Thermal atomic layer etching of silicon nitride using an oxidation and “conversion etch” mechanism

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ABSTRACT

Thermal atomic layer etching (ALE) of silicon nitride was achieved using sequential exposures of oxygen (O₂) or ozone (O₃), hydrofluoric acid (HF), and trimethylaluminum [TMA, Al(CH₃)₃]. Thermal Si₃N₄ ALE was performed with Si₃N₄ thin films deposited on silicon wafers using low pressure chemical vapor deposition. In situ spectroscopic ellipsometry (SE) was employed to monitor the changes in the Si₃N₄ film thickness as well as the SiO₂ layer thickness. The SE results at 290 °C yielded an Si₃N₄ etch rate of 0.25 Å/cycle with an O₂-HF-TMA reactant sequence using partial pressures of 250, 0.65, and 1.2 Torr for O₂, HF, and TMA, respectively. The O₂, HF, and TMA reactants were held statically at the indicated partial pressures for 10, 5, and 5 s, respectively. Larger etch rates were observed using O₃ instead of O₂ as the oxidant. A higher Si₃N₄ etch rate of 0.47 Å/cycle was measured at 290 °C using an O₃-HF-TMA reactant sequence at the same partial pressures and static exposure times as the O₂-HF-TMA sequence. The Si₃N₄ etch rate was observed to decrease at lower temperatures. An Si₃N₄ etch rate of 0.07 Å/cycle was measured at the lowest temperature of 210 °C using an O₃-HF-TMA reactant sequence. The Si₃N₄ etch rate was dependent on the reaction sequence. When an O₃-TMA-HF sequence was employed with reactant partial pressures of 250, 0.65, and 1.2 Torr for O₃, HF, and TMA, respectively, the Si₃N₄ etch rate was 0.20 Å/cycle at 290 °C. Thermal Si₃N₄ ALE adds to the growing list of materials that can be etched with atomic layer control using thermal chemistry.

I. INTRODUCTION

Atomic layer etching (ALE) is typically based on two sequential, self-limiting surface reactions. A schematic of a model ALE process is shown in Fig. 1. The first reaction typically modifies the surface by halogenation or oxidation. The second reaction then removes the modified surface species and produces volatile etching products. The sequential application of the surface modification and removal reactions leads to ALE. There are two main versions of ALE based on either plasma ALE or thermal ALE.

Plasma ALE is an established etching process that employs energetic ions or neutrals to remove the modified surface species by a sputtering process and produces anisotropic etching. The origins of plasma ALE can be traced back to the pioneering work of John Coburn and Harold Winters on Si etching with XeF₂ and Ar⁺ ions. They observed a synergy in Si etching when the XeF₂ and Ar⁺ ions were incident on the Si substrate at the same time. They could have tried to convert their Si etching process to a plasma Si ALE process by performing sequential XeF₂ and Ar⁺ ion exposures. However, self-limiting behavior would not have been observed because XeF₂ spontaneously etches silicon. Subsequent work demonstrated plasma Si ALE using halide adsorption and Ar⁺ ion exposures. Many other plasma ALE processes have also been developed for a variety of materials including SiO₂, HFO₂, InP, Al₂O₃, W, Cr, graphene, and polymers.

Thermal ALE is a newer etching process that utilizes thermal reactions to accomplish etching and achieves isotropic etching. Isotropic etching is useful to conformally etch three-dimensional structures. Several different pathways have been documented for thermal ALE. One mechanism for thermal ALE utilizes...
fluorination and ligand-exchange reactions. This mechanism has been demonstrated for Al₂O₃, HfO₂, ZrO₂, AlN, GaN, and VO₂. Another pathway for thermal ALE involves conversion reactions that convert the initial material to a new material prior to etching. This conversion mechanism has been developed for ZnO, SiO₂, TiN, W, WO₃, and Si ALE.

