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Thermal Atomic Layer Etching of Aluminum Oxide (Al₂O₃) Using Sequential Exposures of Niobium Pentafluoride (NbF₅) and Carbon Tetrachloride (CCl₄): A Combined Experimental and Density Functional Theory Study of the Etch Mechanism

Varun Sharma,* Simon D. Elliott, Tom Blomberg, Suvi Haukka, Michael E. Givens, Marko Tuominen, and Mikko Ritala*

ABSTRACT: Thermal atomic layer etching (ALEt) of amorphous Al₂O₃ was performed by alternate exposures of niobium pentafluoride (NbF₅) and carbon tetrachloride (CCl₄). The ALEt of Al₂O₃ is observed at temperatures from 380 to 460 °C. The etched thickness and the etch rate were determined using spectroscopic ellipsometry and verified by X-ray reflectivity. The maximum etch rate of about 1.4 Å/cycle and a linear increase of the removed film thickness with the number of etch cycles were obtained at a temperature of 460 °C. With the help of density functional theory calculations, an etch mechanism is proposed where NbF₅ converts part of the Al₂O₃ surface into an AlF₃ or aluminum oxyfluoride layer, which upon reacting with CCl₄ is converted into volatile halide-containing byproducts, thus etching away the converted portion of the material. Consistent with this, a significant surface fluorine content of about 55 at. % was revealed when the elemental depth profile analysis of a thick NbF₅-treated Al₂O₃ layer was performed by X-ray photoelectron spectroscopy. The surface morphology of the reference, pre-, and postetch Al₂O₃ surfaces was analyzed using atomic force microscopy and bright-field transmission electron microscopy. Moreover, it is found that this process chemistry is able to etch Al₂O₃ selectively over silicon dioxide (SiO₂) and silicon nitride (Si₃N₄).

INTRODUCTION

In an era of emerging nano-technologies, the fabrication of sub-10 nm, complex, and 3-D device structures demands unprecedented thickness control in the atomic regime. Specific advances in semiconductor manufacturing techniques are therefore required, and several techniques are being actively developed, such as thermal atomic layer deposition (ALD), plasma enhanced ALD, plasma-based atomic layer etching (ALE), and the recently explored thermal atomic layer etching (ALEt). Complementary to ALD, ALEt is a technique that utilizes either partial or complete self-limiting sequential gas–solid reactions to allow the removal of material from the surface with atomic-level precision. Due to the self-limiting nature of at least one of the ALEt half-reactions, it can be preferred over plasma-based ALE for isotropic etching of material from non-line-of-sight features.

Several thermal ALEt processes have been developed that employ a conversion-etch reaction mechanism. During the conversion step, the surface is converted into a more reactive material, which during the etch step is exposed to a coreactant and forms volatile products. In ALEt, the conversion step can form an oxide, fluoride, or another type of reactive surface that differs from the actual etch target. In the etch step, ligands from the coreactant molecules can undergo surface reactions such as ligand-exchange transmetalation, fluorination, or chlorination to form species that may leave the surface.

In most of the reported ALEt reactions, hydrogen fluoride (HF) is used as a fluorinating agent in either the conversion or the etch step. However, the use of HF can be restricted due to the safety concerns associated with its handling and storage. Moreover, its corrosive nature can pose some compatibility issues with gas-feed as well as exhaust lines, pumps, and other reactor parts, especially when kept at elevated temperatures. Therefore, alternatives to HF-based...
ALEt chemistries would prove to be beneficial. Several other highly reactive and toxic fluorinating agents such as SF₆, XeF₂, F₂, CCl₂F₂, and CHClF₂ have been proposed.

In this paper, we explore a novel ALEt chemistry for etching amorphous Al₂O₃. It is proposed that NbF₅ can be used as a fluorinating agent, replacing HF. CCl₄ is used to carry out the halide-exchange reactions with the fluorinated aluminum oxide surface in order to form volatile AlF₅Cl₂ species. Moreover, CCCI₃ is relatively more stable than the trimethyl aluminum (TMA) used in the ALE literature, which decomposes below 400 °C. Despite NbF₅ being solid, it has sufficient vapor pressure (about 0.1 Torr at 45 °C) and forms volatile species upon fluorinating the Al₂O₃ surface (at least at 460 °C) and thus leads to almost no surface contaminations. Moreover, it is relatively safer to handle and store and is compatible with the semiconductor vacuum processing equipment.

