Thermal atomic layer etching of amorphous and crystalline \( \text{Al}_2\text{O}_3 \) films

Cite as: J. Vac. Sci. Technol. A 39, 042602 (2021); \texttt{doi:10.1116/6.0000995}
Submitted: 21 February 2021 · Accepted: 17 May 2021 · Published Online: 9 June 2021

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Note: This paper is part of the 2022 Special Topic Collection on Atomic Layer Etching (ALE).

ABSTRACT
Thermal atomic layer etching (ALE) can be achieved with sequential, self-limiting surface reactions. One mechanism for thermal ALE is based on fluorination and ligand-exchange reactions. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have demonstrated the thermal ALE of amorphous \( \text{Al}_2\text{O}_3 \) films. However, no previous investigations have explored the differences between the thermal ALE of amorphous and crystalline \( \text{Al}_2\text{O}_3 \) films. This study explored the thermal ALE of amorphous and crystalline \( \text{Al}_2\text{O}_3 \) films. HF, SF\(_6\), or XeF\(_2\) were used as the fluorination reactants. Trimethylaluminum (TMA) or dimethylaluminum chloride (DMAC) were used as the metal precursors for ligand-exchange. Spectroscopic ellipsometry measurements revealed that the amorphous \( \text{Al}_2\text{O}_3 \) films had much higher etch rates than the crystalline \( \text{Al}_2\text{O}_3 \) films. When using HF and TMA at 300 °C, the amorphous \( \text{Al}_2\text{O}_3 \) film was removed at an etch rate of 0.78 Å/cycle. For the crystalline \( \text{Al}_2\text{O}_3 \) film, an etch rate of 0.06 Å/cycle was initially observed prior to the stoppage of etching after removing about 10 Å of the film. Thermal ALE with HF and DMAC resulted in similar results. Etch rates of 0.60 and 0.03 Å/cycle were measured for amorphous and crystalline \( \text{Al}_2\text{O}_3 \) films at 300 °C, respectively. Other fluorination agents, such as SF\(_6\) or XeF\(_2\), were also used together with TMA or DMAC for \( \text{Al}_2\text{O}_3 \) ALE. These reactants for fluorination and ligand-exchange were able to etch amorphous \( \text{Al}_2\text{O}_3 \) films at 300 °C. However, they were unable to etch crystalline \( \text{Al}_2\text{O}_3 \) films at 300 °C beyond the initial 10–20 Å surface layer. The investigations also examined the effect of annealing temperature on the etch rate per cycle using HF and TMA as the reactants at 300 °C. Amorphous \( \text{Al}_2\text{O}_3 \) films were etched at approximately the same etch rate of 0.78 Å/cycle until the crystallization of amorphous \( \text{Al}_2\text{O}_3 \) films at ≥ 880 °C. The differences between amorphous and crystalline \( \text{Al}_2\text{O}_3 \) thermal ALE could be used to obtain selective thermal ALE of amorphous \( \text{Al}_2\text{O}_3 \) in the presence of crystalline \( \text{Al}_2\text{O}_3 \).

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I. INTRODUCTION

ALE is a technique that can remove thin films with Ångstrom-level precision using sequential, self-limiting surface reactions. There are two major types of ALE: plasma- and thermal. Plasma ALE is an anisotropic etching technique based on surface modification followed by an exposure of energetic ions or neutrals that remove material.1,2 Thermal ALE is an isotropic etching technique and is often viewed as the opposite of atomic layer deposition (ALD).3,4 Similar to ALD, thermal ALE utilizes sequential exposures of gaseous reactants with inert gas purging in between the reactant exposures.3,4

A common thermal ALE mechanism is based on fluorination and ligand-exchange reactions to achieve etching.3,4 For metal oxides, the fluorination reaction converts a thin surface layer of the metal oxide into a metal fluoride.9,10 The ligand-exchange reaction then creates a volatile metal product that results in the removal of the surface metal fluoride layer.11 The ligand-exchange step involves a metal precursor accepting a fluoride ligand while donating one of its ligands to the metal fluoride surface. Etching occurs when this ligand-exchange creates stable, volatile products.11

Thermal ALE using the fluorination and ligand-exchange pathway has been used to etch many metal oxides, such as \( \text{Al}_2\text{O}_3 \), ZrO\(_2\), \( \text{HfO}_2 \), and \( \text{Ga}_2\text{O}_3 \). The same fluorination and ligand-exchange process has also successfully etched metal nitrides such as AIN (Ref. 17) and GaN.18 Other mechanisms for
thermal ALE utilize conversion reactions. During conversion reactions, the surface of the thin film of interest is converted into a new material. Conversion reactions have been used to etch SiO$_2$ (Ref. 20) and ZnO. In addition, thermal ALE of W, Si, Sn, In, Hf, and Ge (Ref. 25) can be accomplished via oxidation and conversion reactions.