In this paper, thermal Si₃N₄ ALE is demonstrated based on an oxidation and "conversion etch" mechanism. In similarity with earlier work on Si ALE, Si₃N₄ is initially oxidized to SiO₂ using O₂ or O₃ as the oxidant. The SiO₂ layer can be converted to Al₂O₃ or an aluminum silicate using Al(CH₃)₃. Hydrofluoric acid (HF) is able to fluorinate the aluminum to form AlF₃ or AlFxOy. The aluminum fluoride layer is then reacted with Al(CH₃)₃ through a ligand-exchange reaction to form volatile AlF(CH₃)₂ products such as dimers of AlF(CH₃)₂ or AlF(CH₃)₂-Al(CH₃)₃. A schematic of this mechanism is shown in Fig. 2 assuming conversion to Al₂O₃ and fluorination to AlF₃.

Thermal Si₃N₄ ALE is important because Si₃N₄ is a key material in semiconductor devices. Si₃N₄ is used as a spacer, mask, diffusion barrier, dielectric, and protection layer. The etching of the silicon nitride spacer that forms the mask for implantation of source and drain and protects the gate sidewalls is one of the most challenging steps in semiconductor processing. Si₃N₄ also has many other uses in optical and optoelectronic devices because of its wide bandgap. In addition, Si₃N₄ is employed extensively in making MEMS devices. Thermal Si₃N₄ ALE should yield isotropic etching that would be extremely valuable for fabricating advanced three-dimensional devices.

Thermal Si₃N₄ ALE should also complement the plasma Si₃N₄ ALE methods. One plasma Si₃N₄ method is based on sequential hydrofluorocarbon plasma exposure and thermal annealing. The second plasma Si₃N₄ method is defined by sequential fluorocarbon plasma exposure and Ar⁺ ion bombardment. The third plasma Si₃N₄ ALE method is constructed from sequential hydrogen plasma exposure and fluorinated plasma exposure. There are also variations of this third plasma Si₃N₄ ALE method where the reaction after the hydrogen plasma exposure involves either ion irradiation or fluorinated plasma exposure followed by annealing. The thermal Si₃N₄ ALE procedure developed in this paper is an isothermal process that avoids both plasma exposures and annealing steps.

II. EXPERIMENT

Thermal Si₃N₄ ALE was conducted in warm wall, hot-stage reactor. A complete description of this apparatus has been given in a previous publication. The walls of the reactor were maintained at 160 °C. The sample temperature was varied between 210 and 290 °C. The sample was held on the horizontal stage by gravity. The reactor was equipped with an in situ spectroscopic ellipsometer (J.A.Woollam, model M-2000UI). This ellipsometer could monitor the changes in the Si₃N₄ film thickness and the SiO₂ layer thickness during Si₃N₄ ALE. The Al₂O₃ layer is not explicitly considered because this layer is ultrathin and is merged with the SiO₂ layer. Ellipsometric measurements were recorded after each Si₃N₄ ALE cycle during the purging step.

One Si₃N₄ ALE cycle consisted of static exposures of O₂ or O₃, HF and trimethylaluminum (TMA) followed by a 30 s nitrogen purge time after each exposure. Static exposure times for O₂ or O₃, HF and TMA were 10, 5, and 5 s, respectively. Industrial grade O₂ (Airgas) was used to perform the oxidation. This O₂ was also the feed gas for the O₃ generator. O₃ was produced by an O₃ONIA ozone generator (Switzerland) with an ozone output of ~15 wt. %
relative to O₂. HF was obtained from the HF vapor pressure above an HF-pyridine solution.²⁴ HF-pyridine (70 wt. %) and trimethylaluminum (97%) were supplied by Sigma-Aldrich.

The etch chamber was pumped with a mechanical pump (Alcatel Adixen 2010C1). The precursor dose valves, nitrogen feed mass flow controller, and the reactor isolation valve were closed simultaneously to achieve the static exposures. The reported reactant pressures refer to their partial pressures with respect to the background N₂ gas pressure of 1 Torr. Ultrahigh purity grade N₂ (99.9999%, Airgas) was used as the carrier gas.

The Si₃N₄ samples (University Wafer Inc.) were prepared using low pressure chemical vapor deposition of Si₃N₄ on silicon wafers. These low stress Si₃N₄ samples had an initial thickness of 100 nm. Rutherford backscattering spectroscopy analysis of the as-received samples confirmed Si-to-N ratios of 3-to-4. Forward recoil energy spectrometry also measured the hydrogen content of the Si₃N₄ films at <3 at. %. X-ray diffraction scans determined that the Si₃N₄ films were amorphous.

