DRY ETCHING OF NOVEL DIELECTRIC FILMS

By

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Ye shall know the truth, and the truth shall make you free.

St. John 8:32
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There has been an extensive effort over the past decade to develop novel dielectric thin films, with the leading candidates being TaO$_x$ and (Ba,Sr)TiO$_3$. These films have many applications, which include their use as both a dielectric layer for storage capacitors in dynamic random access memory (DRAM) or gate insulators in metal oxide field effect transistor (MOS-FET).\(^{(1-8)}\) For wide use of these kinds of films, etching techniques for submicron patterning are required. This thesis reports an investigation in of the etching processes for novel high dielectric thin films.

First, Inductively Coupled Plasma etching of Ta$_2$O$_5$ was performed in a variety of different chemistries, including SF$_6$ with additions of O$_2$, Ar, CH$_4$ or H$_2$ ; Cl$_2$/Ar ; N$_2$/Ar and CH$_4$/H$_2$/Ar. Etch rates up to \(~1200\ \text{Å} \cdot \text{min}^{-1}\) were achieved with either SF$_6$ or Cl$_2$ based chemistries. Under these conditions the etch rates for Si were approximately 4-7 times faster, although equi-rate etching was achieved at low source powers and low
halogen gas percentages in the plasma chemistry. The etched Ta$_2$O$_5$ surfaces were smooth over a broad range of conditions of source power, chuck power and process pressure. There was no effect of post deposition annealing on the Ta$_2$O$_5$ etch rates, at least up to 800 °C.

Additionally, the effect of ultra violet (UV) illumination effect during dry etching was examined and produced significant enhancements (up to a faster of 2) in etch rates due to photo-assisted desorption of the TaF$_x$ products. UV illumination is an alternative to employing elevated sample temperatures during etching to increase the volatility of the etch products and may find applications where the thermal budget should be minimized during processing.

Finally, high density plasma etching of (Ba,Sr)TiO$_3$ (BST) and LaNiO$_3$ (LNO) thin films was performed in two different plasma chemistries, Cl$_2$/Ar and CH$_4$/H$_2$/Ar. While the latter chemistry produced extremely low etch rates ($\leq$ 100 Å·min$^{-1}$) under all conditions, the Cl$_2$/Ar produced smooth anisotropic pattern transfer. The etching was still strongly ion-assisted, but maximum removal rates of ~900 Å·min$^{-1}$ for both materials were achieved with selectivities of ~16 for BST and ~7 for LNO over Si. A single layer of thick (~7 µm) photoresist proved to be an effective mask under these conditions.
CHAPTER 1
INTRODUCTION

1.1. Tantalum Pentoxide Thin Film

There has been an extensive effort over the past decade to develop Ta$_2$O$_5$ as a dielectric for storage in dynamic random access memories\(^{(1-5)}\) as well as a gate insulator in metal-oxide-semiconductor devices.\(^{(6-10)}\) Additional applications include its use as an insulating layer in thin film electroluminescent display devices,\(^{(11-15)}\) as an antireflective layer for optical materials,\(^{(14-15)}\) and as a detection layer in biological and chemical sensors.\(^{(16-19)}\)

The projected semiconductor industry association roadmap for future generations of Metal-Oxide-Semiconductor Field Effect Transistor (MOSFET)-based integrated circuits calls for 30-40 Å gate oxide equivalent thickness by 2000, and ≤15 Å by 2009.\(^{(20)}\) The thickness of SiO$_2$ must be scaled to obtain the designed speed improvements, higher device currents and reduced short-channel effects demanded by future complementary MOS circuits. However, a limit exists as to how thin SiO$_2$ layers can be reproducibly formed and the necessity for a new gate insulating material arises. For a MOSFET to perform as a transistor, the gate must have greater control over the channel than does the drain, i.e. the gate-to-channel capacitance must be larger than the drain-to-channel capacitance suggested by the model of Liu et.al.\(^{(21)}\)

\[
L_{\text{min}} \sim T_{\text{ox}} \cdot X^j_f
\]
Where $L_{\text{min}}$ is the minimum acceptable gate length, $T_{\text{ox}}$ is the gate oxide thickness and $X_j$ the junction depth. Gate oxide thickness must be scaled down with channel lengths to suppress short-channel effects.\(^{(22,23)}\) There are questions concerning the integrity of very thin SiO$_2$ layers, specifically in regard to breakdown mechanisms, dopant penetration and higher leakage currents.\(^{(24,25)}\) Due to the various limitations of SiO$_2$, alternate gate dielectrics with reduced gate leakage currents will be required for future sub-100 nm CMOS generations. Materials with high dielectric constants, $K$, such as Si$_3$N$_4$, TiO$_2$, and Ta$_2$O$_5$ may prove to be the most desirable solution. Higher dielectric materials offer large potential improvement in reducing tunneling currents. Regardless of the dielectric materials, the same gate capacitance is desired for a MOSFET device in order to maintain the same drive current. Therefore, for the same capacitance,

$$C = \frac{\varepsilon_d}{t_{\text{ox}}}$$

$$t_{\text{ox}} = \frac{\varepsilon_d}{C} \sim \varepsilon_d$$

In principal, a high-$K$ dielectric would allow a proportionately higher power supply voltage at a comparable or higher capacitance for the same voltage.\(^{(26)}\) Although integrating such materials has proven to be difficult due to interface states, leakage, and high thermal cycle incompatibilities, other manufacturability limits may be eased. For example, Ta$_2$O$_5$ with a relative dielectric constant around 25 can be deposited approximately 6.5 times thicker than SiO$_2$ for the same effective gate capacitance. Therefore, a 6.5 nm Ta$_2$O$_5$ dielectric layer with an equivalent $t_{\text{ox}}$ of 1 nm would require less precision in controlling the thickness and, hence, greater reproducibility. In fact,
Ta$_2$O$_5$ has been thoroughly studied over the past three decades due to its extensive use in classical capacitor technology for storage in dynamic random access memories$^{(9,10,27)}$ and electro-luminescent displays.$^{(15)}$ In 1987, Angle and Tally$^{(28)}$ reported electrical and storage characteristics of the Ta$_2$O$_5$-SiO$_2$ device for use in nonvolatile memory technologies. Further motivation for the study of Ta$_2$O$_5$ has begun to emerge more recently during the past decade, as the scaling of integrated circuits has pushed the conventional dielectric films, like SiO$_2$ and Si$_3$N$_4$ close to their physical limitations.