Thermal ALE of amorphous Al$_2$O$_3$ is typically performed using fluorination and ligand-exchange reactions. Previous studies have used HF for fluorination, and Sn(acac)$_2$ trimethylalumium (TMA), or dimethylaluminum chloride (DMAC) for ligand-exchange. The process for etching Al$_2$O$_3$ with HF and TMA is shown in Fig. 1. There have been no reports of thermal ALE for crystalline Al$_2$O$_3$. However, other crystalline materials, such as AlN and GaN, have been etched with thermal ALE.

One previous study examined the difference in thermal ALE between crystalline and amorphous HfO$_2$, ZrO$_2$, and HfZrO$_4$. Amorphous HfO$_2$, ZrO$_2$, and HfZrO$_4$ were observed to etch more rapidly than their corresponding crystalline counterparts using HF and TiCl$_4$ as the reactants at 250 °C. The differences were not as great using HF and DMAC as the reactants at 250 °C. In particular, ZrO$_2$ showed very little difference between the amorphous and crystalline forms. A similar study comparing crystalline and amorphous Al$_2$O$_3$ will be presented in this paper.

Al$_2$O$_3$ has many different crystalline structures. Amorphous Al$_2$O$_3$ is a glassy, disordered state of Al$_2$O$_3$ that can be formed by either physical vapor deposition (PVD) or atomic layer deposition (ALD). Upon annealing >800 °C, amorphous Al$_2$O$_3$ films deposited using electron beam evaporation crystallize into gamma-Al$_2$O$_3$ and other phases such as delta-Al$_2$O$_3$. The annealing of Al$_2$O$_3$ ALD films also results in a mixture of crystalline phases including gamma-Al$_2$O$_3$. As the Al$_2$O$_3$ film is annealed to higher temperatures, the crystalline structure evolves and finally reaches the alpha-Al$_2$O$_3$ crystalline phase at temperatures >1100 °C. The crystalline Al$_2$O$_3$ films used in this study were prepared by annealing in the range of 800–1000 °C and displayed x-ray diffraction peaks that were consistent with gamma-Al$_2$O$_3$ and delta-Al$_2$O$_3$.

The etching of crystalline Al$_2$O$_3$ films is important because obtaining ultrathin films of crystalline metal oxides can be difficult. The crystallization temperature typically increases as the Al$_2$O$_3$ film thickness decreases. For example, for a 60 s annealing process, an 8 nm Al$_2$O$_3$ ALD film could be crystallized at 850 °C as determined by x-ray diffraction analysis. In contrast, for the same 60 s annealing process, a 5 nm Al$_2$O$_3$ ALD film required 900 °C to crystallize, and a 3.5 nm Al$_2$O$_3$ ALD film required 1000 °C to crystallize. Crystallization temperatures that increased for thinner Al$_2$O$_3$ film thicknesses were also observed using differential scanning calorimetry studies.

The trend that thinner films require higher temperatures to crystallize is well established for other metal oxide films. The increase in crystallization temperature as the film decreases in thickness is explained by the increase in surface-to-volume ratio. Al$_2$O$_3$ ALE could avoid the high thermal budget necessary for crystallizing ultrathin Al$_2$O$_3$ films. A thicker Al$_2$O$_3$ film could be grown using Al$_2$O$_3$ ALD and then annealed for crystallization. Subsequently, the thicker crystalline Al$_2$O$_3$ film could be etched back to the desired ultrathin thickness.

Differences between amorphous and crystalline thermal ALE etch rates are also important for selective ALE. Selectivity is achieved when two materials have different etch rates under the same conditions. Selectivity could be observed for the crystalline and amorphous forms of the same material if the two have different etch rates. Crystalline thin films of HfO$_2$, ZrO$_2$, and HfZrO$_4$ have been shown to etch more slowly than their corresponding amorphous thin films. A similar trend may be observed for Al$_2$O$_3$ ALE. A possible application would be the selective etching of ultrathin Al$_2$O$_3$ films. For example, a low temperature anneal of Al$_2$O$_3$ films of various thicknesses would only crystallize the thicker films. The thinner amorphous Al$_2$O$_3$ films that did not crystallize would then be etched via thermal Al$_2$O$_3$ ALE.

For this study, fluorination and ligand-exchange reactions were used to etch amorphous and crystalline Al$_2$O$_3$ films. The fluorination reactions were HF, SF$_6$, and XeF$_2$. The ligand-exchange reactions were TMA and DMAC. The experiments were all conducted at 300 °C. Film thickness measurements were performed versus number of thermal ALE cycles using ex situ spectroscopic ellipsometry (SE). Plots of film thickness versus number of ALE cycles were used to determine the etch rates.

**II. EXPERIMENT**

The thermal ALE experiments were performed in a viscous flow reactor. The reaction temperatures were maintained by a proportional-integral-derivative (PID) temperature controller (2604, Eurotherm). A constant flow of ultrahigh purity (99.999%) N$_2$ gas was employed as the carrier and purge gas. Mass flow controllers (Type 1179A, MKS) regulated the nitrogen gas flow. A mechanical pump (Pascal 2038D, Alcatel) was attached to the back of the reactor. The reactor pressure with flowing N$_2$ carrier gas was ~1 Torr. The reactor pressure was measured by a capacitance manometer (Baratron 121A, MKS).