The silicon wafer coated with the Si₃N₄ film was cut into 2 × 2 cm² coupons before use. Prior to Si₃N₄ ALE, the samples were dusted off using high purity nitrogen gas without using any solution-based cleaning. The nitride oxidation experiment was conducted using a solution pre-etched Si₃N₄ sample. For this purpose, the native oxide was removed using a 1 min dip in a 10 wt. % HF solution followed by rinsing in DI water.⁵²

X-ray photoelectron spectroscopy (XPS) (PHI 5600, RBD Instruments) measured the film composition after the Si₃N₄ ALE process. A monochromatic Al Kα x-ray source (1486.6 eV) was used to collect survey scans with a pass energy of 93.9 eV and a step size of 0.400 eV. Auger Scan software package (Auger Scan, RBD Instruments) was employed to collect the data. Casa XPS software (Casa XPS, Casa Software) determined the surface concentrations using the peak areas and the corresponding sensitivity factors.

III. RESULTS AND DISCUSSION

A. Thermal Si₃N₄ ALE using O₂

Figure 3 displays the Si₃N₄ thickness change and corresponding thickness for the SiO₂ layer during Si₃N₄ ALE at 290 °C using O₂-HF-TMA sequential exposures. O₂, HF, and TMA were exposed at partial pressures of 250, 0.65, and 1.2 Torr, respectively. The etch temperature of 290 °C was chosen to avoid potential problems with TMA decomposition that may occur at higher temperatures.³³⁻⁵⁴ Figure 3 shows that the Si₃N₄ thickness change occurs at a rate of 0.25 Å/cycle. In addition, the SiO₂ layer levels off at a thickness of ~9 Å after 40 Si₃N₄ ALE cycles.

For comparison, crystalline silicon can be etched at a higher etch rate of 0.45 Å/cycle using similar reactant conditions at 290 °C.²⁶ The lower etch rate for Si₃N₄ probably arises from the difference in oxidation rates for silicon and silicon nitride. The oxidation rate of Si₃N₄ CVD films in dry and wet oxygen ambient is much lower than the oxidation rate for Si.⁵⁵⁻⁵⁹ The lower oxidation rate of Si₃N₄ limits Si₃N₄ oxidation and reduces the Si₃N₄ etch rate.

Previous studies have observed that higher O₂ pressures lead to larger Si₃N₄ oxidation rates.⁶⁰ In an attempt to increase the Si₃N₄ etch rate, higher O₂ pressures of 350 and 450 Torr were used with the same temperature, HF and TMA partial pressures, reactant sequence, and exposure times as in Fig. 3. Figure 4 shows that the increase in O₂ pressure resulted in only a slight increase in the Si₃N₄ etch rate from 0.25 Å/cycle at 250 Torr to 0.28 Å/cycle at 450 Torr. This result suggested that a more powerful oxidizing agent is needed to increase the Si₃N₄ oxidation rate and the Si₃N₄ etch rate. Several studies have reported that Si₃N₄ has a significantly higher oxidation rate in H₂O than in O₂.⁵⁵⁻⁵⁶ In addition, thermochemical calculations indicate that ozone (O₃) can be more favorable for Si₃N₄ oxidation.⁵⁹
B. Thermal Si₃N₄ ALE using O₃

Figure 5 shows the Si₃N₄ thickness change and values for the SiO₂ layer thickness versus number of ALE cycles at 290 °C using an O₃-HF-TMA reactant sequence. Partial pressures for O₃, HF, and TMA were 250, 0.65, and 1.2 Torr, respectively. O₃ was held statically for 10 s. HF and TMA were held statically for 5 s. The Si₃N₄ film thickness is etched at an etch rate of 0.47 Å/cycle. The etch rate of 0.47 Å/cycle using O₃ is higher than the etch rate of 0.25 Å/cycle using O₂ as observed in Fig. 3. In addition, the etch rate of 0.47 Å/cycle is comparable with the etch rate of 0.45 Å/cycle observed for Si ALE using the O₃-HF-TMA sequence at similar reaction conditions.\(^6\) Figure 5 also reveals that the SiO₂ layer thickness is fairly constant at \(\sim 11\) Å during the 80 Si₃N₄ ALE cycles. This SiO₂ thickness of \(\sim 11\) Å using O₃ is higher than the SiO₂ thickness of \(\sim 9\) Å using O₂ as observed in Fig. 3.