The crystalline form of tantalum pentoxide has two principle phases, an orthorhombic ($\beta$) phase and hexagonal ($\delta$) phase. The orthorhombic phases can be divided into two distinct forms, a high temperature form and a low temperature form (called $\alpha$-Ta$_2$O$_5$), with a reversible transition occurring at approximately 1360 °C. The lattice parameters for the orthorhombic phase are $a=6.198$ Å, $b=40.209$ Å and $c=3.888$ Å. The lattice parameters for the hexagonal phase are $a = 3.87$ Å, $b = 3.87$ Å. The crystalline structure has been reported to depend significantly on the deposition temperature, as well as the post-deposition annealing temperature. The orthorhombic $\beta$-Ta$_2$O$_5$ is preferentially formed in films deposited by PVD or LPCVD with a post-deposition anneal. Yet, for films deposited by PECVD and annealed the crystalline structure is generally hexagonal $\delta$-Ta$_2$O$_5$. $^{(27)}$

Most of the work to date has focussed on improving the electrical properties of Ta$_2$O$_5$ deposited by various chemical vapor deposition methods, in particular the use of post-growth O$_2$-based annealing processes to reduce leakage currents in capacitor structures. $^{(29-32)}$ There has been relatively little work on developing etching processes for Ta$_2$O$_5$. Wet etching has generally been performed at elevated temperatures (200-500 °C)
in HF-based solutions\textsuperscript{(33-36)} or with anodic oxidation.\textsuperscript{(37)} None of these processes is particularly attractive from the viewpoint of selecting appropriate mask materials. A few reports have appeared on reactive ion etching (RIE) using fluorocarbon gas chemistries (CH\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, CHF\textsubscript{3}, CF\textsubscript{3}Cl and CCl\textsubscript{2}F\textsubscript{2}).\textsuperscript{(38-40)}

In recent times, high density plasma processing has gained popularity due to the ability to have essentially independent control of ion energy and ion flux. These tools typically operate at lower pressures (1-10 mTorr) than RIE (50-200 mTorr), with less need to employ sidewall-polymer-forming gas chemistries in order to achieve anisotropic etching.\textsuperscript{(41)}

In this thesis we report on a study comparing etch rates, etched surface morphologies of Ta\textsubscript{2}O\textsubscript{5} and selectivities over electrodes in Inductively Coupled Plasma (ICP) discharges, using a number of differential chemistries. Also, we report on the use of ultraviolet (UV) light irradiation during Inductively Coupled Plasma (ICP) etching to produce enhancements in etch rate in both Cl\textsubscript{2}- and F\textsubscript{2}- based chemistries.

2) (Ba,Sr)TiO\textsubscript{3} Thin film

High dielectric constant materials are under intense development as a replacement for SiO\textsubscript{2} as gate materials in metal oxide field-effect transistors or as storage capacitors in advanced dynamic random access memories (DRAM).\textsuperscript{(42-46)} Another application is for decoupling capacitors in device packages.\textsuperscript{(27,45)} The leading candidates are TaO\textsubscript{x} and (Ba,Sr)TiO\textsubscript{3} (BST), based on their dielectric breakdown strength, area capacitance and measured leakage current densities.\textsuperscript{(42-55)} While dry etching process are well-developed for conventional SiO\textsubscript{2}-based dielectric structures, there is much less known about the etching
characteristics of the newer materials. In this paper we report on high density plasma etching of thin film (Ba,Sr)TiO$_3$ and LaNiO$_3$ (LNO) in two different chemistries, namely Cl$_2$/Ar and CH$_4$/H$_2$/Ar. In a conventional DRAM capacitor technology, doped polysilicon is generally employed as the electrode material. However with oxide ferroelectrics this is not feasible because of interfacial reactions to form SiO$_x$, which reduces the effective dielectric constant of the capacitor stack. There have been two basic classes of electrode materials employed to date, namely those based on elemental metals, predominantly Pt (Ir and Ru have also been reported) or those based on metallic oxides such as IrO$_2$, RuO$_2$ or high-Tc superconductors.$^{(45)}$ The metallic oxides have a potential advantage in improving the fatigue performance of capacitors. In this work we have chosen LaNiO$_3$ as the metallic oxide for use with BST films, since it displays several advantages as an electrode material.$^{(56-60)}$

Our etching experiments have focussed on comparing the Cl$_2$ and CH$_4$/H$_2$ chemistries for achieving practical etch rates for the two materials. In the former case the etch products would be expected to be metal chlorides and O$_2$, while in the latter case metalorganics, metal hydrides, water vapor and O$_2$ may be expected to form. Under high density conditions, the etching reactions are generally strongly ion-assisted so that fully chlorinated products need not be formed before ion impingement helps desorb surface species. We find that highly anisotropic pattern transfer is possible in both materials using ICP etching, with Cl$_2$/Ar providing much higher removal rates.
2.1. Review of Plasma Properties

Dry etching processing using a plasma is one of the most important processes for integrated circuit manufacturing. Plasma-driven chemical reactions and/or reactive ion beams are used to remove material in dry etching. Dry etch processing has become popular in semiconductor manufacturing because of advantages relative to wet etching, usually vertical pattern transfer, good uniformity, high reproducibility and good controllability. It also provides much higher resolution potential by overcoming the problem of isotropy. All semiconductor manufacturers need advanced plasma etching for increasing circuit density and creating narrower line-widths.

A plasma is a partially ionized gas, fundamentally a conducting gas known as the fourth state of matter, and has properties which are different from ordinary neutral gas or non-conducting fluids\(^{(61)}\). A plasma is usually formed when high energy electrons have an average Coulombic force higher than the electron binding energy. An electric field is applied to the plasma which receives the energy and dissipates it in various ways. Free electrons in the plasma have a much higher energy. In the gas phase, the electrons are accelerated so that they collide with gas molecules where they can cause electron ejection or bond-breaking, and positive ions and molecular fragments are generated in the many different processes that occur in the chamber. For example, for a molecule XY, the following may occur due to electron collisions.
Dissociation: \[ e + XY \leftrightarrow X + Y + e \]

Ionization: \[ e + X \leftrightarrow X^+ + 2e \] ; \[ e + XY \leftrightarrow XY^+ + 2e \]

Excitation: \[ e + X \leftrightarrow X^* + e \] ; \[ e + XY \leftrightarrow XY^* + e \]

Where \( X^+ \), \( XY^+ \) are ions and \( X^* \), \( XY^* \) are radicals. These ions and radicals have energies much larger than the ground state, and are very reactive because of their incomplete bonding state.

For most plasma etching, the extent of ionization is very small. Typically, the ionization rate is one charged particle per \( 10^5 \) - \( 10^6 \) neutral atoms and molecules \(^{62}\). In the plasma, the range of electron energies is usually between 1 - 20 eV and the ion density is normally between \( 10^9 \) - \( 10^{12} \) cm\(^{-3}\) \(^{63}\).

Due to a mass difference between electrons and ions, the electrons can move more rapidly than the ions. This is especially true in high frequency and radio frequency systems where the electrons can obtain much higher energies than ions. The high mobility of electrons means that most of the applied potential appears across a momentary negative sheath, and the plasma is a fairly good conductor where most of the potential drop occurs across the dark space sheath. This dark space sheath will form at both electrodes and behaves like a capacitor which is governed by the electrode areas, cathode \( (A_1) \) and anode \( (A_2) \). The self bias voltage will be divided approximately according to the ratio \( (A_2/A_1)^4 \) \(^{64}\). The potential distribution in the plasma chamber system is shown in the Figure 1-1.

In a plasma, electrons will tend to escape to the electrode and chamber walls and be collected more rapidly than ions, establishing a net negative current flow from the plasma volume to ground. This loss of negative charge in the plasma creates a potential difference,
called the plasma potential \((V_p)\). The magnitude of this potential is determined by the geometry of the contacting volume in plasma chamber system. Generally, the smaller the volume of the enclosing structure, the larger is \(V_p\).

Figure 2-1. Potential distribution in rf discharge.
The potential changes happen fast in the sheath region. The width of the sheath depends on the voltage applied to establish the plasma and the ion density of the plasma. Ions in the sheath region are dramatically accelerated - in this case, positive ion energies are typically 1-1000 eV \(^{(61)}\) towards the negatively charged electrode producing secondary electrons on impact. The secondary electrons are accelerated out into the plasma by the same space charge sheath and may obtain considerable energy from the sheath \(^{(63)}\). So ions from the plasma region pass into the sheath region and are accelerated towards the electrode. If an inert gas is used then accelerated ions bombard the electrode surface or sample wafers removing material by physical sputtering.

