrier gas with XeF$_2$ in vapour phase, which is introduced into the process chamber.

This changes the way in which processing can be accomplished. In the literature, etch rates in pulsed processing can reach 10 µm/min when etching polysilicon films, and up to 1.9 µm/min when etching single crystal silicon [62,70]. To our knowledge, there is little information regarding hardware configurations utilising the continuous-flow design, and certainly no description of the process behaviours or their contrast to “pulsed” methods. This is not only in relation to silicon etch rates, but also in material compatibilities and the general process behaviours.
One report of a continuous flow XeF\textsubscript{2} system as part of the release stage for a device was described in 2007 [67]. This reported the release of a device using the memsstar Xeric silicon etch system. The group investigated the etch properties of undercutting polysilicon films with a process pressure of 3.5 Torr and 100 sccm of nitrogen carrier gas through the solid source bubbler during the etch process. The group compared etching rates of silicon by both XeF\textsubscript{2} and SF\textsubscript{6} from an inductively coupled plasma etching process. They used a range of aperture sizes to assess the effect on etch rates in their test design with etch rates of 11.6 \(\mu\text{m/m}\) being reported, which is substantially larger than the 1.9 \(\mu\text{m/m}\) reported previously [70]. The group also found that apertures could affect the etch rates depending on etch pressures. It was shown that SF\textsubscript{6} is more readily affected by loading effects with smaller open areas than the behaviour of XeF\textsubscript{2} etching, however in both cases, reduced process pressures minimised the loading effects seen on silicon etching. The biggest benefit the team gained from XeF\textsubscript{2} etching was etch selectivities of 1000:1 against thermally grown oxide films against the 300:1 result of SF\textsubscript{6}. This highlights a step forward in showing the benefits of XeF\textsubscript{2} etching in the fabrication of next generation devices.

In this chapter, the results of continuous flow XeF\textsubscript{2} etching on the memsstar Alpha Silicon system is described. The behaviours associated with etching processes are reported alongside material selectivities towards key functional materials.

### 6.2 Hardware Design and Configuration

The etch system used for the work in this chapter is the memsstar Orbis Alpha silicon etch system. This is a compact version of the memsstar production system, which has the same overall functionality but with a footprint more suited to research and development. The difference between the two systems is not significant, and the method by which the etching is conducted is the same. As already described, a carrier gas of nitrogen, production grade (99.95% Purity), is introduced into the bubbler. Within the bubbler, there is a dip tube with a cross head and mesh design, which allows better saturation of the carrier gas with XeF\textsubscript{2}.

Figure 6.1 shows the schematic design for the “bubbler” as used in this work. The specific details have been omitted due to confidentiality regarding the design.
Figure 6.1 Schematic of a solid source bubbler for XeF2 systems [139].

Figure 6.2(a) is a schematic of the continuous flow process system used in this work. Figure 6.2(b) for comparison is a generalised design of the pulsed-processing hardware configuration as described in a number of previous reports. Although the exact design of pulsed based systems through literature varies, the key components are highlighted in Fig. 6.2(b).

The continuous flow system uses two gas inputs: nitrogen and hydrogen as shown in Fig 6.2(a). Nitrogen is a common inert gas that can be used as the carrier gas for the bubbler. The hydrogen is used as part of a newly developed method for improved selectivity between silicon/polysilicon films and silicon dioxide and/or silicon nitride films. The work described in this chapter will highlight the benefits of the continuous flow hardware configuration and its process for manufacturing.
For etching, the process gasses are introduced into the chamber using a showerhead based gas inlet as shown in Fig 6.3. This design is commonly used in PECVD systems due to its ability to distribute reactant gasses more evenly across the surface of a wafer. The hole-pattern is typically size specific to the wafer diameter in order to improve etching performance.
Distribution of the holes is size specific and extends to the edge of the relevant wafer size (100, 150 or 200mm diameter). Any holes beyond the edge of the wafer will increase the loading effect and cause a detrimental effect to overall etch uniformity. This leads to having size specific showerhead parts that reduce this effect on the wafers. The loading effect causes problems when aiming to achieve uniform etching profiles across wafers. This loading effect, which can be best described as an excess of etch vapour at the edge of a wafer such that the local etching rate observed at the edge of the wafer is higher than at the centre the wafer. At the centre of the wafer, the XeF$_2$ can be utilised evenly across the exposed region, however at the edge, this is not the case and the XeF$_2$ is more concentrated at the edge of the wafer resulting in a fast etch.

As shown in the Fig. 6.4, XeF$_2$ molecules are evenly distributed across the wafer. If there were an excess of the molecule past the edge of the wafer, an enhanced edge effect would be observed with greater etching occurring around the edge than the centre of the wafer.
6.3 Sample Preparation

Samples were prepared for investigation of XeF$_2$ etching behaviours. The samples were fabricated using the method described in Chapter 4. The samples were blanket films, multiple deposited layers, patterned structures using lithography and RIE based processes.

To assess undercut etching, a patterned photoresist layer was used on the surface of $<$100$>$ silicon wafers. Blanket etching rates for single crystal silicon cannot be measured since it is difficult to accurately measure the etch depth and hence the etch behaviour. The parameters for photoresist deposition and patterning were described in Chapter 4. For polysilicon etching, both the blanket and patterned structures can be used. Blanket films can reveal the effect of unpatterned polysilicon film etching behaviours in situations where thinning of the whole surface may be required. The process configuration of the polysilicon deposition system has been described in Chapter 3 to achieve a thickness of 1 µm.

Additionally, PECVD films of silicon dioxide and nitride were deposited as the masking layers on both single crystal and polysilicon samples. These layers were then patterned by photolithography and subsequently RIE patterning of the oxide or nitride layer. After RIE processing, the photoresist layer was removed by oxygen plasma, leaving only the patterned nitride mask on top of the polysilicon or single crystal silicon wafer. These samples can be used to investigate selectivity of etching silicon with respect to oxide or nitride masking layers. As discussed in Chapter 2, oxide and nitride films can be used as masking layers or functional dielectric layers. Control of the film
thickness therefore can be a critical concern where specific electrical or mechanical properties are required.

Metal films were deposited onto silicon wafers to assess etch compatibility in XeF₂ processing. Metal deposition was performed on the OPT Plasmalab 400 system as shown in Fig. 6.5. This system is capable of depositing films of Cr, Cu, Al, Al (with 1% Si content), Ta and Mo films by sputtering of the respective metal targets. A layer of thermally grown silicon dioxide, with a thickness of 0.1 µm was used as the adhesion layer on which the metals were to be deposited. All of the metal layers were deposited to a thickness of 300 nm. This thickness would be sufficient for studying the etching capabilities and provide additional selectivity information on selected standard CMOS materials against silicon films.

![Figure 6.5 Oxford Instruments plasmalab system for metal sputter deposition.](image)

6.4 Experimental Method

To ensure a substantial etch measurement for bulk silicon and to reduce the measurement error of the undercut result, an etch time of 10 minutes was used. The optical measurement method for samples has been described previously in Chapter 3.

A simple process flow was developed to gain insight into the fundamental behaviours of each XeF₂ etch test. This would help to understand possible key interactions that might exist in the process. The primary process parameters that will be investigated are process pressures between 2 Torr and 9 Torr and nitrogen carrier gas flow into the XeF₂ bubbler from 50 sccm to 150 sccm. When etching polysilicon films, due to their ease of
etching in contrast to the single crystal silicon, the etch times are reduced under the same process pressure and gas flow conditions. This allows for understanding of the differences between the two types of silicon material.

An additional area of analysis will be the investigation of selectivity with silicon dioxide and silicon nitride films as well as the metals outlined previously. Films of PECVD silicon dioxide and silicon nitride were deposited on <100> single crystal silicon wafers. There were two types of wafer samples: blanket films, which have no structure on the surface and wafers that are patterned by RIE as stated in Chapter 3. The etch depth was measured using a 9-point measurement method before and after etching the wafer in order to assess uniformity and relative etching rates. Optical measurement of the undercut process is not easy for the films since the films are not optically clear at the deposited thicknesses. Therefore, assessment of undercut etch profiles require that the masking films be removed by a wet HF etch method. These tests are repeated in the study of hydrogen as an additional process gas. This new reaction mechanism is used as a means to improve selectivity between silicon and either silicon dioxide or silicon nitride films as discussed further in section 6.5.3.