C. Effect of reactant pressure on etch rate

Figure 6 displays the dependence of the Si₃N₄ etch rate on TMA and HF partial pressures at 290 °C. Figure 6(a) shows the Si₃N₄ etching as the TMA pressure is varied from 0.6 to 1.9 Torr with the O₃ and HF pressures held constant at 250 and 0.65 Torr, respectively. The Si₃N₄ etch rate increased from 0.38 Å/cycle to 0.47 Å/cycle as the TMA pressure increased from 0.6 Torr to 1.2 Torr. The TMA pressure increase from 1.2 to 1.9 Torr did not increase the etch rate. At both pressures, the etch rate stayed constant at 0.47 Å/cycle. In comparison, the Si etch rate during Si ALE was also larger at higher TMA pressures. The Si etch rate increased from 0.2 Å/cycle at a TMA pressure of 30 Torr to 0.4 Å/cycle at a TMA pressure of 250 Torr.\(^3\)

Figure 6(b) shows the Si₃N₄ etching at 290 °C as the HF pressure is varied from 0.40 to 0.81 Torr with the O₃ and TMA pressures held constant at 250 and 1.2 Torr, respectively. The increase in HF pressure from 0.40 to 0.65 Torr resulted in an increase in the etch rate from 0.40 to 0.47 Å/cycle. Further increase in the HF pressure from 0.65 to 0.81 Torr resulted in a slight increase from 0.47 to 0.50 Å/cycle. In comparison, the Si etch rate was constant at 0.4 Å/cycle at HF pressures from 0.5 Torr to 1.5 Torr.\(^3\)

Slightly higher Si₃N₄ etch rates are expected at higher TMA and HF pressures. Higher TMA pressures lead to more conversion of SiO₂ to Al₂O₃.\(^3\) Higher HF pressure is also known to yield larger fluorination thicknesses and higher Al₂O₃ etch rates.\(^2\) The TMA and HF pressures also have little effect on the SiO₂ thickness. The SiO₂ thickness remained constant at \(\sim 11–13\) Å independent of TMA pressure during the experiments shown in Fig. 6(a). The SiO₂ thickness increased slightly from \(\sim 12\) Å at an HF pressure of 0.65 Torr to \(\sim 16\) Å at an HF pressure of 0.40 Torr during the experiments shown in Fig. 6(b). These SiO₂ thicknesses are approximate because the measurements of SiO₂ thickness may be affected by surface roughness.\(^6\)
In contrast to the dependence of the Si$_3$N$_4$ etch rate on TMA and HF pressure, there is no observable dependence of the Si$_3$N$_4$ etch rate on the O$_3$ pressure. Figure 7 shows the dependence of the Si$_3$N$_4$ etch rate on O$_3$ pressure at 290 °C. The partial pressures of TMA and HF were fixed at 1.2 and 0.65 Torr, respectively, as the O$_3$ pressure was varied from 37 to 250 Torr. These results illustrate that the Si$_3$N$_4$ etch rate is independent of the O$_3$ pressure. This behavior suggests that O$_3$ is a powerful oxidation agent. O$_3$ is able to produce enough Si$_3$N$_4$ oxidation to maintain high Si$_3$N$_4$ etch rates even at lower O$_3$ pressures. The SiO$_2$ thickness also stayed constant at $\sim$12 Å over the 80 Si$_3$N$_4$ ALE cycles for each O$_3$ pressure. These results argue that the oxidation of Si$_3$N$_4$ by O$_3$ is self-limiting.

D. Temperature dependence of etch rate

Figure 8 shows the Si$_3$N$_4$ thickness changes for sample temperatures of 210, 230, 250, 270, and 290 °C. These experiments were conducted using the O$_3$-HF-TMA reactant sequence and partial pressures of 250, 0.65, and 1.2 Torr, for O$_3$, HF, and TMA, respectively. The Si$_3$N$_4$ etch rate increases from 0.07 Å/cycle at 210 °C to 0.47 Å/cycle at 290 °C. This trend is consistent with a thermally activated process. An Arrhenius plot of the temperature-dependent Si$_3$N$_4$ etch rates is shown in Fig. 9. This Arrhenius plot yields an activation barrier of $E_a = 13.4$ kcal/mol for the combined oxidation, conversion, fluorination, and ligand-exchange reactions.