2.2. Dry Etching Techniques

All dry etch processes and reactors are basically alike in that the wafer is placed in a vacuum chamber, gases are admitted to the chamber, and a plasma is initiated in the gas. For an etch process to proceed successfully there are four required conditions. The first is that the plasma must generate species. The second is that the reactant radicals must be transferred to the sample surface. The third is the atoms on the sample must react with the radicals in the plasma, and finally the by-products must be moved away from the surface of sample. Of these four events, the slowest step primarily determines the etch rate, which may be diffusion or chemical-reaction limited.

In recent years there have been many dry etching methods developed according to different techniques and different reactors; for example, plasma etching (Barrel), reactive ion etching (RIE), magnetically enhanced reactive ion etching (MERIE), trielectrode
(TRIODE), rf down stream, microwave down stream, co-axial downstream, surface wave plasma (SWP), triode downstream, split power reverse phase (SPRP), electron cyclotron resonance (ECR), transformer cyclotron resonance (TCP), inductively coupled plasma (ICP), helicon - type etc. However, only some of the most popular dry etching techniques will be explained in this chapter. Figure 2-2. shows schematics of chamber diagrams of representative techniques.

2.2.1. Plasma Etching

Until the 1970's, pure plasma etching was known as one of the most popular etching techniques, together with wet etching. Typically, plasma etching is performed over 100 millitorr in pressure, and is purely chemical in nature meaning and there is no charged particle bombardment of the surface to enhance the etch rate or to promote directionality. Nowadays, this technique is usually used to strip the photo resist mask layer after patterning transfer, called plasma ashing.

Reactive species generated in plasma react with the sample surface and create volatile etch products that are then swept away. If the gases were carefully selected, then it is possible to achieve very high selectivity through this process. Pure plasma etching has significant advantages, such as reducing the damage to the samples during the etching process. Also, one frequently uses plasma etching for dry cleaning of damaged wafers after high energy ion bombardment. For example, deep contact hole formation, trench etching and gate material etching for field effect transistors performed without surface treatment after ion assisted bombardment etching.
Figure 2-2. Schematic chamber diagrams of representative etching techniques.
Figure 2-3. Schematic diagram of DC self-bias in RIE system.
lead to devices suffering from serious electrical or physical degradation. These include high metal contact resistance, high leakage current in the trench etched surface and source or drain junction leakage in transistors.

In spite of its great advantages, there is the critical issue that the films tend to etch in all directions at once, so one can not achieve vertically fine sub-micron patterning using a pure plasma type etching process. The result is an isotropic etch, therefore, this process is limited to isotropic pattern transfer in semiconductors.

2.2.2. Reactive Ion Etching (RIE)

Ions from the plasma can bombard the surface to be etched at normal incidence and with energy of hundreds of volts, so it is easy to achieve an anisotropic pattern transfer.

The two electrodes, one with the radio frequency power supply and a blocking capacitor are shown in figure 2-3. The blocking capacitor eliminates DC current from the electrode. Typically, the pressure is between 10-100 millitorr, and a 13.56 MHz radio frequency power (rf) through coupling discharge is applied to generate plasma discharges. In this process, there are $\sim 10^{13}$ cm$^{-3}$ neutral atoms for each 1 millitorr gas pressure, whereas the ion density is typically $10^{10} - 10^{11}$ cm$^{-3}$ in most conventional rf discharges.

Fig.3 shows the voltage drop between nodes Va and Vb. For the purpose of illustration it will be supposed that the rf waveform is square and varies from $+V_x$ to $-V_x$. When the supply voltage Va is negative, the electrode voltage Vb must follow Va, then the electrode attracts an ion current. When Va switches to positive, the electrode will attract electrons instead. If it is repeatedly switched many times until the time-average current is zero, the node Vb will oscillate about a negative value called the DC self-bias of the electrode. This occurs because of
the difference in mobility between electrons and ions. So there is a nearly continuous ion bombardment of the powered electrode. It should be noted that this effect derives from the different mobility of the electrons and ions, which is a fundamental characteristic of the discharge. If the electrode's sizes are unequal to each other, the potential difference is concentrated at the smaller electrode.

For reactive ion etching, the sample is put on the powered electrode (negatively biased cathode) and accelerated ions bombard the samples and anisotropic pattern transfer can be achieved. RIE takes advantage of a synergism between the physical and chemical etching mechanism and achieves etch rates that are faster than the sum of the two components. However, this technique has a serious disadvantage which is damage to the samples because of the high energy ion bombardment. In order to decrease the sample damage and increase the etch rates, one needs much lower ion energy and a high density plasma technique, therefore new techniques are needed to solve those kinds of problems.

2.2.3. Chemically Assisted Ion Etching

Chemically assisted ion etching techniques are popular processes because of their great advantages. In the past, one usually used plasma or RIE-type etching techniques. However one of the disadvantages of the RIE process is that the chamber pressure is high and the ion damage to the samples is severe. At pressures of a few hundred millitorr, where it is relatively straightforward to create a plasma, it is difficult to get reliable etch process for ULSI devices or sub-micron feature size-devices. Nowadays, to increase pattern density and reduce the power consumption, devices have continuously scaled down and the structures have become laterally much smaller and vertically much higher\(^{(66,67)}\).
Figure 2-4. SEM micrographs of DRAM; trench type storage node (top), fin type storage node (bottom).
(from Samsung Electronics).
For example, dynamic random access memory (DRAM) structures are shown in Figure 2-4. The structure at left is trench type for storage node and the one at right is stacked capacitor profile. The DRAM processes usually lead technology development in semiconductor industries because of its more advanced technologies; for example, ultra sub-micron patterns (under 0.1 um), lower damage process, high selectivity techniques, high etch rate, higher aspect ratio, deep trench etching and small deep contact hole (diameter ~ 0.1 um depth ~ 5um) and using new advanced materials. To achieve advanced etching processes, low pressures (~ mtorr) and high density plasma techniques are necessary. However in case of the RIE method, the plasma is generated in the etch reactor with only a single source power applied to the electrode so it is not easy to obtain high density plasma and low ion energy conditions in RIE system without extremely high applied power and damage.

In the 1980s - 1990s many kinds of high density etching techniques were developed, such as ICP, ECR, and helicon resonance. ECR and helicon sources employ an external magnetic field to shape and contain the plasma, while ICP sources do not (68). One of the methods involves the addition of magnetic fields configured to reduce electron loss from the plasma and the sample where electrons in the plasma are forced to orbit about magnetic field lines while absorbing microwave energy. External magnetic fields constrain the electron's motion and fewer are lost by collisions with the reactor wall than in conventional RIE, and therefore the plasma potential is much lower than ground potential. Typically, ion energies are ≤15 eV and there is a higher ion density of $10^{11}$-$10^{12}$ cm$^{-3}$ compared with RIE tools ($\sim 10^9$ cm$^{-3}$). In ECR tools, rf or dc bias of the substrate chuck controls the ion energy while the plasma density is controlled by varying the microwave power and neutral gas pressure.
In spite of the advantages of the ECR system, a major problem of the ECR is bad uniformity due to the limitation of power supply. In this point, ICP has a better characteristics than ECR. In inductively coupled plasma tools, the reactor chamber is encircled with rf coils which carry rf current and generate a magnetic field in the up and down directions. The magnetic field then generates an electric field which confines the accelerated electrons in a circular motion. The electrons, in a circular path, will have only a small chance to be lost to the chamber walls, resulting in low dc self bias. Ion energy, separated from the ion flux, can be controlled by applying another rf source at the chuck. Separate control of the chemical etching and ion bombardment can be obtained in this manner.