Undercut and uniformity data is calculated with a 9-point measurement profile across a test sample. The definitions of what is considered an undercut is described in Fig. 6.6 and for clarification, the 9 positions of measurement across each sample wafer is shown in Fig. 6.7. A 10 mm edge exclusion zone is observed in all measurements taken in this work. With all wafers and blanket films in particular, there is an “Edge Exclusion” zone. This region is a defined area at the edge of a wafer where measurement and analysis are excluded due to known deposition or handling interactions that cause particle, etch and defects at the edge of the wafer. In large foundries, a 3 mm edge exclusion zone is more typical. For the memsstar Alpha silicon system, the tolerances are not as stringent and utilise 10 mm exclusion zone. All measurements at positions 1, 5, 6 and 9 are measured 10 mm from their relative edge. These measurements are then used to calculate wafer uniformity to 1-sigma (σ). This relates to the standard deviation divided by the mean of the series multiplied by 100 to give a uniformity percentage as described in equations (6.1) and (6.2).
Figure 6.6 Profile examples of single crystal silicon before (a) and after (b) etching, polysilicon before (c) and after (d) etching.

Figure 6.7 Diagram of 9-point measurement locations on a 150 mm wafer.

Examples of the observed undercut profiles after etching are shown in Fig. 6.8. Figure 6.8 (a) and (b) show optical pictures of polysilicon etching using a photoresist mask layer. Figure 6.8(c) and (d) show polycrystalline silicon etching profiles and 6.8(e) and (f) show single crystal silicon etching profiles.
Figure 6.8 Examples of undercut profiles by optical inspection of polysilicon etching (a), (b) and Scanning Electron Microscopy (SEM) method for polysilicon (c), (d) and bulk silicon (e), (f).

Figure 6.8(a) shows the optical view of polysilicon undercutting with a photoresist mask. The thermally grown oxide is now visible as the blue material, while the etch front is also clearly visible. The undercut is measured by software and shown as the red
line, also described in Fig. 6.6(d). Under SEM analysis after photoresist removal, the same features can be observed in Fig. 6.8(b). Figure 6.8(c) shows the undercut profile of bulk silicon after etching by XeF₂. Images under SEM were angled at 10° to attain suitable definition of both the cleaved side of the structure and the surface features of the sample.

Uniformity is calculated by first, calculating the standard deviation of the 9 point measurement.

\[
\sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}}
\]  

(6.1)

where x is a data point, x-bar is the mean of the series and n is the number of data points in the series. Uniformity is then given by:

\[
Uniformity (%) = \left(\frac{\text{Standard Deviation}}{\text{Mean}}\right) \times 100
\]  

(6.2)

6.5 Results and Discussion

6.5.1 Reaction Mechanism

The behaviours of both single crystal silicon and polysilicon films are investigated using the silicon etch system. The same process will be used for both types of silicon to assess comparative behaviours and contrasts in the materials. In both cases, the reaction follows the same process and is defined by the following reaction equation:

\[
2\text{XeF}_2 + \text{Si} \rightarrow 2\text{Xe} + \text{SiF}_4
\]  

(6.3)

This reaction requires the physical absorption of the XeF₂ molecule into the silicon as described previously [52, 64, 70]. The XeF₂ molecule is known to dissociate through one of two mechanisms: either full dissociation into Xe and two F⁻ molecules, or partial dissociation into XeF⁺ and F⁻ molecules.
6.5.1.1 Results of Etching Single Crystal Silicon

An initial screening experiment on undercut etching was performed with patterned bulk silicon wafers. The process factors were described with lower and upper values: 2 Torr and 9 Torr for pressure and 50 sccm and 150 sccm for carrier gas flow rates.

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Etch rate (µm/min) for 50 sccm carrier gas</th>
<th>Etch rate (µm/min) for 150 sccm carrier gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.68</td>
<td>1.05</td>
</tr>
<tr>
<td>9</td>
<td>1.86</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Table 6.1 Etch rate of bulk silicon under screening process conditions.

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Uniformity (%) for 50 sccm carrier gas</th>
<th>Uniformity (%) for 150 sccm carrier gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.68</td>
<td>3.69</td>
</tr>
<tr>
<td>9</td>
<td>1.56</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Table 6.2 Etch uniformity of bulk silicon under screening process conditions.

The screening experiments described in Tables 6.1 and 6.2 show that etching rates are found to be higher in regimes using an increased process pressure. As pressure increases, the residence time of the reaction gasses in the etch chamber increase as the automatic pressure controller (APC) imposes a greater restriction in the pumping line to maintain higher pressures, as already described in Chapter 4. The increase in residence time, allows for a higher rate interaction between the XeF₂ molecules and the exposed silicon surfaces. Uniformity results show similar trends in Table 6.2. These initial results describe starting points for process conditions, which are expanded further within this work.

To understand the effects of increasing carrier gas flows make in the undercut etching behaviour observed in Table 6.1, the operation of the solid source bubbler was investigated. Figure 6.9 shows the output from the XeF₂ bubbler with increasing nitrogen carrier gas flow. As the carrier flow increases, the XeF₂ output from the bubbler also increases.
The XeF$_2$ output is calculated by the etch system based on the set nitrogen carrier gas flows. It calculates the time taken to reach a fixed pressure value from base vacuum pressure with the nitrogen gas flow on its own and then repeated with XeF$_2$ also flowing.

In a similar behaviour to liquid bubblers for catalysts in Chapter 4, as nitrogen flow increases in the solid source bubbler, the XeF$_2$ output flow does not increase linearly as can be seen in Fig. 6.9. It is observed that as the carrier gas flow increases, the XeF$_2$ concentration is reduced in the overall gas being introduced into the process chamber as shown in Fig. 5.10.
This shows that low nitrogen carrier gas flows provide a higher relative concentration of XeF$_2$ in the process module. Undercut performance would therefore appear to benefit in regimes utilising low carrier gas flows as initial screening results indicated in Fig. 6.8(a). Higher carrier gas flows produce lower XeF$_2$ concentration and this will lead to etching rates changing over the course of this range of carrier flows.

![Figure 6.11](image_url)

**Figure 6.11** Relative partial pressure of XeF$_2$ at 2, 5 and 9 Torr pressures with increasing carrier gas flow.

The relationship to XeF$_2$ concentration can give an approximate partial pressure inside the process module. Figure 6.11 shows the relationship to partial pressure of XeF$_2$ to carrier gas flow. XeF$_2$ partial pressure, like concentration, decreases with increasing carrier gas flows. The measurements were taken at a chamber pressure of 9 Torr.

The uniformity results suggest different process conditions than those used for high undercut etching rates would be required in bulk silicon etching. Low-pressure regimes appear to improve uniformity across the sample more effectively. In manufacturing, this is a critical parameter on both deposition and etching systems. Many commercially available systems typically have a specification to meet a uniformity variance across a wafer of below 5% uniformity. A complete analysis was performed to further describe the etching behaviours as shown in Fig. 6.12.
From these results, etch rates are shown to be higher with increased process pressures. Undercut etching rates for single crystal silicon achieve an etching rate of 2.25 μm/min with both a high pressure and high carrier gas flow as shown in Fig. 6.12(a). This shows a single crystal silicon etching preference towards higher partial pressures of XeF₂ in the chamber shown in Fig. 6.11, but also that higher levels of XeF₂ can improve the etching rate, showing potential for increasing the etch of silicon if more XeF₂ were supplied to the process than the hardware is capable of providing.
Previous work has always aimed to process silicon in as high a pressure as possible; yet have been limited by hardware limitations. In early work, this was in the millitorr (mTorr) range, and as work has progressed, now reaching pressures close to 5 Torr [57, 58, 62, 70].

6.5.1.2 Results of Polysilicon Etching

Unlike single crystal silicon, it is possible to measure the thickness of polysilicon films deposited above thermal oxide layers using the Nanospec thin film measurement method described in Chapter 3. The same process described for etching single crystal silicon was performed for the etching of blanket films of polysilicon. The blanket polysilicon films were etched for two or four minutes. This difference in the etching time allows assessment on whether the etch rate and uniformity changes over time. Etch times greater than four minutes are not suited, as etching of the polysilicon would clear the edge exclusion zone and adversely affect the results.

The results are shown in Fig. 6.13(a) for an etch time of 2 minutes. The results show etching behaviours similar to bulk silicon. Increased process pressures result in higher etching rates. The etch rates also appear to be more influenced by increasing carrier gas flow than increasing pressures. Figure 6.11 would suggest that higher partial pressures are capable with lower carrier gas flows and Fig. 6.12(a) does show that increased pressures do affect the etching rate more than carrier gas flows. One explanation for this change in behaviour lies in the generation of XeF$_2$ partial pressure. In an undercut etch regime, there is a much smaller open area of reactant material exposed due to the masking layer, this reduces the reaction sites across the wafer which can lead to an increase in the partial pressure of XeF$_2$. With a 100% open area etch such as the blanket polysilicon film; a partial pressure cannot build to the same level, as there is an immediate and high level of XeF$_2$ utilisation as soon as it is introduced into the process module.
Figure 6.13 Blanket polysilicon Etch Rate (a) and Uniformity (b) behaviours with increasing carrier gas flow, 2-minute process time.