The fluorination reactions used either HF-pyridine solution (70 wt. % HF, Sigma-Aldrich), SF$_6$ (>98.5%, SynQuest Laboratories), or XeF$_2$ (99.5%, Strem Chemicals). All fluorination reactions were performed in a viscous flow reactor using a constant flow of ultrahigh purity N$_2$ gas as the carrier and purge gas.
agents were maintained at room temperature. The HIF-pyridine solution was contained in a gold-plated stainless steel bubbler to prevent corrosion. The pressure transients of HF from the HIF-pyridine source were adjusted to ∼90 mTorr using a metering valve (SS-4BMG, Swagelok). The XeF₂ pressure transients were ∼10 mTorr without a metering valve. The SF₄ pressure was metered to ∼200 mTorr. The ligand-exchange precursors were TMA (97%, Sigma-Aldrich) and DMAC (97%, Sigma-Aldrich). Both ligand-exchange reactants were held at room temperature. Metering valves were used to maintain pressure transients of ∼40 mTorr for both TMA and DMAC.

Crystalline and amorphous aluminum oxide thin films on native oxide silicon wafer coupons were used for these studies. Some of the Al₂O₃ ALD films were grown using methyl or chloride-based aluminum precursors and water at temperatures in the range of 200–250 °C. An SSI Solaris 200 Rapid Thermal Processing system was used for crystallizing the amorphous Al₂O₃ films. The first set of crystalline Al₂O₃ films were obtained by subjecting the Al₂O₃ ALD films to rapid thermal annealing at 1000 °C. These Al₂O₃ films had a thickness of approximately 5 nm.

The second set of samples consisted of Al₂O₃ ALD films deposited using TMA and H₂O at 200 °C. The growth of these Al₂O₃ ALD films was performed in the same reactor that was employed for the ALE studies. These Al₂O₃ ALD films were then thermally annealed at various temperatures (400, 600, 800, and 1000 °C) in an N₂ ambient for 60 s. The thickness of these Al₂O₃ ALD films was approximately 17 nm.

Grazing incidence x-ray diffraction (GI-XRD) scans were recorded using an x-ray diffractometer (Bede D1, Jordan Valley Semiconductors) with radiation from the Cu Kx line at λ = 1.5405 Å. The x-ray tube filament voltage was 40 kV and current was 35 mA. The incident angle was 0.3°. GI-XRD scans for these samples are shown in Fig. 2. Only the Al₂O₃ ALD film annealed at 1000 °C displayed a diffraction peak. The diffraction peak at 67° is consistent with the gamma-Al₂O₃ or delta-Al₂O₃ structure.

The third set of samples were grown using the same method as the first set of samples except that the films were annealed to 800, 840, 880, 920, 960, and 1000 °C using a rapid thermal anneal process in an N₂ ambient for 60 s. All the samples used in this study were analyzed with XRD to determine film structure and x-ray reflectivity (XRR) to measure the film densities. The XRR measurements were recorded using the same diffractometer and parameters as described for the GI-XRD scans. The XRR scan range was 500–6000 arc sec and recorded with a step size of 10 arc sec.

The film densities derived from the XRR scans are displayed in Fig. 3. The initial Al₂O₃ ALD films have densities around 3.0 g/cm³ as expected for Al₂O₃ ALD films. The films that obtain crystallinity after annealing have densities around 3.63 g/cm³. This density is consistent with a number of Al₂O₃ polymorphs including gamma-Al₂O₃ or delta-Al₂O₃. These crystalline Al₂O₃ films are not as dense as alpha-Al₂O₃ which has a density of 3.99 g/cm³.

The silicon wafers with the Al₂O₃ thin films were cut into coupons with dimensions of 2 × 2 cm². For each experiment, multiple samples were placed in the reactor. Running multiple samples concurrently allowed for direct comparisons between amorphous and crystalline Al₂O₃ films.

The ALE experiments were performed with a reaction sequence of x-30-2-30. This sequence signifies a fluorination reactant exposure of x seconds, then a 30 s N₂ purge, a metal precursor exposure of 2 s, and then another 30 s N₂ purge. The metal precursor exposure of 2 s was determined from previous studies of Al₂O₃ ALE. Experiments using HF or SF₄ as the fluorination reactant had a reaction sequence of 1-30-2-30. When XeF₂ was used as the fluorination reactant, the reaction sequence was 3-30-2-30.

The film thicknesses were measured using ex situ spectroscopic ellipsometry (SE) measurements. A spectroscopic ellipsometer (M-2000, J. A. Woollam) measured Ψ and Δ from 240 to 880 nm.
1000 nm with an incidence angle of 70°. The CompleteEASE software was used to model the data to determine the film thickness and the optical constants, n (refractive index) and k (extinction coefficient). The etch rate was determined using film thickness measurements versus number of ALE cycles.