Finally, the chemically assisted ion etching technique can achieve anisotropic, fine pattern transfer of the deep and ultra-sub micron structures as well as new advanced materials devices.

2.2.4. Ion beam Milling

Ion beam milling is a purely physical technique, with no chemical reactive etching factor. A relatively high energy (500-800 eV) inert ion beam transfers large amounts of energy and momentum to the substrate. If the force is strong enough these ions can physically remove material from the sample surface. Usually, the pressure used in ion milling is under the 0.1 millitorr. Since the pressure is low, the mean free path of the particle is long and the ejected sputtered material can cross the reactor vessel and reach opposing walls. When uniform ion beams bombard a sample, it provides an anisotropic profile in pattern transfer. But, poor selectivity, low etch rate and severe damage on the sample are critical disadvantages to widely
use the ion milling process, because of physical sputtering, and the etch rate is strongly dependent on the beam angle.

Ion beam milling is used to make ultra thin samples for material analysis, such as transmission electron microscopy (TEM). Sometimes it is used as a planarization process to fill high aspect ratio features by opening the edge boundary more widely (decreasing the aspect ratio), thereby allowing deposition in the deep valley regions.
CHAPTER 3
INDUCTIVELY COUPLED PLASMA ETCHING OF Ta$_2$O$_5$

3.1. Materials and Experimental Procedure

a-Ta$_2$O$_5$ layers ~1000 Å thick were deposited on (100), B-doped (1 Ω-cm) Si wafers by plasma enhanced chemical vapor deposition using Ta(C$_2$H$_5$O)$_5$ and O$_2$ precursors. The deposition temperature was ~350 °C. Post-growth annealing at 600-800 °C for 1 min in an O$_2$ ambient was performed to examine whether there was any effect of film densification on the etching properties, as previously reported for wet etching experiments.$^{(35)}$ The 800 °C annealing is close to the recrystallization condition.

For etch rate experiments, a small section of the 5x5 mm$^2$ samples was masked with Apiezon wax, and the etch depth measured by stylus profilometry after removal of the mask in acetone. The etched surface morphology was measured by tapping mode atomic force microscopy (AFM). We generally included some Si samples in each run to give some idea of Ta$_2$O$_5$/Si etch selectivity.

The dry etching was performed in a PlasmaTherm 790 series reactor. Samples were thermally bonded to a He backside-cooled, rf powered (13.56 MHz) chuck. The plasma was generated in a 3 turn ICP source operating at 2 MHz. Gas injection into this source was metered through electronic mass flow controllers at a typical load of 15-20 standard cubic centimeters per minute (sccm). The process pressure was held constant at 2-5 mTorr, and Cl$_2$/Ar, SF$_6$/Ar, SF$_6$/O$_2$, N$_2$/Ar and CH$_4$/H$_2$/Ar chemistries were investigated.
The Ar is generally added to facilitate plasma ignition at low pressure, while O\textsubscript{2} addition enhances the atomic neutral fluorine density in F\textsubscript{2}-based discharges.

### 3.2. Results and Discussion

#### 3.2.1. SF\textsubscript{6}-based etching

Figure 3-1 shows a comparison of Ta\textsubscript{2}O\textsubscript{5} and Si etch rates, with the resultant selectivities, as a function of discharge composition in SF\textsubscript{6}/Ar (top) and SF\textsubscript{6}/O\textsubscript{2} (bottom). The etch rates for Ta\textsubscript{2}O\textsubscript{5} increase more slowly with increasing SF\textsubscript{6} concentration than do the rates for Si, with the consequence that the maximum selectivity for Si over Ta\textsubscript{2}O\textsubscript{5} is achieved in pure SF\textsubscript{6} discharges. The dc self-bias increases in both chemistries as the SF\textsubscript{6} concentration increases, indicating that the positive ion density is decreasing. Note that Ta\textsubscript{2}O\textsubscript{5} etch rates of \(~1200 \text{ Å} \cdot \text{min}^{-1}\) are achieved in the SF\textsubscript{6}-based mixtures, at self-biases in the range \(-215\) to \(-290\) V. We could not detect the etch products for Ta\textsubscript{2}O\textsubscript{5} with optical emission spectroscopy, but assume they are probably TaF\textsubscript{x} and O\textsubscript{2}. In the case of Si, we readily observed the SiF\textsubscript{x} etch products, with emission lines in the range 400-430 nm.

The effect of ICP source power on the etch rates is shown in Figure 3-2 for fixed plasma composition. The Si etch rate increases either modestly or not at all over the range 300-1000 W, while the Ta\textsubscript{2}O\textsubscript{5} etch rate tends to decrease at the higher powers. This decrease is at least partially caused by the fall-off in dc self-bias, which is suppressed as the positive ion density in the discharge increases at high powers. It is clear that because Si etches in atomic fluorine even without ion bombardment, whereas Ta\textsubscript{2}O\textsubscript{5} does not, that there will always be a faster etch rate for the former in non-polymer-forming plasma.
Figure 3-1. Etch rates and selectivities for Si over in SF$_6$/Ar (top) and SF$_6$/O$_2$ (bottom) discharges (250 W rf chuck power, 750 W source power, 2 mTorr), as a function of SF$_6$ percentage.
Figure 3-2. Etch rates and selectivity for Si over Ta$_2$O$_5$ in SF$_6$/Ar (top) and SF$_6$/O$_2$ (bottom) discharges (250 W rf chuck power, 2 mTorr) as a function of ICP source power.
Figure 3-3. Etch rates and selectivity for Si over Ta$_2$O$_5$ in SF$_6$/Ar (top) and SF$_6$/O$_2$ (bottom) discharges (750 W source power, 2 mTorr) as a function of rf chuck power.
chemistries. To achieve selectivity for Ta$_2$O$_5$ over Si in F$_2$-based chemistries, it will likely be necessary to try mixtures such as SF$_6$/CH$_4$ or CF$_4$/H$_2$.

The rf chuck power controls the incident ion energy, with the latter being approximately equal to the sum of the plasma potential (roughly –25 V in this tool, from Langmuir probe measurements) and the dc self-bias. One would expect an increase in the etch rates of both Ta$_2$O$_5$ and Si because of the improved efficiency of ion-assisted reactions (both initial bond-breaking and etch product desorption). This is indeed the trend observed, as shown in Figure 3-3 for both SF$_6$/O$_2$ and SF$_6$/Ar. Selectivity generally is found to decrease with increasing ion energy because of the larger contribution of physical process relative to chemical etching (Figure 3-3).

![Figure 3-4](image)

Figure 3-4. RMS roughness of Ta$_2$O$_5$ and Si surfaces before and after etching in SF$_6$/Ar or SF$_6$/O$_2$ discharges (250 W rf chuck power, 750 W source power, 2 mTorr).
The etched surface morphologies were examined by AFM, and Figure 3-4 shows the measured root-mean-square (RMS) roughness (measured over 1 \( \text{\mu m}^2 \) area) after exposure to SF\(_6\)/O\(_2\) or SF\(_6\)/Ar discharges (250 W rf chuck power and 750 W source power). The Ta\(_2\)O\(_5\) surface roughnesses are unchanged from their control values, whereas the Si shows some etch-induced texture. In each case the etch was performed for 30 secs, corresponding to etch depths of \( \sim 450 \) Å for Ta\(_2\)O\(_5\) and 2500-3000 Å for Si.