The real process control in this regime is the rate at which XeF$_2$ is introduced into the process chamber. As N$_2$ carrier gas flow is increased from 50 sccm to 150 sccm, blanket polysilicon etch rates increase by 20% from 0.15 µm/min to 0.18 µm/min. This shows that blanket film etching continues to increase with an increase N$_2$ carrier gas flow which results in increasing levels of XeF$_2$ in the chamber, which is utilised as quickly as possible to maintain high etching rates. If the hardware was capable of greater gas flows into the bubbler, it is expected the trend would continue.

Uniformity results in Fig. 6.13(b) show a variance from 4% at 2 Torr to less than 3% at both 5 and 9 Torr, and these are considered well within standard semiconductor and
MEMS specification. Again, the uniformity of the undercut agrees with the results of the single crystal silicon undercut process by showing a more even etch profile in high-pressure regimes.

At a four minute etch time, the undercut etch rates are reduced by 100 nm/min as shown in Fig. 6.14. This would suggest that the initial etch period is quicker and stabilises to a reduced etching rate as time progresses for blanket film etching. Continuing the etching for longer to assess the overall effects begins to change the etch behaviour however. As the loading effect continues and the polysilicon films begin to clear the edge of the wafer, the observable speed at which the film etches appears to increase as the volume decreases with increasing process time. Measurements for uniformity at this stage provided no clear trend. Ideally, performing this test on a blanket silicon wafer would give a clearer indication of etch performance of longer times on a blanket wafer. However, with no means of accurately measuring step change without patterning the wafer, this test would also not be an accurate experiment.

In terms of uniformity for blanket polysilicon etching, in both the two and four minute etch process tests, the results show uniformities with results below 5%. There is a small amount of variability between the results by pressure values, but in both etch times, a low pressure regime caused the poorest uniformity results of the tests.
Figure 6.14 Blanket polysilicon etch rate (a) and uniformity (b) behaviours with increasing carrier gas flow, 4-minute process time.

Undercut etching of polysilicon films shows a contrasting behaviour to the blanket film etching behaviours. While etching 100% exposed polysilicon layers, the change in pressure has less effect on etching rates, the flows used for carrier gas into the solid source bubbler are key as seen in the etching rate of blanket layers. Fig. 6.15(a) shows the effect of both pressure and carrier gas flow controls and the differing process behaviours when performing undercut etch processes on polysilicon films to those in Fig. 6.13 with blanket films.
Figures 6.9 to 6.11 show the effect that carrier gas flows have on concentration of the XeF$_2$ within the process module. This concentration can be associated with the relative partial pressure within the reaction environment. In contrast to blanket film etching where the flow of N$_2$ into the solid source bubbler is key due to the speed of XeF$_2$ introduction and consumption, undercut etch rates are affected more in line with the behaviours shown in Fig. 6.11.

In undercut designs, the photoresist mask layer acts as a protection for the unexposed regions of the wafer and also as a physical restriction for the XeF$_2$ molecules, forcing
the etch reaction to move from a reaction limited regime where XeF$_2$ immediately reactions with exposed material, to a transport limited reaction where the XeF$_2$ molecule must first pass through the access holes in the masking layer before reaching the material interface. With a much smaller open area of etch material, the XeF$_2$ is capable of building a greater partial pressure, which can increase the concentration of the XeF$_2$ interacting at these smaller open regions, increasing the etch rate of the film. As the N$_2$ carrier flow is increased, the partial pressure of this XeF$_2$ concentration is diluted by the additional inert N$_2$ and a decrease in etch rate is seen.

Figures 6.16(a) to (c) more clearly describe the effect of XeF$_2$ partial pressures. As shown in all three examples, as the partial pressure of the XeF$_2$ increases, the etching rate of polysilicon also increases. In Fig. 6.17, plotting the partial pressure charts in Figs. 6.16(a) to (c) on a single chart shows this effect of etch rates for undercut structures affected more predominantly by XeF$_2$ partial pressure. At 5 Torr, with an XeF$_2$ partial pressure of 2.08 Torr, an undercut etch rate of 13.89 µm/min is measured, while at 9 Torr, with an XeF$_2$ partial pressure of 2.01 Torr, the undercut etch rate is measured as 11.82 µm/min. This shows that control of the relative partial pressure within the etch chamber can be used to maintain high etching rates.

When these figures are plotted on a single chart as shown in Fig. 6.17, a clear upward trend in undercut etching behaviour is discovered, thus showing the strong interplay that exists between both pressure and carrier gas flow in the etch process. In fact, a clear trend can be observed of this behaviour and relationship between XeF$_2$ partial pressures and undercut etching rates of polysilicon deposited by the LPCVD method.
Figure 6.16 Effects of increasing partial pressure on undercut etch rates at 2 Torr (a), 5 Torr (b) and 9 Torr (c) of total pressure.
Figure 6.17 Effects of undercut etch rate of polysilicon films with increasing XeF\(_2\) partial pressure.

Control of a continuous high XeF\(_2\) concentration throughout the etch process is one key benefit of the continuous-flow etch method. A pulsed regime would introduce XeF\(_2\) into the etch chamber, the XeF\(_2\) is then consumed until the chamber is evacuated to its base vacuum pressure. This means that the XeF\(_2\) partial pressure is continually being reduced as it is consumed, as there is a finite amount of XeF\(_2\) available. To maintain high etch pressures in a pulsed system, a large number of short pulses would be required. These would allow for short periods of high XeF\(_2\) partial pressure to etch the material quickly without seeing the decrease in etch rate with decreasing partial pressure, however, the amount of XeF\(_2\) wasted in this regime would be substantial.

The results of this section show the behaviours of single crystal and polysilicon films. Both types of film etch differently due to the difference in the structure of each material. In single crystal silicon, etching will continue down as far as the etch progresses laterally, while polysilicon films will only etch to the oxide layer in depth shown in Fig. 6.6. In single crystal etch structures, there is no etch stop layer such as thermally grown oxide. In polysilicon designs, when the etch stop layer is reached, the lateral etch rate increases exposing more silicon to etch in a polysilicon design hence a greater observed undercut etching rate.

The main discovery in these tests describe the benefit of maintaining a high partial pressure of XeF\(_2\) in the chamber: this will lead to a clear increase in undercut etching.
 rates of silicon based films. When etching single crystal films, the silicon is absorbing as much XeF$_2$ as can be supplied in a clear reaction limited regime, such that the partial pressure of XeF$_2$ when etching single crystal silicon material is continually being depleted in a way that is not observed in the polysilicon undercut processes.

This can be improved by lowering pressure and reducing the etch rate across the wafer thus enhancing a more even utilisation of XeF$_2$ across a whole wafer. Slowing the etch process by decreasing carrier gas flows also improves uniformity. Tables 6.3 and 6.4 show the results of the undercut etching rates for single crystal and polysilicon.

<table>
<thead>
<tr>
<th>Process Pressure</th>
<th>Carrier Gas Flow 50 sccm</th>
<th>Carrier Gas Flow 100 sccm</th>
<th>Carrier Gas Flow 150 sccm</th>
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<td>9</td>
<td>1.86</td>
<td>2.11</td>
<td>2.25</td>
</tr>
</tbody>
</table>

Table 6.3 Undercut etching rates in $\mu$m/min for <100> bulk silicon.

<table>
<thead>
<tr>
<th>Process Pressure</th>
<th>Carrier Gas Flow 50 sccm</th>
<th>Carrier Gas Flow 100 sccm</th>
<th>Carrier Gas Flow 150 sccm</th>
</tr>
</thead>
<tbody>
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<td>3.46</td>
</tr>
<tr>
<td>5</td>
<td>13.89</td>
<td>6.90</td>
<td>6.85</td>
</tr>
<tr>
<td>9</td>
<td>18.78</td>
<td>14.12</td>
<td>11.82</td>
</tr>
</tbody>
</table>

Table 6.4 Undercut etching rates in $\mu$m/min for LPCVD polysilicon films.

The obtained results in the case of etch rates for both cases of single crystal and polysilicon films have shown improvement over previously reported etch rates as shown in Tables 6.5 and 6.6. These results were obtained under pulsed process configurations.

<table>
<thead>
<tr>
<th>Reported Etch Rate ($\mu$m/min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.25</td>
<td>This work</td>
</tr>
<tr>
<td>10</td>
<td>Xuan et. al. [66]</td>
</tr>
<tr>
<td>1.9</td>
<td>Easter et. al. [70]</td>
</tr>
</tbody>
</table>

Table 6.5 Reported undercut etching rates for bulk silicon in literature.
Table 6.6 Reported undercut etching rates for polysilicon from literature.