E. Surface roughness and composition after etching

Figure 10 displays AFM results for the as-received and etched Si$_3$N$_4$ substrates. Si$_3$N$_4$ ALE was performed at 290 °C using an O$_3$-HF-TMA reactant sequence with pressures of 250, 0.65, and 1.2 Torr for O$_3$, HF, and TMA, respectively. Figure 10(a) indicates that the root-mean-square (RMS) surface roughness of the as-received Si$_3$N$_4$ substrate is 4.7 Å ± 0.2. After 100 cycles of Si$_3$N$_4$ ALE, Fig. 10(b) reveals that the RMS surface roughness decreased to 3.1 Å ± 0.2.

The results in Fig. 10(b) demonstrate that the Si$_3$N$_4$ ALE process smoothes the surface of the Si$_3$N$_4$ film. Surface smoothing by thermal ALE processes have been previously reported for a number of systems including Al$_2$O$_3$ ALE (Refs. 4 and 21).
and HfO$_2$ ALE.$^{24}$ No increase in surface roughness was observed for thermal Si ALE at higher O$_2$ pressures of 250 Torr at 290 °C.$^{36}$

Figure 7 shows that the O$_3$ pressure can be reduced from 250 to 37 Torr without affecting the Si$_3$N$_4$ etch rate. However, a low O$_3$ pressure of 37 Torr did not significantly reduce the surface roughness. The RMS roughness after 100 Si$_3$N$_4$ ALE cycles using an O$_3$ pressure of 37 Torr was 4.3 Å. This roughness is only slightly less than the RMS surface roughness of 4.7 Å for the as-received substrate. The surface smoothing is dependent on the O$_3$ pressure. Higher pressures of O$_3$ may produce more uniform SiO$_2$ films that yield surface smoothing during Si$_3$N$_4$ ALE.

XPS analysis was used to quantify the species on the Si$_3$N$_4$ surface after Si$_3$N$_4$ ALE. An XPS scan of the Si$_3$N$_4$ surface was performed after 100 Si$_3$N$_4$ ALE cycles using an O$_3$-HF-TMA reactant sequence with partial pressures of 250, 0.65. and 1.2 Torr, respectively, at 290 °C. After the Si$_3$N$_4$ ALE ending with a TMA exposure and subsequent atmospheric exposure, the compositions from XPS were: 37.2 at. % (Si-2p); 28.9 at. % (N-1s); 19.1 at. % (O-1s); 10.9 at. % (C-1s); 2.8 at. % (Al-2p); and 1.2 at. % (F-1s).

Oxygen is attributed to remaining SiO$_2$ and Al$_2$O$_3$ from O$_3$ exposure and conversion during Si$_3$N$_4$ ALE. In addition, additional oxygen may be produced from Si$_3$N$_4$ oxidation resulting from atmospheric exposure. The aluminum results from the conversion of SiO$_2$ to Al$_2$O$_3$ during the TMA reaction.$^{33}$ Adventitious carbon is present due to ambient air exposure when transferring from the ALE reactor to the XPS chamber for analysis.

F. Removal of residual surface oxide

The Si$_3$N$_4$ ALE process produces an SiO$_2$ layer when Si$_3$N$_4$ is oxidized by O$_2$ or O$_3$ as shown in Fig. 2. This SiO$_2$ layer remains on the Si$_3$N$_4$ film during and after etching. Some applications may benefit from the removal of this SiO$_2$ layer. The SiO$_2$ layer can be removed from the Si$_3$N$_4$ surface by performing SiO$_2$ ALE. An earlier study has characterized SiO$_2$ ALE at 300 °C with TMA and HF as the reactants.$^{33}$