### 3.2.2. Cl\(_2\)-based etching

The results for Cl\(_2\)/Ar etching at fixed source power (750 W) and rf chuck Power (250 W) are shown in Figure 3-5 as a function of discharge composition. The rates increase as Cl\(_2\) is added, which is often an indicator of some chemical contribution to the etch mechanism. Indeed the enhancement factor is 10-20 for etch rates obtained in pure Cl\(_2\) relative to pure Ar, much larger than expected based on a purely physical sputtering enhancement due to the heavier mass of Cl\(_2^+\) (74) versus Ar\(^+\) (40), which are the most abundant ions present. The ratio of molecular to atomic chlorine is in the range 5-10 under our conditions. The selectivity for Ta\(_2\)O\(_5\) over Si is in the range 0.3-1. Similar maximum etch rates (\( \sim 1200 \) Å·min\(^{-1}\)) for Ta\(_2\)O\(_5\) in Cl\(_2\) were obtained as with SF\(_6\) discharges. The bottom of Figure 3-5 shows the calculated etch yields, with the strong enhancement upon Cl\(_2\) addition evident.

Figure 3-6 shows the effect of both source power (top) and rf chuck power (bottom) on the Ta\(_2\)O\(_5\) and Si etch rates at fixed plasma composition (10Cl\(_2\)/5Ar). The etch rates for both materials decrease at high values of either parameter, a phenomenon often observed in high density processes and often ascribed to ion-assisted desorption of the reactants.
Figure 3-5. Etch rates and selectivity for Ta$_2$O$_5$ over Si (top) and etch yields (bottom) as a function of Cl$_2$ percentage in Cl$_2$/Ar discharges (250 W rf chuck power, 750 source power, 2 mTorr).
Figure 3-6. Etch rates and selectivity for Ta₂O₅ over Si in Cl₂/Ar discharges as a function of source power (top) or rf chuck power (bottom).
(neutral atomic chlorine in this case) before they can react with the substrate.\(^{(69)}\) The Ta\(_2\)O\(_5\)/Si selectivities again fall in the range 0.3-1 over the whole range of conditions investigated. Note that conventional RIE, which corresponds to 0 W source power, produces etch rates for both materials of only a few tens of angstrom per minute.

3.2.3. Other chemistries : CH\(_4\)/H\(_2\)/Ar and N\(_2\)/Ar

The CH\(_4\)/H\(_2\)/Ar /Ar chemistry has proven useful for dry etching materials such as InSnO\(_x\) and III-V compound semiconductors (GaN, GaAs, InP) through the formation of metal organic and hydride etch products. In the case of Ta\(_2\)O\(_5\), possible products include (CH)\(_x\)Ta\(_y\), H\(_2\)O and O\(_2\). We examined the effect of varying source and chuck power, at fixed discharge composition (chosen from past experiments in other materials). Figure 3-7 shows that under all of our conditions, Ta\(_2\)O\(_5\) etches at a slower rate than Si. The rf power results show that this is essentially a sputtering process, and the calculated ion yields were very low <0.1.

Another possible etch chemistry is based on N\(_2\)/Ar, in the hope that reactive nitrogen neutrals would extract oxygen as N\(_2\)O or NO\(_2\), with the Ta being removed by Ar\(^+\) sputtering. Figure 3-8 shows that the etch rates for Ta\(_2\)O\(_5\) are again very low, and slower with N\(_2\)/Ar mixtures than with simple Ar\(^+\) sputtering. We also examined the rate of source power and chuck power, but again always found that the Ta\(_2\)O\(_5\) etched slower than Si, with selectivities for Ta\(_2\)O\(_5\)/Si of 0.4-0.8.
Figure 3-8. Etch rates and selectivity for Ta<sub>2</sub>O<sub>5</sub> over Si (top) and etch yields (bottom) as a function of N<sub>2</sub> percentage in N<sub>2</sub>/Ar discharges (250 W rf chuck power, 750 W source power, 2 mTorr).
Figure 3-9. AFM scans of Ta$_2$O$_5$ surfaces before and after etching in CH$_4$/H$_2$/Ar, Cl$_2$/Ar or N$_2$/Ar discharges (350 W rf chuck power, 750 W source power, 2 mTorr).
The etched $\text{Ta}_2\text{O}_5$ surface morphologies with the CH$_4$/H$_2$/Ar, N$_2$/Ar and Cl$_2$/Ar chemistries were similar to those of control samples, as shown in the example of Figure 3-9. This is consistent with equi-rate removal of the Ta and O, or else one would expect significant surface roughening.

A final point of interest is the effect of annealing of the $\text{Ta}_2\text{O}_5$ on the dry etch rates. Figure 3-10 shows that over the range 600-800 °C there was no measurable effect on etch rates, given that the error in the etch rate measurements use ±10%. While this result is not consistent with the previous results on wet etching of $\text{Ta}_2\text{O}_5$, it is perhaps not surprising because dry etching is less influenced by material quality.
CHAPTER 4
COMPARISON OF PLASMA CHEMISTRIES FOR DRY ETCHING OF Ta$_2$O$_5$

4.1. Materials and Experimental Procedure

Amorphous Ta$_2$O$_5$ films were deposited at 350 °C on B-doped (1 Ω cm), (100) Si wafers using Ta(C$_2$H$_5$O)$_5$ and O$_2$ precursors in a plasma enhanced chemical vapor deposition system. Section ~5x5 mm$^2$ from these wafers were masked with Apiezon wax for the etch rate experiments, while etched surface morphology was obtained from tapping mode Atomic Force Microscope (AFM) measurements. In each run a Si sample was included so we could calculate the Ta$_2$O$_5$/Si etch selectivity.

All of the etching was performed in a Plasma Therm 790 system in which the samples are thermally bonded to an rf-powered (13.56 MHz, 350 W), He backside-cooled chuck (4” diameter). The 3 turn ICP source operates at 2 MHz and powers up to 1000 W, with direct injection of gases into this source through mass flow controllers at a typical total flow rate of 15-20 standard cubic centimeters per minute.

4.2. Results and Discussion

Table 4-1 summarizes the maximum etch rates achieved for Ta$_2$O$_5$ in the different plasma chemistries investigated, along with the selectivity over Si. Both SF$_6$- and Cl$_2$-based mixtures produce etch rates at least an order of magnitude higher than CH$_4$/H$_2$/Ar or N$_2$/Ar, and there is always reverse selectivity with respect to Si i.e. the latter etches 2-6
Table 4-1. Comparison of maximum etch rates achieved for ICP etching of Ta$_2$O$_3$ in different plasma chemistries, and selectivity over Si under same conditions.

<table>
<thead>
<tr>
<th>Plasma Chemistry</th>
<th>Maximum Ta$_2$O$_3$ Etch Rate (Å·min$^{-1}$)</th>
<th>Ta$_2$O$_3$ Selectivity over Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_6$ / Ar</td>
<td>1200</td>
<td>0.16</td>
</tr>
<tr>
<td>SF$_6$ / O$_2$</td>
<td>1200</td>
<td>0.20</td>
</tr>
<tr>
<td>SF$_6$ / CH$_4$</td>
<td>1000</td>
<td>0.25</td>
</tr>
<tr>
<td>SF$_6$ / H$_2$</td>
<td>950</td>
<td>0.16</td>
</tr>
<tr>
<td>Cl$_2$ / Ar</td>
<td>1050</td>
<td>0.32</td>
</tr>
<tr>
<td>CH$_4$ / H$_2$ / Ar</td>
<td>50</td>
<td>0.45</td>
</tr>
<tr>
<td>N$_2$ / Ar</td>
<td>100</td>
<td>0.65</td>
</tr>
</tbody>
</table>

times faster than Ta$_2$O$_3$ in all of the plasma chemistries. There was little difference in the results obtained with O$_2$ or Ar addition to SF$_6$, even though O$_2$ addition is often found to enhance the atomic neutral fluorine density in F$_2$-based discharges. In an attempt to slow the Si etch rate and possibly achieve selective Ta$_2$O$_3$-to Si etching, we tried both CH$_4$ and H$_2$ addition to SF$_6$ to enhance polymer deposition on the Si.