II EXPERIMENTAL SECTION

Substrates and Process Gases. The target films deposited on p-type 200 mm silicon wafers that were used in the etch experiments are thermally grown SiO₂ (TOx), high-quality low-pressure chemical vapor deposited Si₃N₄, and ALD-grown Al₂O₃. The SiO₂ and Si₃N₄ films were about 20 and 30 nm thick, respectively. The Al₂O₃ films were deposited at 300 °C by the TMA and water (H₂O) ALD process.

The fluorinating agent was 99.5% pure NbF₅ purchased from abcbr GmbH (Germany). The CCCI₃ (anhydrous) was bought from Merck KGaA (Germany) and had a purity ≥ 99.5%. The NbF₅ vessel was kept at 45 °C, and the CCCI₃ source vessel was operated at room temperature, CCCI₃ has a vapor pressure of about 90 Torr at room temperature and was therefore used in a vapor-draw mode, whereas NbF₅ was used in a vapor-push mode. Nitrogen (99.999%) was used as an inert purge gas. Both the purge gas flows as well as CCCI₃ dose were controlled by needle valves.

Experimental Setup. The etch experiments were conducted on a Pulsar 2000 (P2000) cross-flow reactor manufactured by ASM International N.V. designed to process 200 mm silicon wafers. The P2000 chamber was operated at isothermal conditions to a maximum Tetch of 460 °C. Prior to any etching, all target substrates were kept in a vacuum chamber for 5 min in order to ensure stabilization of the wafer surface temperature. The chamber pressure was between 2 and 4 Torr.

Characterization Techniques. The thickness and optical constants of the films were evaluated using SE-800 spectroscopic ellipsometer from SENTECH Instruments GmbH, (Germany). X-ray reflectometry (XRR) was performed for confirming the removed thickness values, measuring the postetched surface roughness, and film densities using Xpert PRO MRD X-ray diffractrometer from Malvern Panalytical Ltd. (United Kingdom). For consistency, the exact center points of the wafers were chosen as measurement spots.

Elementary surface composition investigations were performed by X-ray photoelectron spectroscopy (XPS) and conducted on PHI Quantera SXM. Monochromatic Al Kα (1486.6 eV/15 kV) X-rays with a take-off angle of 45° were used. The analysis chamber pressure was 3 × 10⁻⁶ Pa. In all XPS depth profile measurements, the argon ion energy was set to 1 keV and the X-ray spot size was 100 μm. The pass energy of 140 eV was used. The detection limit of this particular tool is about 0.1–0.5 at. %.

Transmission electron microscopy (TEM) imaging was performed by EVANS Analytical Group (California, USA) on FEI Tecnai TF-20 FEG/TEM operated at 200 kV in a bright-field imaging mode. The TEM lamellas for imaging were prepared by using the focused ion beam lift-out technique. The thicknesses of the TEM lamellas were around 100 nm. For preserving the contrast and structural integrity of the sample, a carbon coating was performed prior to the ion-milling.

Computational Techniques. The chemical mechanism of the ALEt process was investigated using first-principles density functional theory (DFT) as implemented in the Schrödinger Materials Science Suite. Atomic-scale models of bulk materials, surfaces, and gas-phase molecules were optimized under periodic boundary conditions with the Perdew–Burke–Ernzerhof (PBE) functional, a plane wave basis to a wavefunction cut-off of 40 Ry, PBE ultrasoft pseudopotentials, and Monkhorst–Pack k-point sets using the Quantum ESPRESSO code.

Total energies from DFT are used to calculate reaction energies (ΔE) for possible chemical transformations of these surfaces by the etchants during ALEt.