The precision of the SE measurements of film thickness was within ±0.05 Å. A Cauchy model was used for all the Al₂O₃ thin films. The etch rates obtained from individual ALE experiments were accurate to ±0.03 Å/cycle. The reproducibility of the etch rates as determined from repeated experiments under the same conditions was ±0.05 Å/cycle.

Atomic force microscopy (AFM) was utilized to evaluate the surface of the amorphous and crystalline Al₂O₃ films before and after ALE. These AFM measurements were performed with a Park NX10 AFM instrument using a noncontact mode. The scan rate was 0.4 Hz with an Olympus microcantilever probe (OMCL-AC160TS).

III. RESULTS AND DISCUSSION

A. Al₂O₃ etching with HF and TMA or DMAC for ligand-exchange

The etch rates were significantly different for the amorphous and crystalline Al₂O₃ samples. The initial experiment compared the first set of samples comprised of the amorphous Al₂O₃ ALD films and the crystalline Al₂O₃ films annealed to 1000 °C. The Al₂O₃ ALE results for these samples using HF and TMA as the reactants at 300 °C are shown in Fig. 4. The etch rate for the amorphous Al₂O₃ film is 0.78 Å/cycle. This etch rate is comparable with earlier measurements for the ALE of amorphous Al₂O₃ ALD films using HF and TMA at 300 °C. In comparison, the etch rate for the crystalline Al₂O₃ is 0.06 Å/cycle only for the first 10 Å of the film thickness. No further etching occurs after removal of the top surface layer. This behavior may occur if the top surface layer is easier to fluorinate and remove than the bulk crystalline Al₂O₃ film.

AFM images compared the surface roughness before and after Al₂O₃ ALE. Figure 5(a) shows an AFM line scan for an initial amorphous Al₂O₃ film. The initial root mean square (RMS) surface roughness was 0.148 nm. Figure 5(b) displays an AFM line scan after Al₂O₃ ALE using HF and TMA at 300 °C removed 5.2 nm of the amorphous Al₂O₃ film. The RMS surface roughness after this etching was marginally smaller at 0.135 nm. Surface smoothing of amorphous Al₂O₃ films has been observed earlier after Al₂O₃ ALE using either HF and TMA as the reactants or HF and Sn(acac)₂ as the reactants.

Figure 6(a) shows an AFM line scan for an initial crystalline Al₂O₃ film. The initial RMS surface roughness was 0.107 nm. Figure 6(b) displays an AFM line scan after Al₂O₃ ALE using HF and TMA at 300 °C removed 0.5 nm of the crystalline Al₂O₃ film. The RMS surface roughness was slightly reduced after this etching to 0.085 nm. The Al₂O₃ ALE was able to smooth the crystalline Al₂O₃ surface. There was no evidence that the crystalline structure

![Amorphous Al₂O₃](image)

**FIG. 4.** Thickness change vs number of ALE cycles for amorphous and crystalline Al₂O₃ films using HF and TMA as reactants at 300 °C.

![AFM line scans](image)

**FIG. 5.** AFM line scans (a) before and (b) after Al₂O₃ ALE that removed a thickness of 5.2 nm for amorphous Al₂O₃ films at 300 °C using HF and TMA as reactants.
and possibly higher etch rates at crystalline grain boundaries caused an increase in the surface roughness after Al₂O₃ ALE using HF and TMA as the reactants.

DMAC is also an effective ligand-exchange reactant for the ALE of amorphous Al₂O₃ ALD films. Figure 7 shows the thermal ALE results using HF and DMAC at 300 °C. The amorphous Al₂O₃ ALD film had an etch rate of 0.60 Å/cycle. This etch rate for the amorphous Al₂O₃ film is comparable to the previous results using HF and DMAC as the reactants at 300 °C. AFM results indicated that the RMS roughness increased slightly using HF and DMAC as the reactants. The RMS roughness increased from 0.148 nm for the initial amorphous Al₂O₃ film to 0.266 nm after 200 ALE cycles.

In contrast to the amorphous Al₂O₃ film, Fig. 7 reveals that the crystalline Al₂O₃ film had a much lower etch rate of 0.03 Å/cycle using HF and DMAC as the reactants. Similar to the results using HF and TMA as the reactants, the crystalline Al₂O₃ films have a much lower etch rate than the amorphous Al₂O₃ films. AFM results showed that the RMS roughness of the crystalline Al₂O₃ films was nearly equivalent after etching using HF and DMAC as the reactants. For the crystalline Al₂O₃ films, the RMS roughness was 0.107 nm for the initial films and 0.136 nm after 200 ALE cycles.