<table>
<thead>
<tr>
<th>Reported Etch Rate (µm/min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.78</td>
<td>This Work</td>
</tr>
<tr>
<td>10</td>
<td>Jeon et. al. [62]</td>
</tr>
<tr>
<td>9.4</td>
<td>Chu et. al. [58]</td>
</tr>
<tr>
<td>8</td>
<td>Arana et. al. [68]</td>
</tr>
<tr>
<td>0.7</td>
<td>Winters et. al. [57]</td>
</tr>
</tbody>
</table>

In both materials, etching rates have been improved from previously reported values in literature by controlling the process parameters. In the case of polysilicon, the highest etch rate measured is 18 µm/min which nearly doubles the previously reported work of 10 µm/min [62]. The etching rates of bulk silicon have also been improved from literature reports of 1.9 µm/min to 2.25 µm/min [70]. The work reported in [66] is the only report of etching rates at 10 µm/min in single crystal silicon using a XeF$_2$ pulsed-processing configuration published in 2006 with no other literature repeating this etching rate in bulk silicon.

As shown in Fig. 6.11, with a low carrier gas flow of 25 sccm N$_2$, the relative partial pressure of XeF$_2$ at 9 Torr of total pressure is in the region of 2.5 Torr. While the polysilicon undercut etches have all shown higher etching rates in high pressure low carrier gas flow regimes, bulk silicon is able to show better undercut etching with high pressure and high carrier gas flow regimes.

6.5.2 Effects of XeF$_2$ etching on SiO$_2$ and Si$_3$N$_4$ films

Selectivity is a recurring theme in this thesis and is equally as important as the effect of etching silicon based films. Chapters 4 and 5 focused on the selectivity silicon dioxide films to silicon nitride as the key sacrificial and functional layers respectively in vapour phase HF etching processes. The XeF$_2$ etching work in this chapter will look at selectivity of silicon based films towards not only silicon dioxide and silicon nitride, but also a range of metals used as functional layers in MEMS devices such as RF MEMS.

6.5.2.1 Results of Etching Blanket Silicon Dioxide and Nitride Films with XeF$_2$

Using 150 mm diameter wafers, 1 µm thick layers of PECVD silicon dioxide and PECVD silicon nitride films are used as the masking layer in the way as photoresist was
used in the previous experiments. The first test was to assess the behaviours of blanket silicon dioxide and silicon nitride films.

In recent work, the localised effect of silicon dioxide film etching has been studied while silicon is etched in the same structure [72]. While much of the early literature describing XeF$_2$ etching noted no measureable etch of oxide films, very few papers have ever previously discussed oxide film etching at very low rates in the presence of silicon etching at the oxide interface [51].

The PECVD blanket oxide and nitride films were etched for four minutes using the same process used for blanket polysilicon films as described in section 6.5.1.2. After the etch process was complete, there was no measureable thickness change of the oxide or nitride films. Without the presence of an exposed silicon source to be etched, the etching of these materials does not appear to occur, which is in agreement with the literature [72].

6.5.2.2 Results of Etching Patterned Silicon Dioxide and Silicon Nitride Films

The lithography method for patterning of the SPR350 negative photoresist as described in Chapter 4 was performed on PECVD silicon dioxide and silicon nitride layers. The mask design was described in Chapter 3 and used in the previous experimental samples in section 6.5.1. These exposed regions of oxide or nitride were then etched anisotropically by reactive ion etching (RIE) with the bulk silicon material 1 µm below. These samples were then etched using the same single crystal silicon etch process as described in section 6.5.1.1. The etch rate of the silicon dioxide films were assessed by 9-point measurement. These samples focused only on the undercut of single crystal silicon. Deposition of PECVD oxide masks on polysilicon is possible, but the accurate measurement of the PECVD layers and thermal oxide layers on top of the top of polysilicon is not possible with this work. The etch data for these oxide films and their subsequent silicon undercut rates are shown in Fig. 6.18 (a) and (b) including the error bars representing the measurement system of ± 5 nm.
In the presence of bulk silicon etching, silicon dioxide etching was observed. The greatest etch depths were measured at 35 nm over a 10 minute etch period. Single crystal silicon etch rates were similar to those shown in Fig. 6.11 where photoresist was the masking layer. As Fig 6.18(a) shows, the etch rate is very low as shown in the literature but can be considered in the manufacture of devices with very thin oxide layers.

Figs. 6.19 (a) and (b), the etch depth measurements of the nitride masking layer and the etch rates of single crystal silicon are given. The nitride masking layers show an etching
behaviour related to exposure to localised silicon etching similar to the samples using an oxide layer as the mask.

From the results, it is found that silicon nitride masking layers are more readily etched than oxide masking layers. While oxide films are etched up to 35 nm, nitride layers under the same process conditions are etched up to 600 nm. The single crystal etching rates when using nitride as a mask appear to have been affected in the same process. Equation (6.3) describes the reaction of XeF$_2$ with silicon films. This reaction as previously discussed initiates with the absorption and dissociation of XeF$_2$ into the
silicon layer. This reaction utilises fluorine to break silicon bonds and generates SiF$_4$ as part of the reaction.

The results can be viewed as an interaction of unreacted fluorine being released at the silicon etch interface etching the nitride mask material. This has also been observed in a pulsed-process reaction system for thermally grown oxide films [72]. As described in Chapters 4 and 5, the reaction mechanism for nitride layer etching relates to cleaving Si-N bonds with fluorine substitution. This reaction is not as prominent with oxide films and this is shown again here by the clear difference in etch behaviour between oxide and nitride films under the same experimental conditions.

Table 6.7 summarises the calculated selectivity values of silicon and polysilicon films to PECVD oxide and nitride films. While these tests were performed only with single crystal silicon, using polysilicon etch rates provided in section 6.5.1.2, relative etching rates of PECVD oxide and nitride films can be calculated.

<table>
<thead>
<tr>
<th>Carrier Gas Flow (sccm)</th>
<th>Polysilicon / PECVD Oxide</th>
<th>Polysilicon / PECVD Nitride</th>
<th>Single Crystal Si / PECVD Oxide</th>
<th>Single Crystal Si / PECVD Nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5366</td>
<td>354</td>
<td>797</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>5884</td>
<td>336</td>
<td>1079</td>
<td>21</td>
</tr>
<tr>
<td>150</td>
<td>3475</td>
<td>281</td>
<td>523</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 6.7 Selectivity values of polysilicon and single crystal silicon using PECVD oxide and nitride masks at 9 Torr.

The selectivity of single crystal and polysilicon films to silicon dioxide is shown to be very high. This allows future designs to use oxide layers as masking layers for future MEMS devices. Selectivities of over 3000:1 for polysilicon and 500:1 for single crystal silicon are certainly higher than previous reports [72]. XeF$_2$ selectivities of over 200:1 for polysilicon films and 20:1 for single crystal silicon towards silicon nitride films are achieved. The value for single crystal silicon is also observed to be substantially higher than that of previous literature [61].
6.5.3 Effects of XeF$_2$ Etching on Metal Films

As described in Chapter 3, metal films were deposited onto thermally oxidised <100> silicon wafers. These blanket wafer samples were processed at 9 Torr and with 50 sccm of N$_2$ carrier gas flow as these conditions provided the highest etching rates for the samples. Due to the nature of the metal deposition process, a void in the metal deposition is always left at the edge of the sample. The step change from the edge of the void was used for film thickness measurements using the Dektak surface profilometer as described in Chapter 5, before and after the etch process. After 30 minutes of etching in XeF$_2$ using the high pressure, low carrier gas flow process from section 6.5.1.2, if a layer was observed to etch, patterned test samples were fabricated to measure undercut etching. Measured rates of undercut etching could then be compared to the rates of both single crystal and polysilicon films thus generating relative selectivity data towards these metal layers.

The OPT metal sputter system was used to deposit aluminium, aluminium containing 1% silicon, chromium, copper, molybdenum and tantalum films. The inclusion of aluminium silicon is of interest since it is used in IC manufacturing in order to avoid PN junction spiking in IC manufacturing as shown in Fig. 6.20. The deposition parameters for the various metal films are given in Table 6.8.

<table>
<thead>
<tr>
<th>Material</th>
<th>Power (Watts)</th>
<th>Pressure (mTorr)</th>
<th>Deposition Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1000</td>
<td>3</td>
<td>60</td>
</tr>
<tr>
<td>Al (1%Si)</td>
<td>1000</td>
<td>3</td>
<td>60</td>
</tr>
<tr>
<td>Cr</td>
<td>500</td>
<td>3</td>
<td>94</td>
</tr>
<tr>
<td>Cu</td>
<td>1000</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>Mo</td>
<td>500</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>Ta</td>
<td>500</td>
<td>5</td>
<td>130</td>
</tr>
</tbody>
</table>

Table 6.8 Deposition conditions for films with a thickness of 300 nm.