Since etching is likely to be driven by entropy (S), it is important to also determine reaction free energies (ΔG) that include the effect of temperature (T) and pressure of reactants (preact) and products (pprod), which for ideal gases at constant volume is given by

\[ ΔG = ΔE - TS \]  

where the sticking coefficient (s) is an unknown precursor parameter that is typically in the range 10⁻⁵ to 10⁻⁴ for ALD precursors. As explained in the Supporting Information, the entropy terms at 100 °C < T < 600 °C and pprod or preact were derived from molecular vibrational analysis of the gas-phase reactant and product molecules at the PBE/LAV3D** level with the Jaguar code.

The (0 1 0) surface of θ-Al₂O₃ was used as the periodic slab model for the alumina surface during ALEt. θ-Al₂O₃ was chosen because ions in this polymorph have a similar coordination environment to those in the amorphous as-deposited Al₂O₃. The 2 × 1 expansion of a 3-layer (0 1 0) slab was selected as a representative model surface on the basis of its stability and level of corrugation when bare or fluorinated (see the Supporting Information).

As shown in Figure 1, half of the Al atoms on the bare surface are exposed (4-coordinate to O) and half are covered (6-coordinate).

![Figure 1](https://example.com/figure.png)

Fluorinated and chlorinated surfaces were generated by progressively replacing O with F or Cl in the topmost layer of the slab, always adding two halide monoanions for each oxide dianion removed so as to preserve stoichiometry and charge neutrality.

The maximum level of chlorination was determined to be 3 Cl per 1 cell, which we designate as 100%-Cl coverage since higher coverages led to the spontaneous desorption of AlCl₃ molecules during optimization. By contrast, fluorination up to 166%-F (20 F per 2 × 1 cell) was energetically favorable, albeit with a substantial reorganization to give a surface resembling AlF₅ structural motifs. In this study, we focus on interconversions between the 166%-
F, 100%-F, 100%-Cl, and 0% (i.e., bare alumina) surfaces depicted in Figure 1.

The aim of the DFT simulations is to map out the general form of the ALEt mechanism. Many reactions and byproducts can be possible, and we seek here to distinguish which surface transformations are thermodynamically favorable as a function of process conditions. This can reveal the nature of the saturating surface after each precursor exposure during the ALEt cycle and hence account for the etch rate. However, ALEt is actually a non-equilibrium process, driven by kinetics and the irreversible removal of byproducts from the surface into the gas flow. Computing the detailed sequence of surface adsorbates, intermediates, reaction pathways, and associated kinetics with DFT would be a possible future step but is beyond the current scope. It is worth remembering, therefore, that a reaction computed with DFT would be a possible future step but is beyond the current window.

RESULTS AND DISCUSSION

Etch-Process Characterization. Al₂O₃ is etched by utilizing sequential exposures of NbF₅ and CCl₄ precursors at elevated temperatures (380–460 °C). An inert gas purging was introduced after each exposure to remove the volatile byproducts and excess of precursor molecules from the reaction chamber. The etch per cycle (EPC) was estimated by subtracting the post-etch thickness from the initial thickness byproducts and excess of precursor molecules from the gas flow. Computing the detailed sequence of surface adsorbates, intermediates, reaction pathways, and associated kinetics with DFT would be a possible future step but is beyond the current scope. It is worth remembering, therefore, that a reaction computed with DFT would be a possible future step but is beyond the current window.

Figure 3. AlF₃[O] film thickness vs variation in total NbF₅ exposure time at 400 and 460 °C. The total NbF₅ exposure time is calculated by multiplying the NbF₅ pulse time by the total number of cycles. The NbF₅ pulse times of 4.5 and 3 s were used at 400 and 460 °C, respectively. Each NbF₅ pulse was separated by a 6 s long N₂ purge step.