The ALE of amorphous and crystalline ZrO₂ films was explored earlier using HF and DMAC as the reactants at 250 °C. There was little difference between the amorphous and crystalline ZrO₂ films at 250 °C. The amorphous ZrO₂ films displayed an etch rate of 1.11 Å/cycle. The crystalline ZrO₂ films yielded only a slightly smaller etch rate of 0.82 Å/cycle. The contrast between the etch rates for amorphous and crystalline films of ZrO₂ and Al₂O₃ may be attributed to the larger molar volume expansion upon fluorination for crystalline Al₂O₃. The ratio of molar volumes for 2AlF₃ and crystalline Al₂O₃ is 2.08. In comparison, the ratio of molar volumes for ZrF₄ and crystalline ZrO₂ is 1.74. The larger expansion upon fluorination of crystalline Al₂O₃ to 2AlF₃ may inhibit fluorination and restrict the etching of crystalline Al₂O₃ films.

B. Al₂O₃ etching versus annealing temperature using HF and TMA as reactants

The second set of Al₂O₃ samples that had been annealed to 400, 600, 800, and 1000 °C was used to determine how the etch rate changes as the Al₂O₃ films become more crystalline. Figure 8 shows the results for Al₂O₃ ALE using HF and TMA as the reactants at 300 °C. These results include the as-deposited Al₂O₃ ALD film. The as-deposited Al₂O₃ film, as well as the Al₂O₃ films annealed to 400, 600, and 800 °C all had an etch rate of 0.78 Å/cycle. In contrast, the Al₂O₃ film annealed to 1000 °C displayed a much lower etch rate of 0.09 Å/cycle.

These etching results correlate well with the GI-XRD results for these same samples shown in Fig. 2. The films annealed up to 800 °C do not display crystallinity as measured by GI-XRD and have nearly the same etch rate. The Al₂O₃ film annealed at 1000 °C was the only crystalline film and yielded a much lower etch rate. The results in Fig. 2 indicate that the crystallization of the
The Al₂O₃ ALE was conducted using HF and TMA as the reactants. The Al₂O₃ films annealed at 800 °C had an etch rate of 0.65 Å/cycle. This etch rate of 0.65 Å/cycle for Al₂O₃ films from the third set of samples annealed at 800 °C is slightly less than the etch rate of 0.78 Å/cycle observed in Fig. 8 for Al₂O₃ films from the second set of samples annealed at 800 °C. This variation is attributed to the different Al₂O₃ ALD conditions employed for the second and third set of Al₂O₃ samples.

Figure 9 also reveals that the Al₂O₃ films annealed at 840 °C had a slower etch rate of 0.34 Å/cycle. This result suggests that the Al₂O₃ films annealed at 840 °C are partially crystalline. In contrast, the films annealed at 880 °C or higher temperatures had a negligible etch rate. Based on these Al₂O₃ ALE results, the Al₂O₃ films may be fully crystalline at annealing temperatures of 880 °C and above.

This suggestion can be tested using diffraction studies to determine the crystallinity of the Al₂O₃ ALD films. GI-XRD scans of the amorphous Al₂O₃ ALD films annealed between 800 and 1000 °C are displayed in Fig. 10. The Al₂O₃ films annealed at 880–1000 °C all display crystallinity with a diffraction peak at 67° that is expected for gamma-Al₂O₃ or delta-Al₂O₃ (Refs. 34 and 42). The peak intensities are lower for these GI-XRD scans compared with the GI-XRD scans shown in Fig. 2 because the film thicknesses were smaller at approximately 5 nm.

The Al₂O₃ film annealed to 800 °C does not display a diffraction peak. The Al₂O₃ film annealed at 840 °C displayed a reduced etch rate of 0.34 Å/cycle in Fig. 9. However, the Al₂O₃ film annealed at 840 °C does not appear crystalline by the GI-XRD scan. The threshold for the film crystallinity as measured by GI-XRD is reached for the Al₂O₃ film annealed at 880 °C.

There are dramatic differences between the ALE of amorphous and crystalline Al₂O₃ films. Figure 3 shows that the amorphous Al₂O₃ film has a lower density of approximately 3.0 g/cm³ compared with the higher density of 3.63 g/cm³ for the crystalline Al₂O₃ film. The lower density may facilitate fluorination because fluorination leads to expansion of the metal oxide.

**amorphous Al₂O₃ ALD films occurs between 800 and 1000 °C. To probe annealing temperatures between 800 and 1000 °C, amorphous Al₂O₃ ALD films were annealed in increments of 40 °C between 800 and 1000 °C. This defined the third set of samples. Figure 9 shows the Al₂O₃ ALE results at 300 °C for the amorphous Al₂O₃ ALD films annealed between 800 and 1000 °C.**
For example, for crystalline gamma-Al₂O₃, the molar volume is 101.96 g/mol/3.63 g/cm³ = 28.088 cm³/mol. In contrast, the molar volume of crystalline AlF₃ is 83.98 g/mol/2.88 g/cm³ = 29.160 cm³/mol. The volume expansion upon fluorination of crystalline Al₂O₃ to 2AlF₃ is 2.08.