Figure 6.20 Example of PN junction spiking due to electromigration [79].
While many of the selected films showed no apparent etching after 30 minutes, copper showed an etching rate of 0.3 nm/min. This in relative terms to the undercut rates seen in polysilicon films greater than 10 µm/min, shows a selectivity of 30000:1 and above. The summary of initial blanket metal etch rates are summarised in Table 6.9.

<table>
<thead>
<tr>
<th>Material</th>
<th>Step Change (nm) from Dektak</th>
<th>Blanket Film Etch Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Aluminium-Silicon (1%)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chromium</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Copper</td>
<td>10</td>
<td>0.3</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>900</td>
<td>15</td>
</tr>
<tr>
<td>Tantalum **</td>
<td>2700</td>
<td>300</td>
</tr>
<tr>
<td>Titanium</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

** 3 minute etch on Ta blanket sample

Table 6.9 Results of blanket metal etching in XeF₂.

Two other films showed higher etching rates when exposed to XeF₂: Mo and Ta. The etching of Mo and Ta films were all observed at etching rates greater than 10 nm/min. The reaction equations for Mo and Ta films are as follows:

\[
\text{Mo} + 3\text{XeF}_2 \rightarrow 3\text{Xe} + \text{MoF}_6 \quad (6.4)
\]

\[
2\text{Ta} + 5\text{XeF}_2 \rightarrow 5\text{Xe} + 2\text{TaF}_5 \quad (6.5)
\]

While much of the current work in etching both Mo and Ta films reside around using RIE processes to generate fluorine ions to etch these films [130-138], XeF₂ has in the past also been reported as a means for etching these films [57, 58, 136]. The etching of both Ta and Mo films follow a similar etching mechanism in which the XeF₂ molecules come into contact with the surface of the metal, leading to dissociation of a fluorine molecule from the XeF₂ molecule and cleaving of the Mo-Mo or Ta-Ta chemical bonds. This interaction, leading to removal of fluorine from the XeF₂, subsequently forms the reaction by-products shown in equations (6.4) and (6.5). As XeF₂ is not physically absorbed into the metals, the initiation and etching rates have been reported in literature to be lower to both single crystal and polysilicon films.
To further assess etch undercut properties of these metal samples, the lithography steps described in Chapter 3 were used to create a masking layer for undercut analysis. The exposure times were modified to accommodate the occurrence of reflected exposure on the photoresist layers due to the high reflectivity of the Mo film. Tantalum required the same exposure time as silicon and poly-silicon. Molybdenum however, required only a 3 second exposure time. It has been found that longer exposure times caused over exposure of the films and subsequently leads to lift-off of the whole photoresist layer at the development stage.

From section 6.5.1, the greatest undercut etching rates for both bulk and polysilicon were found in high pressure regimes. Samples of each metal layer with a patterned photoresist mask were etched at the various carrier gas flows as described previously. From this, etching rates and behaviours were assessed with the same process flows as for the silicon films and hence selectivity values can be calculated. The films were etched for 60 minutes to allow for a substantial level of etching to occur in the undercut design. Table 6.10 summarises undercut etch rates for molybdenum and tantalum films. The etch rates are in the region of 12-18 nm/min for molybdenum and 40-90 nm/min for tantalum films. For comparison, both single crystal and polysilicon rates under the same process conditions are also included.

<table>
<thead>
<tr>
<th>N\textsubscript{2} Carrier Gas Flow at 9T (sccm)</th>
<th>Single Crystal Silicon Etch Rate (µm/min)</th>
<th>Poly-Silicon Etch Rate (µm/min)</th>
<th>Molybdenum Etch Rate (µm/min)</th>
<th>Tantalum Etch Rate (µm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.9</td>
<td>18.8</td>
<td>0.016</td>
<td>0.04</td>
</tr>
<tr>
<td>100</td>
<td>2.1</td>
<td>14.1</td>
<td>0.018</td>
<td>0.07</td>
</tr>
<tr>
<td>150</td>
<td>2.3</td>
<td>11.8</td>
<td>0.012</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 6.10 Undercut etch rate comparison of molybdenum and tantalum to silicon films under same process conditions.

Table 6.11 summarises the selectivities of molybdenum and tantalum to silicon films. The results show selectivity of polysilicon towards tantalum as greater than 100:1 and it is greater than 25:1 for single crystal silicon. The selectivities towards molybdenum are substantially higher at over 750:1 for polysilicon and greater than 100:1 for single crystal silicon.
The selectivity values however, are relative selectivities. Much like previous reported figures, these are based on the relative etching rates of two films. The difficulty of measuring the selectivities of these metal films to silicon layers is finding a means to assess the relative change of both the metal and silicon interfaces when etching both materials simultaneously. As both films will etch, these metals cannot be used as adequate masking layers. As can be seen in Table 6.10 and 6.11 however, the high etching rates of these films as compared to the other metal films makes them suitable as alternative sacrificial materials should the need arise.

### 6.5.4 Improvement of Selectivity to SiO₂ and Si₃N₄ by Addition of H₂ in Gas Flow

As discussed in section 6.5.2, the reaction of XeF₂ with silicon is a multi-stage process. After the initial absorption of XeF₂ into silicon there is a subsequent dissociation of fluorine from XeF₂ molecules and the formation of the primary reaction by-product in SiF₄. As previously described, the reaction and subsequent formation of SiF₄ is never exactly 100% complete [72]. This leads to the generation of alternative moieties in the form of SiFₓ where x could vary between 1-4. Incomplete forms such as SiF₃ have incomplete bonds, which will look to complete their bonds when possible. These free bonds are capable of acting as a mechanism by which films such as silicon nitride and silicon dioxide subsequently react and etch. The addition of process gas that could react and complete the formation of the SiFₓ molecule before interacting with either of these films, could greatly improve the ability to obtain high selectivities between silicon and silicon dioxide or silicon nitride layers. As shown in section 6.5.2, the etch rates of silicon dioxide films are negligible when blanket films are exposed to XeF₂, but have an approximate etching rate of 3.4 nm/min when silicon is etched at the same time. With silicon nitride films, etching of films has been observed at rates of up to 61 nm/min when patterned and used as a mask for silicon etching. This highlights a susceptibility to the influence of localised etching effects during the XeF₂ etching process.

<table>
<thead>
<tr>
<th>N₂ Carrier Gas Flow at 9T (sccm)</th>
<th>Single Crystal Silicon to Molybdenum</th>
<th>Polysilicon to Molybdenum</th>
<th>Single Crystal Silicon to Tantalum</th>
<th>Polysilicon to Tantalum</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>116:1</td>
<td>1173:1</td>
<td>47:1</td>
<td>469:1</td>
</tr>
<tr>
<td>100</td>
<td>117:1</td>
<td>784:1</td>
<td>30:1</td>
<td>201:1</td>
</tr>
<tr>
<td>150</td>
<td>187:1</td>
<td>984:1</td>
<td>25:1</td>
<td>131:1</td>
</tr>
</tbody>
</table>

Table 6.11 Selectivities of single crystal and polysilicon films towards Mo and Ta films.
The addition of hydrogen is investigated as an additional component in the processing gas. This new process modifier has not been previously in literature. Its use is to react with the SiF\textsubscript{x} molecules and to reduce its interaction with other films such as oxide and nitride films acting as masking layers. The etch system can deliver up to 50 sccm of hydrogen in the gas flow for the XeF\textsubscript{2}. However the addition of the hydrogen gas changes etching of silicon and the related oxide and nitride films by diluting XeF\textsubscript{2} concentration of the resultant gas flow in the etch chamber.

The concentration and partial pressure figures with an additional 25 sccm of hydrogen are shown in Figs. 6.21 and 6.22. The difference in concentration change is more drastically affected with lower carrier gas flows of N\textsubscript{2} into the solid source bubbler. With hydrogen, the concentration of XeF\textsubscript{2} is almost half of that in Figs. 6.8 and 6.9. As the N\textsubscript{2} carrier gas flow increases, this change is less substantial but is still less than the concentration of XeF\textsubscript{2} when not using hydrogen at a 9 Torr of process pressure. In both regimes however, the trend of decreasing concentration with increasing carrier gas flow is still found. The experiments are expected to show similar trends in terms of silicon etching rates, while providing information on the effects of silicon dioxide and silicon nitride etching using the same processes as described in section 6.5.2.

![Figure 6.21 XeF\textsubscript{2} concentration with increasing N\textsubscript{2} carrier gas flow with and without 25sccm of hydrogen gas.](image-url)
Figs. 6.11 (a) and (b) have highlighted the effects of XeF$_2$ partial pressure on the etching rates of single crystal silicon. With the increase of hydrogen gas shown above in Figs. 6.21 and 6.22, these experiments were performed on similar samples to assess the effects of hydrogen as a means to improve selectivity towards oxide and nitride films. Additionally, tests on standard patterned single crystal silicon and polysilicon films were run to compare the effects of the etching rates when oxide and nitride films are not present.