Figure 4-1 shows the effect of SF$_6$ percentage (by flow) in SF$_6$/CH$_4$ discharges at fixed source power (500 W), chuck power (150 W) and pressure (2m Torr) an Ta$_2$O$_3$ and Si etch rates. The Si rate is always higher than that of Ta$_2$O$_3$, even at high CH$_4$ percentages (90 %), with the Ta$_2$O$_3$/Si selectivity decreasing with increasing SF$_6$ percentage.
We also examined the effect of process pressure on the etch rates in SF\textsubscript{6}/CH\textsubscript{4} discharges at fixed flow rate of etch gas (2 SF\textsubscript{6}/13 CH\textsubscript{4} in this case). Figure 4-2 shows the resulting rates. The etch rates of the both Ta\textsubscript{2}O\textsubscript{5} and Si go to zero at pressures > 20 mTorr and at lower pressures the Ta\textsubscript{2}O\textsubscript{5}/Si is again always less than unity.

% in SF\textsubscript{6} (Total flow rate is 15 sccm)

![Graph showing etch rate and Ta\textsubscript{2}O\textsubscript{5} / Si selectivity in SF\textsubscript{6}/CH\textsubscript{4} discharges as a function of SF\textsubscript{6} percentage.]

Figure 4-1. Etch rate and Ta\textsubscript{2}O\textsubscript{5} / Si selectivity in SF\textsubscript{6}/CH\textsubscript{4} discharges (500 W source power, 150 W chuck power, 2 mTorr) as a function of SF\textsubscript{6} percentage.

![Graph showing etch rate and Ta\textsubscript{2}O\textsubscript{5} / Si selectivity in SF\textsubscript{6}/CH\textsubscript{4} discharges as a function of process pressure.]

Process pressure (mTorr)
Somewhat similar trends were obtained with SF$_6$/H$_2$ mixtures, in which the intent was to decrease the chemical etch component of Si by F$^0$ neutrals by introducing H$_2$. We did actually achieve a Ta$_2$O$_5$/Si selectivity slightly greater than one at very low SF$_6$ percentages, but under these conditions the etch rates are extremely low (≤ 100 Å·min$^{-1}$) for both materials (Figure 4-3).

Some representative results for the N$_2$/Ar plasma chemistry are shown in Figure 4-4. The hope in this case was that reactive nitrogen neutrals would extract oxygen as N$_2$O or NO$_2$, with Ta being removed by Ar$^+$ sputtering. Figure 4-4 shows that the etch rates for Ta$_2$O$_5$ were very low, in fact slower than with simple Ar$^+$ sputtering under the same conditions.
Figure 4-3. Etch rates and Ta$_2$O$_5$/Si selectivity in SF$_6$/H$_2$ discharges (500 W source power, 150 W rf chuck power, 2 mTorr), as a function of SF$_6$ percentage.
Figure 4-5. AFM scans of Si and Ta$_2$O$_5$ before and after etching in 10 SF$_6$/O$_2$ or 10 SF$_6$/Ar discharges (750 W source power, 150 W rf chuck power).
Figure 4-6. RMS roughness of Ta$_2$O$_5$ surface after etching in different plasma chemistries, as a function of pre-etch anneal temperature of the Ta$_2$O$_5$ (top) or plasma composition (bottom).
The Cl₂/Ar etching produced rates comparable to those achieved with SF₆ mixtures. The rates were found to increase as Cl₂ was added, which is often an indicator of some chemical contribution to the etch mechanism. The enhancement factor was ~10-20 for etch rates obtained in pure Cl₂ relative to pure Ar, which is considerably larger than expected on the basis of the most abundant ions present (Cl₂⁺, mass 74; Ar⁺, mass 40).

The etched Ta₂O₅ surface morphologies were good (<0.5 nm root-mean square, RMS roughness) over a broad range of conditions. Figure 4-5 shows some representative AFM scans for both Ta₂O₅ and Si surfaces after etching in either SF₆/Ar or SF₆/O₂ under the same conditions (500 W source power, 150 W rf chuck power). The surfaces of both materials show very low RMS roughnesses although there is a more granular texture with SF₆/O₂. Figure 4-6 shows the RMS roughness dependence on either pre-etching annealing temperature (top) or plasma composition (bottom) for several different plasma chemistries. The roughness remains below 0.5 nm over a broad range of conditions.
5.1. Materials and Experimental Procedure

Amorphous Ta$_2$O$_5$ films ~1000 Å thick were deposited on (100), p-type (B-doped, 1 Ω-cm) Si wafers by plasma enhanced chemical vapor deposition. The precursors used were Ta(C$_2$H$_5$O)$_5$ and O$_2$, and the deposition temperature was ~350°C. We found no dependence of subsequent dry etch rate on the post-growth annealing temperature of the films up to 800°C, which is close to the recrystallization condition.

Samples ~5x5 mm$^2$ were masked with Apiezon wax for etch rate experiments. The etch depth was established by stylus profilometry to an accuracy of ±10% after removal of the mask in acetone. All of the etching was performed in a PlasmaTherm 790 series reactor. The samples were thermally bonded to a Si carrier wafer on a He backside cooled, rf powered (13.56 MHz) chuck. This power was used to control the incident ion energy. The ion flux and plasma dissociation was controlled by the power into the ICP source (2 MHz, 100-1000W). Gas injection into this source was metered through electronic mass flow controllers at a typical load of 15 standard cubic centimeters per minute (sccm). Two different gas chemistries were used SF$_6$/Ar and Cl$_2$/Ar. The process pressure was held constant at 2 mTorr. In some cases a Hg arc lamp (400 W) was installed on 1 inch diameter quartz window on the top of the ICP source, ~20 cm from the sample position. This was used to provide UV illumination of the sample surface during
plasma etching. Sample heating due to the lamp is minimal (<10 °C), as determined by a fluoro-optic probe mounted on the Si carrier wafer.

5.2. Results and Discussion

Figure 5-1 shows the Ta₂O₅ etch rates in 10 SF₆/5 Ar discharges as a function of rf chuck power. The enhancement in etch rates as a result of UV illumination is most pronounced at low chuck powers, corresponding to ion energies of ~150 eV (the sum of dc self-bias voltage and the plasma potential of ~22 eV).