Molecular dynamics simulations have also examined the structure of amorphous and gamma-Al₂O₃. These studies indicate that the surfaces of amorphous and gamma-Al₂O₃ are very similar. First principles calculations also point out the similarity between (Al₂O₃)ₙ clusters and gamma-Al₂O₃. Therefore, the surfaces on amorphous and gamma-Al₂O₃ would not be expected to lead to differences in the etch rates. However, the simulations confirm the higher density of gamma-Al₂O₃ compared with amorphous Al₂O₃. The computations also can examine the coordination number and ring distribution in amorphous and gamma-Al₂O₃. An n-fold ring is defined as the shortest path of alternating Al-O bonds and an n-fold ring consists of 2n alternating Al-O bonds. The coordination number and ring distribution change between amorphous Al₂O₃ and gamma-Al₂O₃.

Amorphous Al₂O₃ has a dominant Al coordination number of 4 and a ring distribution of mostly fourfold rings. Amorphous Al₂O₃ is also largely composed of AlO₄ polyhedra. In contrast, gamma-Al₂O₃ has a dominant Al coordination number of 6 and a ring distribution of mostly twofold and threefold rings. Gamma-Al₂O₃ is also largely composed of AlO₄ polyhedra. The etching of Al₂O₃ may be more difficult for the more highly coordinated Al centers in gamma-Al₂O₃. These highly coordinated Al centers may be less accessible for the fluorination reaction. Thinner fluoride layers on Al₂O₃ during Al₂O₃ ALE have earlier been shown to lead to smaller etch rates.

A previous study investigated the thermodynamics of HF fluorination of Al₂O₃. This study found that desorption of water was the step with the highest energy barrier during HF fluorination. The denser structure of crystalline gamma-Al₂O₃ compared with amorphous Al₂O₃ may also inhibit the desorption of water and reduce the HF fluorination of Al₂O₃.

\[
\text{Al}_2\text{O}_3 + 6\text{HF}(g) \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O}(g), \Delta G^*(300 \, ^\circ\text{C}) = -49.0 \, \text{kcal},
\]

\[
\text{Al}_2\text{O}_3 + 3/2\text{SF}_4(g) \rightarrow 2\text{AlF}_3 + 3/2\text{SO}_2(g), \Delta G^*(300 \, ^\circ\text{C}) = -155.9 \, \text{kcal}.
\]

C. Al₂O₃ etching with SF₄ or XeF₂ as fluorination reagent

Other fluorination agents can be utilized in place of HF during thermal ALE. For example, SF₄ is another possible fluorinating agent that has been previously used in thermal ALE. SF₄ is known to be a stronger fluorination agent for metal oxides. The standard free energy changes during fluorination of Al₂O₃ to AlF₃ using HF or SF₄ illustrate this difference.

A more favorable fluorination reaction could result in a thicker fluoride layer. The ligand-exchange reaction could then remove more of the fluoride layer and yield a higher etch rate.

Thermal ALE using SF₄ and TMA as the reactants at 300 °C is shown in Fig. 11. Amorphous Al₂O₃ has an etch rate of 0.43 Å/cycle. In contrast, crystalline Al₂O₃ does not display any etching. The etch rate for amorphous Al₂O₃ is also lower with SF₄ than with HF. The etch rates for amorphous Al₂O₃ using HF or SF₄ and TMA as the reactants are 0.78 or 0.43 Å/cycle, respectively. The etch rates are not correlating with the standard free energy changes for fluorination. The use of SF₄ as the fluorination reagent also led to an increase in the RMS roughness. The RMS roughness increased from 0.148 nm for the initial amorphous Al₂O₃ film to 0.624 nm after 150 ALE cycles using SF₄ and TMA. Although there was no measurable etching of the crystalline Al₂O₃ film using SF₄ and TMA, the crystalline Al₂O₃ film increased in RMS roughness to 0.502 nm after 150 ALE cycles.

Earlier etch rates for Al₂O₃ using Sn(acac)₂ as the ligand-exchange reagent and either HF or SF₄ as the fluorination reagent also did not scale with the standard free energy changes for fluorination. The etch rate for amorphous Al₂O₃ using IIF or
SF₆ and Sn(acac)₂ as the reactants at 200 °C were 0.28 or 0.20 Å/cycle, respectively. ⁴,¹⁵,⁴⁶ Perhaps there are additional kinetic factors that favor fluorination using HF. For example, H₂O is the product of HF fluorination of Al₂O₃ ¹⁰ in contrast, SF₆ is postulated to release SO₂ according to Eq. (2). Another possible sulfur-containing etch product is SOF₂. ⁴³ The kinetic pathways leading to SO₂ or SOF₂ desorption may be more difficult than the kinetic pathways leading to H₂O desorption. These kinetic bottlenecks may reduce the etch rate using SF₆ as the fluorination reactant.