### 6.5.4.1 Results of Etching Single Crystal Silicon with Hydrogen

Samples as described in section 6.5.1 were fabricated to assess the change in process behaviour with H$_2$ in the processing gas. As the highest etching rate of 2.25 µm/min was obtained at 9 Torr, this pressure regime was used in the analysis of hydrogen in the reaction gas on the etching rate and selectivity.

As shown in Fig. 6.20, the addition of H$_2$ reduces the overall XeF$_2$ concentration. The level of N$_2$ and XeF$_2$ from the bubbler is independent of the hydrogen flow, which is on a separate gas line as shown in Fig. 6.2(b) and as such, the results will highlight the effects of the concentration dilution on the undercut results. The etching rates with and without hydrogen gas for single crystal silicon samples with a photoresist are given in Table 6.12.
Carrier Gas Flow (sccm) | Etch Rate Without H₂ (µm/min) | Etch Rate With H₂ (µm/min)
---|---|---
50sccm | 1.86 | 1.09
100sccm | 2.11 | 1.12
150sccm | 2.25 | 1.12

Table 6.12 Comparison of undercut etch rates of single crystal silicon with and without hydrogen at 9 Torr of chamber pressure.

From Table 6.12, the effects of adding hydrogen gas in the processing gas can be seen. The hydrogen dilutes the total gas mixture as shown in Figs. 6.21 and 6.22, which affects the total etch rate of silicon etching. The dilution reduces the XeF₂ partial pressure.

Table 6.13 shows the percentage drop in the relative XeF₂ concentration of the whole gas mixture in the chamber at 9 Torr. The same results along with those for chamber pressures of 2 Torr and 5 Torr are shown in Fig. 6.21.

<table>
<thead>
<tr>
<th>Carrier Gas Flow (sccm)</th>
<th>Relative XeF₂ Concentration (%)</th>
<th>Partial Pressure of XeF₂ at 9 Torr (Torr)</th>
<th>Relative XeF₂ Concentration (%)</th>
<th>Partial Pressure of XeF₂ at 9 Torr (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Hydrogen</td>
<td>With Hydrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>26.4</td>
<td>2.37</td>
<td>19.3</td>
<td>1.73</td>
</tr>
<tr>
<td>100</td>
<td>18</td>
<td>1.62</td>
<td>14.9</td>
<td>1.34</td>
</tr>
<tr>
<td>150</td>
<td>14.7</td>
<td>1.32</td>
<td>12.9</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Table 6.13 Comparison of XeF₂ concentration and partial pressure with the inclusion of hydrogen gas.

In equation (6.3), the reaction of XeF₂ with silicon indicates the need for absorption of XeF₂ molecules into the silicon to initiate reaction. As already described in previous work [72], it is suggested that the absorption of the XeF₂ and the subsequent desorption of Xe and F is in fact a two-stage reaction. The hydrogen, while diluting the total gas mixture of the process environment, will also interact with the reaction by-products.
### 6.5.4.2 Results of Etching Polysilicon Films with Hydrogen

The same test outlined in section 6.5.3.1 was performed on polysilicon test samples with a photoresist mask. The results of testing at 9 Torr with increasing gas flows are compared with those obtained under the same process parameters without hydrogen.

Similar to the results in Table 6.12, the etching rates of polysilicon were lower with the inclusion of hydrogen in the reaction gas. In relative terms on both tests, the partial pressure of XeF$_2$ are the same to those shown in Table 6.13, it is the effect of the material and the structure under etch that shows a change in the etching behaviour.

<table>
<thead>
<tr>
<th>Carrier Gas Flow (sccm)</th>
<th>Etch Rate Without H$_2$ (µm/min)</th>
<th>Etch Rate With H$_2$ (µm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>18.8</td>
<td>6.43</td>
</tr>
<tr>
<td>100</td>
<td>14.1</td>
<td>6.97</td>
</tr>
<tr>
<td>150</td>
<td>11.8</td>
<td>6.75</td>
</tr>
</tbody>
</table>

Table 6.14 Comparison of undercut etch rates of polysilicon with and without hydrogen in process gas flow.

In polysilicon etching, the change in partial pressure of XeF$_2$ shows a similar behaviour to that of the bulk single crystal silicon. While the etch rates decreased by 50% with H$_2$ in the gas flow etching single crystal silicon, the effects with polysilicon are more pronounced however. The decrease in polysilicon suggests that etching of polysilicon can be inhibited to a certain degree but that the inclusion of H$_2$ cannot to the same extent slow the etching rate of films of polysilicon. Due to the levels of XeF$_2$ available, high etching rates will be possible with polysilicon films due to the ease at which the films react with XeF$_2$ in contrast to single crystal silicon. In comparing this to the results of Table 6.4, the etching rates in Table 6.14 are found to be similar, thus showing even with the inclusion of H$_2$ gas, the configuration utilised here in this work is a highly efficient method of etching silicon films in contrast to pulsed processing configurations.

Fundamentally, the mechanism slowing the reaction should be the same when etching silicon with oxide or nitride masking layers. While there is no full spectrum *in-situ* monitoring system such as a full Fourier Transform Infra-Red system (FTIR) to analyse every present chemical bond on the current system, one can certainly postulate the
reaction path that hydrogen has on the process as a whole. Within equation (6.3), there are two equally possible intermediate reaction stages [72]:

\[
\begin{align*}
2\text{XeF}_2 + \text{Si} &\rightarrow 2\text{XeF}^+ + F^- + \text{SiF}_x \\
2\text{XeF}_2 + \text{Si} &\rightarrow 2\text{Xe} + 2F^- + \text{SiF}_x
\end{align*}
\] (6.6a) (6.6b)

In equations (6.6a) and (6.6b), the reaction by-product is described as \( \text{SiF}_x \), where \( x \) denotes the number of fluorine molecules ranging from 1 to 4. It has been suggested that one of the conditions in which silicon dioxide and silicon nitride films etch is the incomplete formation of \( \text{SiF}_4 \) molecules. The free or incomplete bonds in this molecule and free \( F^- \) molecules that may not already have reacted with the silicon interface could be the source for localised etching of these films.

As previously discussed in Chapter 4, hydrogen-fluorine bonds are incredibly strong due to the effects of the high electronegativity value of the fluorine atoms. This, when in the presence of hydrogen, can provide three further balanced reaction equations due to the ease in which these bonds are able to form.

\[
\begin{align*}
5\text{XeF}_2 + \text{Si} + 3\text{H}_2 &\rightarrow 5\text{XeFH} + \text{HF} + \text{SiF}_4 \\
3\text{XeF}_2 + \text{Si} + \text{H}_2 &\rightarrow 3\text{Xe} + 2\text{HF} + \text{SiF}_4 \\
3\text{XeF}_2 + 2\text{Si} + \text{H}_2 &\rightarrow 3\text{Xe} + 2\text{SiF}_3\text{H}
\end{align*}
\] (6.7a) (6.7b) (6.7c)

Equation (6.7a) results from (6.6a) in showing that hydrogen appears to form complete molecules of \( \text{XeFH} \) and \( \text{HF} \) while generating \( \text{SiF}_4 \) as expected from equation (6.3). Equation (6.7b) shows an alternative reaction route should the \( \text{XeF}_2 \) fully dissociate during the absorption stage of the Si-XeF\(_2\) etch stage, again with the possibility of forming the HF molecule. In both of these equations, it should be noted that there is no concern for either high levels of HF formation causing any reactions with oxide and nitride films. As described in Chapters 4 and 5, a catalyst is required to initiate the reaction, which is not normally introduced into the XeF\(_2\) reaction chamber.
Equation (6.7c) is the most plausible route of the three reaction paths described here as the formation of SiFx molecules is in part, a pre-existing reaction by-product that would take place during the breakdown of Si-Si bonds. In reality, there is a strong likelihood that all three paths occur, however, without an \textit{in-situ} means of monitoring the process, gauging the most accurate or most predominant path would require a substantial investment and re-design of the system.

\textbf{6.5.4.3 Results of Etching Oxide and Nitride Films with Hydrogen in Gas Flow}

The experiments in section 6.5.2.2 were repeated with the inclusion of hydrogen in the gas flow. The same process conditions as used in section 6.5.3.1 were used to study the effects of XeF$_2$ etching firstly on blanket PECVD oxide and nitride films and subsequently with patterned oxide and nitride films. As shown in Fig. 6.18(a), blanket oxide film etch rates were found to be negligible due to the total etch depth being within measurement error of \(\pm 5\) nm of the metrology system. Blanket silicon nitride films were etched up to 600 nm of depth under the same process conditions. With the inclusion of hydrogen in the reaction gas, blanket silicon nitride films now also show a negligible etch rate after etching. This important result shows that etching of PECVD nitride films can be effectively stopped with the inclusion of H$_2$ in the reaction gas.