As shown in Figure 2, an increase in EPC is observed with increasing NbF₅ pulse time at an etch temperature (Tₚₑᶜʰ) of 460 °C. In the figure, NbF₅ pulse time is varied from 0 to 3 s, while the CCl₄ pulse time is fixed to 3 s. For each data point plotted in Figure 2, a total of 150 etch cycles were performed. In the absence of NbF₅, no Al₂O₃ etching was observed as confirmed by XRR, TEM, and XPS. When the NbF₅ pulse time is increased to 0.5 s, an etch rate of about 0.5 Å per cycle is noticed. Further increase in the NbF₅ pulse time to 3 s provides an etch rate of about 1.4 Å/cycle. Longer NbF₅ pulse times were not tested. The figure shows that at a Tₚₑᶜʰ of 460 °C, the EPC did not show strong self-limiting characteristics but may still indicate a soft saturation behavior. A non-saturative fluorination behavior may affect the etch uniformity across the wafer especially in a cross-flow reactor. This non-self-limiting behavior can be explained by enhanced diffusion of fluoride ions at 460 °C. The thickness of the converted layer may depend on factors such as surface temperature, partial pressure, as well as flux of the precursor molecules, reaction time, adsorbate concentration, interaction between surface and diffusing adspecies, presence of defects, being accompanied by phase transitions, and so forth. Thus, in thermal-based ALE processes there may not exist an ALE window.

For studying the temperature-dependent kinetics of the fluorination step, excess fluorination was carried out by exposing the aluminum oxide surface to NbF₅ at 400 and 460 °C (Figure 3). At 400 °C, excess fluorination was performed for 150 and 600 cycles of 4.5 s NbF₅ pulse times, while 150 and 800 cycles of 3 s NbF₅ pulse times were used at 460 °C. After performing the excess fluorination step, the thickness of the formed AlF₃[O] layer was measured by ex situ SE. About 11 and 14 nm thick fluorinated layers were obtained after 450 and 2400 s of total NbF₅ exposure time, respectively, at 460 °C. The formation of thick (>10 nm) AlF₃[O] layers must be due to the prolonged fluorination step and the fluoride ions diffusing deeper into the aluminum oxide layer. The diffusion of fluoride is evidently dependent on the temperature and thus may hint at the existence of no ALE window. According to Morelock et al., aluminium tri fluoride adopts a cubic form above 440 °C, which upon cooling changes to a rhombohedral phase. The X-ray diffraction (XRD) analysis of about 11 nm AlF₃[O] layer revealed the rhombohedral phase (see the Supporting Information S4) and is thus consistent with the literature. On the contrary, at 400 °C, the thickness of the fluorinated layer stayed around 3 nm even after prolonged total NbF₅ exposure of 2700 s. Chen et al. showed the fluoride ions penetrating up to 2 nm thick aluminum oxide after treating fluorinated alumina at 400 °C, and neutral/ions beams-assisted fluorination lead to a thicker AlF₃[O] layer. Moreover, up to 0.5 nm thick AlF₃ layer was obtained at a lower temperature of 300 °C with HF as a fluorinating agent. This temperature-dependent thickness of
the converted fluorinated layer suggests that the conversion step is diffusion-limited.

The fluorination step produced a very hydrophilic surface with water contact angles ≤15°, which is consistent with earlier reports from Roodenko et al. The low water contact angle of the AlF[X\(\text{O}\)] surface is attributed to the high Lewis acidity of Al–F species, resulting in strong adsorption of H\(_2\)O molecules at under-coordinated aluminum sites.

Figure 4 reveals the effect of variation in the CCl\(_4\) pulse time on EPC at 460 °C. The NbF\(_3\) pulse and N\(_2\) purge lengths were set to 3 and 6 s, respectively, and the CCl\(_4\) pulse time was changed from 0.5 to 3 s. The figure shows that an EPC around 1.1 Å is observed for CCl\(_4\) pulse times between 0.5 and 1.75 s. However, when 3 s CCL\(_4\) pulse time is used, an etch rate of 1.4 Å/cycle is achieved.