Figure 11 shows the Si$_3$N$_4$ thickness change and the SiO$_2$ layer thickness during Si$_3$N$_4$ ALE followed by SiO$_2$ ALE at 290 °C. Si$_3$N$_4$ ALE was conducted for the first 40 cycles using an O$_3$-HF-TMA reactant sequence with O$_3$, HF, and TMA pressures of 250, 0.65, and 0.7 Torr, respectively. Subsequently, SiO$_2$ ALE was performed for the next 80 cycles using an HF-TMA reactant sequence.$^{33}$ The only difference between the Si$_3$N$_4$ ALE process and the SiO$_2$ ALE process was the omission of the O$_3$ exposure during SiO$_2$ ALE.$^{33}$

Figure 11 reveals that the first 15 cycles of SiO$_2$ ALE decrease the SiO$_2$ layer thickness from 14 Å to a thickness of 7.5 Å. This apparent SiO$_2$ thickness then remains constant during the next 65 cycles. The apparent SiO$_2$ thickness from ellipsometry analysis may be associated with surface roughness instead of a true SiO$_2$ film thickness.$^{31,62}$ Atomic force microscope images are needed to distinguish between surface roughness and a true film thickness for these ultrathin film thicknesses.

There is also a slow reduction of the Si$_3$N$_4$ film thickness during SiO$_2$ ALE. An Si$_3$N$_4$ etch rate of 0.05 Å/cycle is observed from the HF-TMA reactant sequence at 290 °C. In contrast, no etch of Si was observed when the same SiO$_2$ ALE approach was applied to remove SiO$_2$ after thermal Si ALE using O$_3$-HF-TMA. The slow etch of Si$_3$N$_4$ during the HF-TMA reactant exposure is believed to proceed through TMA conversion of Si$_3$N$_4$ to AlN. The HF then fluorinates the AlN to AlF$_3$ prior to the removal of AlF$_3$ by a ligand-exchange reaction with the subsequent TMA exposure.

In the Si$_3$N$_4$ ALE process using HF and TMA, the TMA exposure would play the dual role of converting the Si$_3$N$_4$ surface to...
AlN and then removing AlF3 during a ligand-exchange reaction. Thermochemical calculations show that both conversion and fluorination reactions are feasible because the standard free energy changes are negative:59

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\begin{align*}
\text{Si}_3\text{N}_4 + 4\text{Al(CH}_3)_3 \text{ (g)} & \rightarrow 4\text{AlN} + 3\text{Si(CH}_3)_4 \text{ (g)} \quad \Delta G^\circ (290^\circ C) = -358 \text{ kcal}, \\
\text{AlN} + 3\text{HF (g)} & \rightarrow \text{AlF}_3 + \text{NH}_3 \text{ (g)} \quad \Delta G^\circ (290^\circ C) = -62 \text{ kcal}.
\end{align*}
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The Si3N4 etch rate may be increased at larger partial pressures of HF and TMA. Figure 12 shows the results for Si3N4 ALE at a higher HF pressure of 1.6 Torr with TMA pressures of 2 and 3 Torr. The higher pressures of HF and TMA only result in marginal increases in the Si3N4 etch rate from 0.05 to 0.06 Å/cycle. These results indicate that the oxidation step with O3 is critical to obtain higher Si3N4 etch rates.

**G. Effect precursor exposure sequence**

The precursor exposure sequence can affect Si3N4 ALE. The O3-HF-TMA exposure sequence yields an Si3N4 etch rate of 0.47 Å/cycle at 290 °C as shown in Fig. 5. Experiments were conducted to determine the effect of changing the precursor exposure sequence to O3-TMA-HF. Figure 13 shows the Si3N4 thickness change and SiO2 layer thickness versus number of ALE cycles at 290 °C for the O3-TMA-HF exposure sequence. The Si3N4 ALE was conducted using O3, HF, and TMA pressures of 250, 0.65, and 1.2 Torr, respectively. The O3-TMA-HF exposure sequence leads to a reduction in the Si3N4 etch rate to 0.20 Å/cycle at the same reactant pressures used for the O3-HF-TMA exposure sequence.

The reduction in the Si3N4 etch rate occurs when the TMA is after the O3 exposure rather than after the HF exposure. The TMA exposure after the O3 exposure may lead to Al2O3 growth on the substrate. This extra Al2O3 may act as a diffusion barrier and restrict the oxidation of silicon during the O3 exposure. The results for the SiO2 thickness in Fig. 13 support this explanation. The SiO2 thickness increases from the initial value of 11 Å over the first 60–70 ALE cycles. The SiO2 thickness reaches a maximum value of 41 Å after about 80 cycles and then slowly reduces to 39 Å after 160 ALE cycles. The Al2O3 growth is included in the SiO2 thickness because there is no separate Al2O3 layer included in the ellipsometry model. In comparison, the SiO2 layer had a thickness of only 11 Å using the O3-HF-TMA exposure sequence.