![Figure 5-1. Ta₂O₅ etch rate with and without UV illumination in ICP 10SF₆/Ar discharges (500 W source power, 2 mTorr) as a function of rf chuck power.](image-url)
Figure 5-2. Ta$_2$O$_5$ etch rate with and without UV illumination in ICP 10SF$_6$/5Ar discharges as a function of source power for two different rf chuck powers, 100 W (top) and 200 W (bottom).
At higher ion energies the etch rates decrease both with and without the UV illumination. This is commonly observed in high density plasma etching of many different materials systems, and is usually ascribed to ion-assisted desorption of the reactive neutrals before they can react with the atoms in the substrate.\(^{70,71}\)

To investigate the effect of ion flux on the \(\text{Ta}_2\text{O}_5\) etch rate, we varied ICP source power for two different chuck powers, as shown in Figure 5-2. At the low chuck power condition (100 W, top), the etch rate enhancement with UV illumination increases with source power and reaches a factor of approximately two in the range 500 - 750 W. By stark contrast, at the higher rf chuck power condition (Figure 5-2, bottom) there is essentially no increase in etch rate as a result of UV illumination. Several groups have reported that UV irradiation dramatically enhances the etch rate of Cu in \(\text{Cl}_2\)-based high density plasmas, through absorption of UV photons by involatile \(\text{CuCl}_x\) etch products, transformation to more volatile species (e.g. \(\text{Cu}_2\text{Cl}_3\)) and subsequent non-thermal desorption of these species.\(^{72,73}\)

In the case of \(\text{Ta}_2\text{O}_5\), an analogous situation would involve photodesorption of \(\text{TaF}_x\) species since the oxygen should be removed as \(\text{O}_2\) or oxyfluorides. The etch rate of the \(\text{Ta}_2\text{O}_5\) was too low for us to detect the etch products by optical emission spectroscopy, although we could determine that the atomic fluorine concentration was not increased by UV illumination, ruling this out as a possible mechanism for the higher rates.

In the case of \(\text{Cl}_2/\text{Ar}\) discharges, Figure 5-3 shows that UV illumination did lead to faster \(\text{Ta}_2\text{O}_5\) etch rates at moderate source power (top) and rf chuck powers (bottom).
This seems plausible from the following scenarios- at very high ion fluxes or energies, the TaF₃ is being efficiently removed by sputter-assisted desorption whether or not the UV illumination is being used, whereas at very low ion fluxes or energies the etch rate may be controlled by diffusion of the etch products through a chlorinated selvedge layer.

To examine the effect of UV illumination on the surface morphology of dry etched Ta₂O₅, atomic force microscopy (AFM) scans were obtained. Figure 5-4 shows examples of surfaces etched in SF₆/Ar discharges either without (top) or with (bottom) the UV irradiation. There is no significant difference in root-mean-square (RMS) surface roughness between the two cases. Similar results were obtained with the Cl₂/Ar plasma chemistry.

![AFM scans of Ta₂O₅ surfaces after etching in ICP 10SF₆/5Ar discharges (750 W source power, 100 W rf chuck power, 2 mTorr) either without (top) or with (bottom) UV illumination.](image)

W/O UV
RMS=0.21

With UV
RMS=0.20

750 W ICP
100 W rf
10SF₆/5Ar/2mTorr
Z: 20nm/div
X: 1 um/div

Figure 5-4. AFM scans of Ta₂O₅ surfaces after etching in ICP 10SF₆/5Ar discharges (750 W source power, 100 W rf chuck power, 2 mTorr) either without (top) or with (bottom) UV illumination.
6.1. Materials and Experimental Procedure

The sample preparation has been described in detail elsewhere, but in brief, both materials were deposited on Si substrates using pulsed laser deposition (KrF excimer laser, 5 Hz pulse frequency) at an O$_2$ partial pressure of 200-300 mTorr and a substrate temperature of 650 °C. Pressed powder targets were used in both cases. The LNO appears to grow predominantly with (110) orientation even on (100) Si, while the BST is polycrystalline. LNO/BST/Si capacitor structures produced from companion samples exhibited an interface state density of ~7x10$^{11}$ eV·cm$^{-2}$ without any post-deposition H$_2$ annealing. The leakage current density was ~10$^{-8}$ A·cm$^{-2}$ at 5x10$^4$ V·cm$^{-1}$.

Etching was performed in a Plasma Therm 790 Inductively Coupled Plasma reactor. The plasma is sustained in a 3-turn, cylindrical geometry source operating at 2 MHz and powers from 500-1000 W. The samples were thermally bonded on an rf-(13.56 MHz) biased chuck, at powers of 50-350 W. These conditions produced dc self biases of approximately −50 to −340 V. In general, dielectric materials have relatively high bond energies and it is necessary to employ high ion energies during etching to break the bonds so that etch products may form. The average ion energy is the sum of the dc self-bias through which the ion is accelerated, plus the plasma potential, which is ~22 eV in our particular system. Two different gas chemistries were investigated, namely CH$_4$/H$_2$/Ar...
and Cl$_2$/Ar. Electronic grade gases comprising these mixtures were injected into the ICP source through mass flow controllers at a total flow rate of either 15 (for Cl$_2$/Ar) or 20 (for CH$_4$/H$_2$/Ar) standard cubic centimeters per minute (sccm).

The etch depths were obtained from stylus profilometry after removal of the mask material, which was Apiezon wax except when we wanted to examine etch anisotropy using scanning electron microscopy (SEM), in which case we employed lithographically patterned photoresist (AZ4620E, cured at 150 °C) as a mask. Etch yield (number of atoms of the target material removed per incident ion) was calculated from a semi-empirical model developed for this reactor that employs ion fluxes measured by the Langmuir probe technique.

6.2. Results and Discussion

6.2.1. Cl$_2$/Ar Plasma Chemistry

Figure 6-1 (top) shows the influence of rf chuck on the etch rates of both BST and LNO films at fixed pressure (2 mTorr), source power (750 W) and Cl$_2$/Ar flow rates (10 sccm/5 sccm). The etch rate of BST increases with the higher ion bombardment energy up to approximately 250 W rf chuck power and decreases thereafter. This is a commonly observed trend with high density plasma etching and is usually ascribed to ion-assisted desorption of the adsorbed chlorine neutrals before the etch products can form. In the case of LNO we do not observe the decrease in etch rate at high rf chuck powers, suggesting the amount or stability of the adsorbed chlorine is different than for BST. The etch yields (bottom) for both materials are low, and emphasise that the etching is dominated by physical sputtering.
Figure 6-2. Etch rates (top) and etch yields (bottom) for BST and LNO in 10Cl₂/5Ar, 5mTorr, 250W rf chuck power discharges, as a function of source power.
The role of source power (which controls ion flux) on the material etch rates is shown in Figure 6-2. Increasing the source power suppresses the dc self-bias because of the higher conductivity of the plasma, and this leads to two competing effects, namely an increase in ion flux but a decrease in ion energy. This competition is reflected in an initial increase in BST etch rate, followed by a decrease when the self-bias falls below approximately –270 V. The latter is consistent with the data of Figure 6-1. Once again the behavior of the LNO is different, with a continuing increase in etch rate over the range of source powers we investigated. The etch yield (Figure 6-2 bottom) of LNO does not change as much with ion flux as does etch rate, suggesting the increased etch rates are mostly due to a higher sputter rate.

6.2.2. CH₄/H₂/Ar Plasma Chemistry

We did not examine this chemistry as carefully as we did with Cl₂/Ar, because it was quickly apparent the etch rates with CH₄/H₂/Ar were extremely low. Figure 6-3 shows the effect of rf chuck power on the etch rates of both BST and LNO—the trend shows that the etching is sputter-limited, with very low yield (≤ 0.04). There is no apparent chemical contribution to the etching with this gas mixture, with results similar to those obtained with pure Ar plasmas.