Figure 5 plots EPC values at various etch temperatures for the Al\(_2\)O\(_3\) ALEt process by NbF\(_3\) + CCl\(_4\) (red curve). The figure also demonstrates that CCl\(_4\) alone (blue curve) does not etch Al\(_2\)O\(_3\) within the tested temperature range of 380–460 °C. The incapability of CCl\(_4\) alone in etching Al\(_2\)O\(_3\) is also confirmed by XRR and TEM images as seen below. However, at 380 °C, the etch rate of Al\(_2\)O\(_3\) by the NbF\(_3\) + CCl\(_4\) ALEt process is comparatively low, at about 0.08 Å/cycle, and no significant etching was observed at temperatures <380 °C. From Figure 5, it can be seen that the EPC increases with the etch temperature and reaches an etch rate of 1.4 Å/cycle at 460 °C. The Figures 2–4 also corroborate the proposed ALEt mechanism, whereby NbF\(_3\) is necessary to fluorinate the Al\(_2\)O\(_3\) and the converted layer is etched by a subsequent pulse of CCl\(_4\). In most of the thermal ALE reports, the ALE window is not observed, and the EPC is dependent on the partial pressure of CCl\(_4\). Similarly, it is evident from our findings that there exists no ALE window. However, a few ALE processes exhibit an ALE window such as ALE of HfO\(_2\), TiO\(_2\), and TiN.

Selective Etching. In thin-film technology, many applications may benefit from thermal ALEt processes that provide selective etching of Al\(_2\)O\(_3\) over SiO\(_2\) and Si\(_3\)N\(_4\). Figure 6 shows that the NbF\(_3\) + CCl\(_4\) ALEt process is able to etch Al\(_2\)O\(_3\) linearly with the number of etch cycles at 460 °C. A total of 150 cycles were performed per data point. A linear fit of Al\(_2\)O\(_3\)-etched thickness with respect to etch cycles yields a constant etch rate of 0.11 nm/cycle when 0.5 s NbF\(_3\) and 3 s CCl\(_4\) pulse times are used. By contrast, under all conditions tested here, no etching of SiO\(_2\) and Si\(_3\)N\(_4\) films was observed. In other words, between 380 and 460 °C, Al\(_2\)O\(_3\) can be etched selectively over SiO\(_2\) and Si\(_3\)N\(_4\) by the NbF\(_3\) + CCl\(_4\) etch process.

Surface Characterization. XPS studies were conducted in order to understand the etch mechanism. An Al\(_2\)O\(_3\) surface exposed to NbF\(_3\) was the test subject. Figure 7 shows the XPS elemental depth profile analysis of the surface that has been fluorinated. The aluminum oxide surface was subjected to a total of 150 cycles of 3 s NbF\(_3\) pulses with intermittent 6 s N\(_2\) purges at 460 °C. Reasons for conducting the fluorination step under such extreme conditions were to ensure a significant as well as meaningful fluorine signal, to understand the fluorination step, and to deduce a reliable reaction mechanism. From the XPS depth profiling and SE measurements, the thickness of the AlF\([X\text{O}]\) layer formed under these conditions was estimated to be around 11 nm.

After 15 s of sputtering, a very high fluorine content of about 55 at. % (similar F content was found by Kim et al.) after fluorinating Al\(_2\)O\(_3\) and a decreased oxygen content of 17 at. % (as compared to roughly 60 at. % oxygen in Al\(_2\)O\(_3\)) is observed.
The fluorine content gradually decreases with sputter time and may indicate the presence of a gradient in the composition of the AlF₃ layer. Furthermore, a very low niobium content of about 1 at. % decreased oxygen, and high fluorine content support the proposed reaction mechanism in favor of reaction R2 described below. This confirms that the NbF₅ molecules impart at least some fluoride ions to aluminum and form a volatile species with oxygen. Moreover, the formation of an about 11 nm thick AlF₃ layer upon excess fluorination may explain the non-self-limiting EPC curve in Figure 2.