Another possible fluorination agent for thermal ALE is XeF₂. ¹⁶ XeF₂ has an even larger standard free energy change for fluorination of Al₂O₃ than HF or SF₆. ⁴⁷

\[
\text{Al}_2\text{O}_3 + 3\text{XeF}_2(g) \rightarrow 2\text{AlF}_3 + 3/2\text{O}_2(g) + 3\text{Xe}(g), \Delta G^\circ(300 \, ^\circ\text{C}) = -266.5 \text{ kcal.} \quad (3)
\]

Figure 12 shows the results for Al₂O₃ ALE using XeF₂ and TMA as the reactants at 300 °C. The etch rate for amorphous Al₂O₃ is 0.66 Å/cycle. This etch rate using XeF₂ is slightly less than the etch rate of 0.78 Å/cycle for amorphous Al₂O₃ using HF and TMA as the reactants from Fig. 4. The etch rate using XeF₂ is also somewhat larger than the etch rate of 0.43 Å/cycle for amorphous Al₂O₃ using SF₆ and TMA as the reactants from Fig. 11. These results again do not argue that the Al₂O₃ etch rate is proportional to the standard free energy changes for Al₂O₃ fluorination. Using XeF₂ as the fluorinating reagent did not increase the RMS roughness for the amorphous Al₂O₃ films. The RMS roughness was 0.148 nm for the initial amorphous Al₂O₃ film and nearly equivalent at 0.133 nm after 50 ALE cycles using XeF₂ and TMA as the reactants.

Figure 12 also shows results for the etching of crystalline Al₂O₃ using XeF₂ and TMA as the reactants at 300 °C. These crystalline samples were annealed to 1000 °C. There is evidence that etching of the crystalline Al₂O₃ proceeds for about 17 Å before the etching stops. Similar behavior was observed for etching crystalline Al₂O₃ with HF and TMA as the reactants in Fig. 4. This behavior suggests that the bulk crystalline Al₂O₃ does not etch. However, a modified or damaged surface of the crystalline Al₂O₃ film may be accessible to etching. This idea is supported by the large increase in RMS roughness observed after 50 ALE cycles using XeF₂ and TMA as the reactants. The RMS roughness increased from 0.107 nm for the initial crystalline Al₂O₃ film to 7.923 nm after 50 ALE cycles using XeF₂ and TMA.

Etching experiments were also performed with XeF₂ and DMAC as the ligand-exchange reactant at 300 °C. Figure 13 shows that the etch rate for amorphous Al₂O₃ is 0.81 Å/cycle. This etch rate using XeF₂ is slightly larger than the etch rate of 0.78 Å/cycle for amorphous Al₂O₃ using HF and TMA as the reactants from Fig. 4.
TABLE I. Etch rates using different fluorination reactants and metal precursors for ligand-exchange at 300 °C for amorphous and crystalline Al₂O₃ films.

<table>
<thead>
<tr>
<th>Fluorination reactant</th>
<th>Ligand-exchange reactant</th>
<th>Amorphous Al₂O₃ (Å/ cycle)</th>
<th>Crystalline Al₂O₃ (Å/ cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>TMA</td>
<td>0.78</td>
<td>0.06</td>
</tr>
<tr>
<td>HF</td>
<td>DMAC</td>
<td>0.60</td>
<td>0.03</td>
</tr>
<tr>
<td>SF₄</td>
<td>TMA</td>
<td>0.43</td>
<td>No etch</td>
</tr>
<tr>
<td>XeF₄</td>
<td>TMA</td>
<td>0.66</td>
<td>0.45*</td>
</tr>
<tr>
<td>XeF₂</td>
<td>DMAC</td>
<td>0.81</td>
<td>No etch</td>
</tr>
</tbody>
</table>

*Initial etching only before etching stops.

The etch rate using XeF₂ and DMAC is also somewhat larger than the etch rate of 0.66 Å/cycle for amorphous Al₂O₃ using XeF₂ and TMA as the reactants from Fig. 12. AFM measurements also revealed that the RMS surface roughness increased after Al₂O₃ ALE using XeF₂ and DMAC. The RMS roughness increased from 0.148 nm for the initial amorphous Al₂O₃ film to 0.832 nm after 150 ALE cycles. A summary of all the Al₂O₃ etch rates for amorphous Al₂O₃ at 300 °C is given in Table I.

Figure 13 also indicates that the crystalline Al₂O₃ does not etch with XeF₂ and DMAC at 300 °C. In fact, there may be a slight deposition on the Al₂O₃ surface under these conditions. The RMS roughness also increased to 0.613 nm after 80 cycles resulting from the XeF₂ and DMAC exposures on crystalline Al₂O₃. Earlier experiments have monitored the deposition of AlF₄ on Al₂O₃ using HF and TMA at much lower temperatures. The lack of etching in Fig. 13 is consistent with all the previous experiments on crystalline Al₂O₃. A summary of all the Al₂O₃ etch rates for crystalline Al₂O₃ at 300 °C is provided in Table I. Either there is no etching of crystalline Al₂O₃ or there is a slight amount of etching before the etching stops after removing 10-17 Å of the top surface layer.