Similar behavior was observed for Si ALE when the reactant exposure sequence was changed from O2-HF-TMA to O2-TMA-HF for the same reactant pressures at 290 °C.36 The Si etch rate was 0.4 Å/cycle for the O2-HF-TMA exposure sequence. The Si etch rate decreased to 0.2 Å/cycle for the O2-TMA-HF exposure sequence. These Si etch rates were measured at 290 °C with pressures of 250, 1, and 1 Torr for O2, HF, and TMA, respectively.36 The decrease in the...
Si etch rate was also attributed to Al₂O₃ deposition occurring when TMA follows the O₂ exposure.

H. Si₃N₄ oxidation by O₃

Si₃N₄ oxidation has predominantly been studied at high temperatures of 900–1400 °C using O₂ and H₂O as the oxidation reactants.55–58,63 Si₃N₄ is very resistant to oxidation and is known to form a thin graded oxidized nitride layer between the film surface and the underlying nitride.63 In addition, very little is known about Si₃N₄ oxidation at lower temperatures with any oxidation reactant.63 To our knowledge, no studies have reported the oxidation of Si₃N₄ with ozone. Because O₃ has been employed as a diffusion barrier that limits further oxidation.64 The kinetics of silicon oxidation are modeled using the Deal–Grove model.65 A similar model may apply for the oxidation of Si₃N₄ by ozone.

IV. CONCLUSIONS

Thermal Si₃N₄ ALE has been demonstrated using an oxidation and "conversation etch" mechanism using O₂ or O₃, HF, and TMA as the reactants. In situ spectroscopic ellipsometry measurements could simultaneously measure the thicknesses of the Si₃N₄ film and the SiO₂ layer on the Si₃N₄ film during thermal Si₃N₄ ALE. O₃ led to higher etch rates than O₂ at the same reactant pressures and exposures times. Etch rates of 0.25 and 0.47 Å/cycle were observed for O₂ and O₃, respectively, at 290 °C using an oxidant-HF-TMA reactant sequence. Using O₂ as the oxidant, the Si₃N₄ etch rates were only weakly dependent on O₂ pressure from 250 Torr to 450 Torr. Using O₃ as the oxidant, the Si₃N₄ etch rates were independent of the O₂ pressure from 37 to 250 Torr. The Si₃N₄ etch rate was dependent on the reaction sequence. The Si₃N₄ etch rate was reduced to 0.20 Å/cycle using an O₂-TMA-HF reactant sequence.

The Si₃N₄ etch rate decreased at lower temperatures. Using an O₂-HF-TMA reactant sequence, the Si₃N₄ etch rate decreased from 0.47 Å/cycle at 290 °C to 0.07 Å/cycle at 210 °C. The Si₃N₄ surface roughness was also reduced after Si₃N₄ ALE at 290 °C using an O₂-HF-TMA reactant sequence. An SiO₂ layer exists on the Si₃N₄ surface with a thickness of ~11 Å during the O₂-HF-TMA reactant sequence at 290 °C. This SiO₂ layer could be removed using sequential HF and TMA exposures. These sequential HF and TMA exposures can also very slowly etch the Si₃N₄ substrate and thermal Si₃N₄ ALE is similar to thermal Si ALE. Both thermal Si₃N₄ ALE and thermal Si ALE are performed using oxidation of their surfaces to form an SiO₂ layer. Subsequently, the SiO₂ surface layer is converted to Al₂O₃ or an aluminum oxide silicate by the TMA exposure. This converted surface layer is then fluorinated by HF. The AlF₃ or AlOxFy fluoride surface layer is then converted to Al₂O₃ or an aluminum oxide silicate by the TMA exposure and is then fluorinated by HF. The AlF₃ or AlOxFy fluoride surface layer is then converted to Al₂O₃ or an aluminum oxide silicate by the TMA exposure and is then fluorinated by HF.

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