Undercut silicon etch processes were performed on PECVD silicon dioxide and nitride films as described in section 6.5.3. The same processes as performed on blanket films of silicon dioxide and nitride films were used on the patterned films to assess the change in etching rates with the inclusion of the H$_2$ gas. As shown in Fig. 6.22, the addition of the hydrogen gas dilutes the total mixture in the process chamber thus the XeF$_2$ partial pressure has also decreased which will affect the silicon etch rate. The results of both etch rate and mask layer etching in the presence of silicon etching are shown with the addition of hydrogen in Figs. 6.23 and 6.24.

Fig 6.23(a) shows the effect of hydrogen during the etching of silicon on the oxide mask layer. While in Fig. 6.18 the oxide mask etch depths were measured as high as 30 nm, with hydrogen the total etch depth reaches a maximum of 8 nm. These etch depth values, as shown by the error bars translate into etching rates that are smaller than the measurement error of the metrology system. This highlights that hydrogen addition when etching silicon reduces the etch rate of oxide films considerably.
In Fig. 6.23 (b), the etching rate of single crystal silicon can be seen with the addition of 25 sccm of hydrogen gas. Table 6.15 highlights the difference in etching rates of single crystal silicon with and without the presence of H$_2$ in the etching chamber.

![Figure 6.23 Etch depth of oxide masking layers (a) and undercut etch rate of single crystal silicon (b).](image-url)
<table>
<thead>
<tr>
<th>Carrier Gas Flow (sccm)</th>
<th>Single Crystal Etch Rate ($\mu$m/min) without H$_2$</th>
<th>Single Crystal Etch Rate ($\mu$m/min) with H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.79</td>
<td>0.69</td>
</tr>
<tr>
<td>100</td>
<td>2.59</td>
<td>0.56</td>
</tr>
<tr>
<td>150</td>
<td>1.78</td>
<td>0.56</td>
</tr>
</tbody>
</table>

Table 6.15 Comparison of etching rates for single crystal silicon with and without H$_2$ in the process gas at 9 Torr using an oxide masking layer.

With single crystal silicon, it was discovered that during the undercut processing, the highest etching rate was obtained at the high process pressure. There was also a trend with higher pressures to show higher etching rates while with lower carrier gas flow as the dilution of the XeF$_2$ concentration with higher carrier flows reduces the etching rate. Table 6.15 shows the effect of adding H$_2$ for single crystal silicon etching with an oxide mask layer. No longer does a high-pressure lead to the high etching rate as shown in Fig. 6.23(b), processes at 2 Torr show the highest undercut etch rates at 1.6 $\mu$m/min while both 5 and 9 Torr of pressure show very similar etching rates as shown in Table 6.15. This can be attributed to the added hydrogen reacting with incomplete SiFx molecules as indicated in equations (7.7a), (7.7b) and (7.7c) more readily at higher process pressures thus actively slowing the etch rate of the silicon due to fluorine being removed from the reaction environment. At lower pressures, the partial pressure of H$_2$ is expected to be insufficient to make the same impact on the etch rate.

The results of silicon nitride mask layer etching with the inclusion of H$_2$ are shown in Fig. 6.24. As with the blanket film, the etching rates of the nitride mask layer show a significant reduction in the etch rate when observed with the inclusion of H$_2$. The maximum total etch depth observed in the presence of silicon etching in this regime was 2 nm, a significant reduction from the values of 600 nm shown in Fig. 6.19. Figure 6.24(a) also indicates that all of the values of the etch depth are within the measurement error under all three pressure levels and as such, there may be no etching occurring at all.

Interestingly, while the etch rate of single crystal silicon decreased compared to etch rates without H$_2$ when using an oxide masking layer in Fig. 6.23(b), the etch rate of silicon when using H$_2$ with a nitride mask increases as summarised in Table 6.16. The results in Fig. 6.19 suggest that the nitride mask was reducing the etch rate of silicon by
reacting some of the free fluorine that would typically be consumed during the etching of silicon resulting in the reaction with Si-N chemical bonds instead. By using the hydrogen to impede the nitride etching, a greater level of free fluorine could be utilised in etching the silicon itself.

Figure 6.24 Etch depth of nitride masking layers (a) and undercut etch rates of single crystal silicon (b) in microns per minute.

With the substantial reduction in nitride etch rate, the etch rate of silicon increases as shown in Table 6.16, this is in agreement with those seen for oxide films in Fig. 6.18. Overall, this leads to a new summary of selectivities towards polysilicon and bulk silicon shown in Tables 6.17.
Table 6.16 Comparison of etching rates for single crystal silicon and PECVD nitride films using H\(_2\) process gas at 9 Torr using a nitride masking layer.

The overall etching behaviours follow the trends as seen in the previous sections: increasing carrier gas flow and process pressure provide an over improvement in etching rates which can again be associated with providing a higher partial pressure of XeF\(_2\) in the process chamber. The addition of hydrogen, while slowing the etching rates, improves the selectivity towards silicon nitride films. Tables 6.17 and 6.18 show comparisons of selectivities of etching single crystal and polysilicon films against oxide and nitride films for the chamber pressure of 9 Torr.

<table>
<thead>
<tr>
<th>Carrier Gas Flow (sccm)</th>
<th>Bulk Silicon Etch Rate (µm/min) without H(_2)</th>
<th>Bulk Silicon Etch Rate (µm/min) with H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.05</td>
<td>1.79</td>
</tr>
<tr>
<td>100</td>
<td>0.9</td>
<td>1.54</td>
</tr>
<tr>
<td>150</td>
<td>1.18</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Table 6.16 Comparison of etching rates for single crystal silicon and PECVD nitride films using H\(_2\) process gas at 9 Torr using a nitride masking layer.

<table>
<thead>
<tr>
<th>Carrier Gas Flow (sccm)</th>
<th>Selectivity to Oxide without H(_2)</th>
<th>Selectivity to Oxide with H(_2)</th>
<th>Selectivity to Nitride without H(_2)</th>
<th>Selectivity to Nitride with H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>797</td>
<td>1150</td>
<td>19</td>
<td>29833</td>
</tr>
<tr>
<td>100</td>
<td>1079</td>
<td>2800</td>
<td>21</td>
<td>19250</td>
</tr>
<tr>
<td>150</td>
<td>523</td>
<td>933</td>
<td>28</td>
<td>7450</td>
</tr>
</tbody>
</table>

Table 6.17 Comparison of single crystal silicon selectivity towards masking layers with and without H\(_2\) in the process at 9 Torr.

<table>
<thead>
<tr>
<th>Carrier Gas Flow (sccm)</th>
<th>Selectivity to Oxide without H(_2)</th>
<th>Selectivity to Oxide with H(_2)</th>
<th>Selectivity to Nitride without H(_2)</th>
<th>Selectivity to Nitride with H(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5366</td>
<td>31303</td>
<td>354</td>
<td>313033</td>
</tr>
<tr>
<td>100</td>
<td>5884</td>
<td>70615</td>
<td>336</td>
<td>176537</td>
</tr>
<tr>
<td>150</td>
<td>3476</td>
<td>19696</td>
<td>281</td>
<td>59090</td>
</tr>
</tbody>
</table>

Table 6.18 Comparison of polysilicon selectivity towards masking layers with and without H\(_2\) in the process at 9 Torr.
In terms of etching silicon in the presence of silicon dioxide and silicon nitride, the use of hydrogen in the gas mixture produces substantial improvement in the selectivity. While there is an observable reduction in etch rate of between 50-67% as shown in Table 6.15 and 6.16 depending on the material to be etched, orders of magnitude of improvement in selectivity of polysilicon to nitride can be obtained.

6.6 Summary
The continuous flow xenon difluoride etching method for silicon and other materials has been studied. Improvements over the pulsed processing method have been shown in terms of etch rates. While the pulsed-processing systems have shown etching rates for single crystal silicon up to 1.9 µm/min, the results for the continuous flow system have demonstrated etching rates of 2.25 µm/min, an 18% increase in etching capability. As part of this, investigations into polysilicon films were conducted. A considerable increase in the etching rate by a factor of almost 2 from 10 µm/min to 18 µm/has been achieved. This benefit appears to come from the increase in the capability of generating high XeF\(_2\) concentration regimes by running at a high pressure within the etch chamber of 9 Torr. This allows for a high partial pressure of XeF\(_2\) to be created thus increasing reactions of XeF\(_2\) with both single crystal silicon and polysilicon materials. Etching of selected metal films was also conducted. These metal films are commonly used in both MEMS and semiconductor manufacturing. The results show no measurable change in the etching of Al, AlSi (1%), Cr and Ti films but show etching rates up to 0.3 nm/min for Cu, 18 nm/min for Mo and 90 nm/min for Ta films respectively. This leads to the selectivities of 187:1 for single crystal silicon and 1173:1 for polysilicon to molybdenum and 47:1 for single crystal silicon and 469:1 for polysilicon to tantalum films. The molybdenum selectivity is higher than the values of 6:1 reported in previous literature [58, 61]. The assessment of selectivity between single crystal silicon and polysilicon with respect to PECVD silicon dioxide and silicon nitride films was made. Selectivities of greater than 1000:1 for PECVD silicon dioxide films and greater than 100:1 for silicon nitride films have been obtained.