The effect of source power is shown in Figure 6-4. Once again, the rates are low (≤ 100 Å·min⁻¹) under all conditions, and ≥ 25 ions are required for removal of one atom of both materials. One problem with trying to use this plasma chemistry for etching of high bond
Figure 6-3. Etch rates (top) and etch yields (bottom) for BST and LNO in 5CH_4/10H_2/5Ar, 5mTorr, 750W source power discharges, as a function of rf chuck power.
Figure 6-4. Etch rates (top) and etch yields (bottom) for BST and LNO in 5CH$_4$/10H$_2$/5Ar, 5mTorr, 250W rf chuck power discharges, as a function of rf chuck power.
strength materials is that polymer deposition from the CH₄ may act to shield the surface from ion bombardment.

6.2.3. Comparison of Plasma Chemistries

Figure 6-5 shows a comparison of the etch rates obtained for both BST and LNO as a function of source power in the two plasma chemistries. The maximum rates with Cl₂/Ar are roughly one order of magnitude higher than with CH₄/H₂/Ar. This has consequences in terms of mask erosion when etching device features, because since the CH₄/H₂/Ar shows no chemical contribution to the etch mechanism, there will be no selectivity over common mask materials such as SiO₂, SiNx or photoresist. By contrast there is some ion-assisted chemical component to the etching with Cl₂.

Since the etching is ion-driven under all conditions for both materials, highly anisotropic features can be formed provided mask erosion is minimized. Figure 6-6 (top) shows a cross-sectional SEM view of a narrow (≤1 μm) feature created in BST using a 10 Cl₂/5 Ar discharge for 9 mins (5 mTorr, 750 W source power, 200 W rf chuck power). In this case a 0.5 μm thick SiNx layer and 1 μm resist bilayer was used as a mask and all the resist and the SiNx 0.15 μm of the SiNx was lost during the etch process. The side walls are slightly sloped from faceting of the edges of the mask during exposure to the plasma. Figure 6-6 (center and bottom) show features etched into BST (center) or LNO (bottom) using the same plasma conditions as above, but with a single 7 μm thick photoresist mask (AZ4614). About one-third of the resist remained at the completion of the etching. This is a simpler masking procedure than the dielectric/resist bilayer, and is still able to produce
anisotropic pattern transfer. We were unable to achieve acceptable etch anisotropy with the CH\textsubscript{4}/H\textsubscript{2}/Ar chemistry because of severe mask faceting that led to sidewall slopes $\geq 30^\circ$ from vertical.

Figure 6-7 shows some typical AFM scans of BST and LNO surfaces before and after exposure to either Cl\textsubscript{2}/Ar or CH\textsubscript{4}/H\textsubscript{2}/Ar discharges. For CH\textsubscript{4}/H\textsubscript{2}/Ar etching the surfaces became slightly rougher, as evidenced by the change in root-mean-square (RMS) roughness. This may result from non-equal rate removal of one or more of the lattice constituents (probably the lighter Ti). By sharp contrast, the surfaces of both materials exhibit a degree of smoothing after exposure to the Cl\textsubscript{2}/Ar plasma, as seen in the raw data of Figure 6-7 and the tabulated RMS values of Figure 6-8. This can result from the angular dependence of ion-milling rate in physically dominated chemistries, whereby sharper surface features are removed faster than flat features.
Figure 6-5. Comparison of BST and LNO in Cl$_2$/Ar and CH$_4$/H$_2$/Ar ICP discharges (5mTorr, 250W rf chuck power), as a function of source power.
Figure 6-6. SEM micrographs of features etched into BST (top and center) using 10Cl$_2$/5Ar, 5mTorr, 750W source power, 250W rf chuck power discharges using either a resist/SiN$_x$ bilayer mask (top) or a single layer resist mask (center). About 0.35µm of the SiN$_x$ remains in the top micrograph. The SEM at bottom shows features etched into LNO using similar plasma conditions and a resist mask, which has been removed.
Figure 6-7. AFM scans of BST and LNO surface before and after dry etching in either Cl₂/Ar or CH₄/H₂/Ar.
Figure 6-8. RMS roughness measured over 5x5 μm² area for BST and LNO samples before and after etching in either Cl₂/Ar or CH₄/H₂/Ar discharges.
A number of different plasma chemistries (SF$_6$/O$_2$, SF$_6$/Ar, Cl$_2$/Ar, N$_2$/Ar and CH$_4$/H$_2$/Ar) were examined for dry etching of Ta$_2$O$_5$ under ICP conditions, the main conclusions of the study are as follows:

(i) The fastest etch rates (~1200 Å· min$^{-1}$) were achieved in SF$_6$ or Cl$_2$ chemistries. The rates with N$_2$/Ar and CH$_4$/H$_2$/Ar were approximately an order of magnitude lower than with SF$_6$ or Cl$_2$.

(ii) Selectivities for Si over Ta$_2$O$_5$ of ~6 were achieved in SF$_6$ discharges, while we were not able to achieve the reverse selectivity, i.e. Ta$_2$O$_5$ etch rates were always slower than those of Si.

(iii) The etched surface morphology of Ta$_2$O$_5$ was smooth under virtually all plasma conditions.

(iv) The Ta$_2$O$_5$ etch rates are much faster under ICP conditions than with reactive ion etching.

(v) There was no effect of post-deposition annealing on the Ta$_2$O$_5$ etch rates, at least up to 800 °C.

Additionally, the dry etching characteristics with UV illumination were examined under ICP condition. UV illumination during ICP etching of Ta$_2$O$_5$ in both SF$_6$/Ar and Cl$_2$/Ar plasma chemistries produces significant enhancements in etch rates. The increased
rates are likely due to photo-assisted desorption of the TaF₅ etch products. The use of UV illumination is an alternative to employing elevated sample temperatures during etching to increase the volatility of the etch products and may find application where the thermal budget should be minimized during processing.

Finally, two common semiconductor plasma chemistries used in etching, namely Cl₂/Ar and CH₄/H₂/Ar, have been examined for dry etching of thin films of (Ba,Sr)TiO₃ and LaNiO₃. The etching in both chemistries is physically-dominated, but only Cl₂/Ar produces reasonable removal rates. Although not presented here, under typical conditions of 750 W of ICP source power and 250 W of rf chuck power (-275 V chuck bias) in our tool, the etch selectivity for BST and LNO over Si is ~16 (BST) and ~7 (LNO) when using Cl₂/Ar. The surfaces of both materials become smoother with exposure to these discharges, and highly anisotropic pattern transfer can be achieved using simple resist masks.
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BIOGRAPHICAL SKETCH

Lee, Kyu-pil was born in Korea on May 28, 1961. He received his B.S. degree in Material Science and Engineering from Han Yang University in Seoul, Korea.

He joined the Semiconductor Research and Development Center of Samsung Electronics Co. in 1985. Since then he has worked as a process architect for the development of CMOS technology and products, such as the 1Mb, 4Mb, 16Mb, 64Mb and 1Gb -DRAM. He was in charge of the development of under 0.15um C-MOS technologies and he has been involved in the development of Silicon On Insulator (SOI)-based CMOS memory devices and Low Voltage Battery Operation (LVBO) memory products.

He has published over 60's patents and many papers related to memory devices and technologies in Samsung, and he received the award of "Samsung technology grand prize" from group president because of his great achievements noting him as the best engineer in Samsung.

With financial support from Samsung Electronics, he enrolled in the Master program at the University of Florida in the Department of Materials Science and Engineering in 1998. He was very fortunate to meet Professor Pearton and do research in the development of dry etching processes for novel dielectric thin films. Under Professor Pearton's close supervision and expert guidance, he has published several journal and conference papers, and is a member of the American Vacuum Society.
Kyu-pil will continue his studies in the Ph.D program and he is interested in development of Magnetic random access memory (MRAM) devices.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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