XeF₂ has been shown to spontaneously etch silicon. A proximity effect also resulted in the spontaneous etching of SiO₂ by XeF₂ in the presence of Si. To determine if XeF₂ alone could spontaneously etch Al₂O₃, both the crystalline and amorphous Al₂O₃ samples were subjected to 100 exposures of XeF₂ at 300 °C. Each XeF₂ exposure was conducted for 3 s followed by a purge of 30 s. After 25 XeF₂ exposures, there was a small thickness loss of 5 Å or less of the top surface layer on each sample. Further XeF₂ exposures beyond 25 exposures showed no thickness change for either sample. These control experiments rule out the spontaneous etching of amorphous Al₂O₃ at 300 °C. Only a small fraction of the 10-17 Å removed from crystalline Al₂O₃ prior to the stoppage of etching could be accounted for by spontaneous etching of Al₂O₃ by XeF₂.

IV. CONCLUSIONS

The thermal ALE for amorphous and crystalline Al₂O₃ films was compared at 300 °C using HF, SF₄, or XeF₂ as the fluorination reactants and TMA or DMAC as the metal precursors for ligand-exchange. The etch rates for the amorphous films were much higher than the etch rates for the crystalline films. For example, the etch rate for amorphous Al₂O₃ prior to any annealing using HF and TMA as the reactants was 0.78 Å/cycle. In comparison, the etch rate for crystalline Al₂O₃ formed by annealing at 1000 °C using HF and TMA as the reactants was approximately 0.06 Å/cycle for the first 10 Å and then negligible for larger Al₂O₃ thicknesses. The RMS surface roughness of both the amorphous and crystalline Al₂O₃ films was slightly reduced by thermal Al₂O₃ ALE using HF and TMA as the reactants.

Etch rates were measured at 300 °C using the following pairs of fluorination/ligand-exchange reactants: HF/TMA; HF/DMAC; SF₄/TMA; XeF₂/TMA; and XeF₂/DMAC. HF/TMA and XeF₂/DMAC resulted in the highest etch rates for amorphous Al₂O₃ prior to any annealing of approximately 0.8 Å/cycle. XeF₂/TMA and HF/DMAC etch rates for amorphous Al₂O₃ were comparable at around 0.6 Å/cycle. The SF₄/TMA etch rate for amorphous Al₂O₃ was the lowest at around 0.4 Å/cycle. Etching the amorphous Al₂O₃ with XeF₂/TMA and SF₄/TMA led to higher RMS surface roughness. In comparison, the etch rates for crystalline Al₂O₃ after annealing to 1000 °C using the same pairs of fluorination/ligand-exchange reactants were much smaller or negligible. However, the RMS surface roughness of the crystalline Al₂O₃ film was noticeably larger after exposures to XeF₂/TMA, XeF₂/DMAC, and SF₄/TMA.

The Al₂O₃ crystallinity and etch rates were also investigated versus annealing temperature. The amorphous Al₂O₃ film remains amorphous for annealing temperatures up to 800 °C. These amorphous Al₂O₃ films also displayed a constant etch rate of 0.78 Å/cycle using the HF and TMA reactants at 300 °C. Crystallinity in Al₂O₃ films starts to appear after annealing at 800 °C. In comparison, the etch rate of the amorphous Al₂O₃ films using the HF and TMA reactants is reduced to 0.34 Å/cycle after annealing at 840 °C. All the films annealed to 880 °C and higher temperatures displayed the same negligible etch rate using HF and TMA as the reactants. In comparison, the intensity of the diffraction peak increases progressively for temperatures higher than 880 °C.

The differences between the etch rates of amorphous and crystalline Al₂O₃ films can be attributed to their different densities. Amorphous materials have a lower density than their crystalline counterparts. The lower density may facilitate fluorination because fluorination leads to a significant molar volume expansion. Lower density and lower coordination of Al centers in amorphous Al₂O₃ may also allow for an easier replacement of oxygen with fluoride during fluorination. A larger fluoride film thickness after fluorination can lead to more fluoride removed during the ligand-exchange reaction and larger etch rates.

The etch rates of Al₂O₃ by the HF, SF₄, and XeF₂ fluorination reactants together with either TMA or DMAC as the ligand-exchange precursor did not correspond with their standard free energy changes for Al₂O₃ fluorination. This lack of correlation suggests that kinetic factors must also be important during Al₂O₃ fluorination. In addition, the difference between the etch rates for amorphous and crystalline Al₂O₃ indicates that amorphous Al₂O₃ could easily be etched in the presence of crystalline Al₂O₃. This structure dependent etching selectivity could be used to remove amorphous Al₂O₃ while retaining crystalline Al₂O₃.
ACKNOWLEDGMENTS
This research was funded by the National Science Foundation (NSF) (No. CHE-1609554).

DATA AVAILABILITY
The data that support the findings of this study are available within the article.

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