A new process has been investigated utilising an additional component in the gas mixture for etching silicon and the related oxide and nitride films. Selectivities were substantially improved to show values of greater than 1000:1 for PECVD silicon dioxide films and 10000:1 for PECVD silicon nitride films thus showing a drastic improvement over all other reported work in the literature regarding selectivity towards
these key functional and structural layers. Although the improvement in selectivity comes with a decrease in etching rate from 18 µm/min to 6 µm/min using H₂ in the reaction gas, the improvement in selectivity far outweighs the moderate reduction in the etching rates.
Chapter 7 Conclusions and Future Work

7.1 Conclusion
The aim of the thesis was to investigate etch process technologies for MEMS and semiconductor manufacturing. As future devices designs emerge and reach the limitations of the existing wet etch process capabilities, new methods are being developed to meet these challenges. This thesis was aimed at improving the understanding of the emerging vapour phase etching methods and to develop new processes for high selectivity between silicon, silicon dioxide and nitride materials in the HF and XeF$_2$ based etching methods.

The effects of catalyst choice within vapour phase HF etching of oxide and nitride films were investigated. The primary focus was to understand the change in oxide and nitride etching rates in order to enhance the selectivity of oxide films to nitride based on the catalyst used in the process. Improvement in the selectivity is a key focus in MEMS devices for a number of reasons. Nitride as a surface passivation layer or as an etch stop are common uses and effective methods in which oxide can be etched with minimal effect on nitride are critical. The inclusion of these two common manufacturing materials will be unavoidable by device designers due to the high levels of information available for these films and the large available access to the deposition systems which are already available.

Etching requires process temperatures of 5°C while utilising high process pressure: 4.5 Torr when using water as the catalyst and 35 Torr when using an alcohol based catalyst. Etching rates up to 200 nm/min were achieved under these respective conditions. Direct comparison of water and alcohol as catalysts under the same process conditions show that alcohol etching processes are substantially slower than water based etching conditions with etching rates as low as 7 nm/min in contrast to 200 nm/min with an alcohol catalyst.

The highest selectivity achieved with an alcohol catalyst is 12:1 in a process at 21°C and a pressure of 11 Torr. For water, the best selectivity is 26:1 at 5°C and a pressure of 11 Torr. Where oxide films were observed to etch at comparable speeds with an alcohol based process, selectivites reached no higher than 7:1 as these conditions were also found to lead to higher nitride etching rates at the same time. By focusing on enhanced
oxide etching rates, the selectivity of 26:1 is higher than those reported previously in literature between PECVD oxide and nitride films.

Investigation of the effects of nitride film modification was also performed as an alternative means of improving the selectivity between these two films in HF etching processes. PECVD nitride films require the use of standard N\textsubscript{2} with silane and ammonia gas flow for deposition. Modifying the silane and ammonia gas flows and performing post process annealing at temperatures from 400°C to 600°C changes the chemical composition of the nitride films and its subsequent etching behaviours. Over the full range of nitride film gas ratios at deposition temperature of 300°C, etching rates decreased from 9.5 nm/min to 2.6 nm/min. This equates to a change in selectivity from 17:1 to 64:1 towards a PECVD oxide film. Etching rates were further reduced to 1 nm/min after annealing films at 600°C leading to attainable selectivities of up to 164:1 between PECVD silicon oxide and nitride films. This is a substantial improvement over work presented in existing literature.

The mechanisms behind these behaviours are that increasing the gas mixture in favour of silane in film deposition leads to an increase in silicon content within the film. As the films were annealed at higher temperatures, these compositional values did not change, and could not explain the further decrease in etch rate due to annealing. FTIR analysis was able to discern a change primarily in incorporated Si-H and N-H bonds, agreeing with existing literature that hydrogen is released from the nitride films in the annealing process under high temperature. This decrease in hydrogen did not continue the trend after an initial anneal at 400°C, thus this also did not explain the change in etching rates with annealing. Ellipsometry again could show the increase in refractive index in relation to increasing the gas mixture in favour of silane, but not with anneal temperature. Measurement of the stress within the film was found to closely follow the nitride etching rate behaviour in each of the seven gas ratio samples. From EDX, ellipsometry and FTIR analysis, it is clear the films do not change their composition significantly as anneal temperatures increase, the change in stress however, suggests further molecular modification induced by the anneal process can improve selectivity results to those higher than described previously.

The etching of silicon in vapour phase by xenon difluoride (XeF\textsubscript{2}) was also investigated. The primary use of this method is the vapour phase etching of silicon-
based films. The focus in this chapter was to understand the benefits of the continuous flow hardware configuration over the designs that have been in place for an established period of time in previous literature. Investigation into the undercut etch rates of both single crystal silicon and polysilicon films was conducted as well as the effects on selectivity towards silicon dioxide and silicon nitride films. Further to this, a selection of metals were also included in the investigation in order to understand their relative etch selectivity towards both silicon and polysilicon including chrome, tantalum, molybdenum, copper and aluminium.

The results of the investigation show that the continuous flow technique was capable of improving the etch rate of single crystal silicon from 1.96 µm/min to 2.25 µm/min, or by 14%, while the polysilicon undercut etching rates were substantially improved by 80% from previously reported literature of 10 µm/min to 18µm/min. This configuration allows for a greater pressure control for etching which increases the residence time of the reactant gas. It was found that the benefit of the hardware configuration allows for the utilisation of increased process pressures in conjunction with the carrier gas flow through the source material. By changing this flow, the concentration could be adjusted, and in conjunction with pressure control, this allows for a more consistent concentration and partial pressure of xenon difluoride unlike in the pulse process system which would immediately begin to lose concentration as the XeF₂ molecules are consumed during the etch process.

A new process that allows for the increase in selectivity by reducing the interaction of free fluorine generated by the reaction with XeF₂ and silicon with the addition of hydrogen gas as a means of improving selectivity towards oxide and nitride films, was conducted. The selectivity of PECVD oxide films towards bulk silicon has been improved from 500:1 to 1000:1 with the addition of hydrogen. The effect is even more remarkable towards PECVD nitride films, the selectivity between bulk silicon and the nitride films can be increased from 19:1 to 10000:1. When etching polysilicon, selectivities of 20000:1 towards the oxide films could be achieved with the inclusion of hydrogen while without hydrogen the value was over 3000:1. Silicon nitride films were found to have a selectivity of greater than 200:1 without hydrogen and over 50000:1 with hydrogen when etching polysilicon films.
7.2 Future Work

The work carried out within the thesis has provided new understanding and discoveries in vapour phase etching technologies for MEMS manufacturing. A number of future considerations are necessary in both HF and XeF₂ etching methods.

The generation of a mathematical model for the etching of oxide and nitride films in vapour phase HF etching would be a substantial area of work to conduct. The major concerns with this would be related to the types of catalyst and films in use. It has been observed that unless these films come from a manufacturing foundry where the tools are high accuracy production level systems, there is a large level of variability in the types of oxide and nitride films available. This leads to an issue in model verification, which could work for one type of film, but not many others. Ideally, this work would use films from production grade deposition systems in the mathematical models to study the differences between the catalysts.

Incorporation of an FTIR or ellipsometer along with the etching chamber would be a very interesting concept. This would allow for in-situ analysis of oxide films as they are etched. One of the factors considered in HF etching is an initiation stage on the surface of the oxide film before etching is established. Using one of these methods could give a greater understanding of the nature of etching initiation in the first few seconds in a chamber and further help understand and improve the etching conditions for improving selectivities to key material pairings.

One over-riding issue for vapour phase HF etching is the inability to use doped oxide films. Investigation into process conditions to etch these films without the formation of residues would be a substantial discovery. One aspect of PECVD nitride modification for improved selectivity that was not investigated in this thesis is the effect of the RF power in the PECVD deposition. This was due to the fact that it was considered a risk to increase the RF power in the current system due to a potential to cause damage to the equipment as the tool is calibrated at one RF value only.

In terms of the xenon difluoride based etching method, one substantial area of understanding not considered was the effect of temperature due to the limitation of the hardware system, but this can be studied in future with a suitable system design.
In both etching methods, further understanding of selectivity between different materials is also necessary. While a study into silicon nitride and oxide films has been carried out, there are many permutations and a substantial library of film materials to consider for further investigation that are beginning to find use within MEMS and NEMS designs. Many of these films are completely uncharacterised within the semiconductor industry.
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