Figure 8 reveals atomic percentages of several elements found on the Al₂O₃ surface as a function of sputtering time after removing about 18 nm of the 56 nm Al₂O₃ support the proposed reaction mechanism in favor of reaction

\[ \text{Al}_2\text{O}_3(s) + 3\text{NbF}_5(g) \rightarrow 2\text{AlF}_3(g) + 3\text{NbOF}_2(g) \]  

(R1) and for this reaction, periodic DFT yields \( \Delta G = +140 \text{ kJ/mol-NbF}_5 \) and \( \Delta G_{300 \text{°C}} = -100 \text{ kJ/mol-NbF}_5 \). The positive value of \( \Delta G \) indicates a net cost in bond energies, while the negative value of \( \Delta G \) reflects the entropy gain in volatilizing the solid. Bulk alumina may be more readily etched by the Cl source alone according to the reaction

\[ \text{Al}_2\text{O}_3(s) + 3\text{CCl}_4(g) \rightarrow 2\text{AlCl}_3(g) + 3\text{COCl}_2(g) \]  

(R7) which has DFT-computed energetics of \( \Delta G = -18 \text{ kJ/mol-Al}_2\text{O}_3 \) and \( \Delta G_{300 \text{°C}} = -248 \text{ kJ/mol-Al}_2\text{O}_3 \). (If the reaction would proceed to completion, CO₂ could be produced, but it seems more likely that COCl₂ would desorb first.) However, no etching is observed experimentally with CCl₄ alone (Figure 4), which suggests that kinetic barriers prevent this reaction from taking place. Consistent with this, periodic DFT simulations show that the CCl₄ molecule resists adsorption to a bare alumina surface probably because the molecule is nonpolar. We therefore exclude these single-etchant reactions from the reaction equations below and restrict our analysis to reactions that etch away either Al or O as volatile products but not both simultaneously. Such reactions are the prerequisite for a successful, self-limiting ALEt process.

The conversion of bulk alumina into solid aluminum fluoride according to

\[ \text{Al}_2\text{O}_3(s) + 3\text{NbF}_5(g) \rightarrow 2\text{AlF}_3(g) + 3\text{NbOF}_2(g) \]  

(R2) is computed to show that \( \Delta G = -24 \text{ kJ/mol-NbF}_5 \) and \( \Delta G_{300 \text{°C}} = -58 \text{ kJ/mol-NbF}_5 \) (Table 1). Although labeled as “conversion” in the ALEt literature, this reaction necessarily involves the etching of oxygen, as one oxide dianion is exchanged with two fluoride monoanions. The thermodynamics of conversion of the bare alumina surface into a 100%...
fluorinated surface is found to be similar in terms of energetics to that of the bulk (R3: $\Delta E = -27$ kJ/mol-NbF$_5$ and $\Delta G_{\text{300°C}} = -60$ kJ/mol-NbF$_5$). Further fluorination of the surface is slightly less favorable (e.g., R4: $\Delta E = +0.8$ kJ/mol-NbF$_5$ and $\Delta G_{\text{300°C}} = -33$ kJ/mol-NbF$_5$ for 100% F to 166% F) but still exoergic, indicating that surface conversion does not self-limit. As shown in Figure 10, there is little variation with temperature in these free energies of fluorination of the bulk and surface by NbF$_5$.

We conclude that continuous conversion of alumina into aluminum fluoride is moderately exoergic under the experimental conditions, but again, the extent to which such conversion actually takes place depends on the kinetics of individual steps that bring NbF$_5$ and alumina into contact. We suggest that this is likely to be dictated by the kinetics of diffusion across the Al$_2$O$_3$–AlF$_3$ interface. The NbF$_5$ pulse therefore produces a surface layer and possibly also subsurface layers that are fluorinated and is experimentally verified in Figures 3 and 8.

We now examine the potential reactions of such fluorinated surfaces (considering the sample surfaces 100% F and 166% F) with gas-phase CCl$_4$ in the next phase of the ALEt cycle. The computations show that the most energetically favorable products are CFCI$_3$ and AlCl$_3$, and the resulting thermodynamics are given in Table 1 and Figure 11.

CCl$_4$ is the likely product of halide-exchange between the CCl$_4$ reagent and the fluorinated surface. The simplest of such reactions produces a chlorinated surface with the same coverage

$$100\% \text{ F-slab} + 12\text{CCl}_4(g) \rightarrow 100\% \text{ Cl-slab} + 12\text{CFCI}_3(g)$$ (R10)

does not depend on whether the conversion is carried out in bulk or at the surface. The reaction becomes more favorable if Si is also etched away as AlF$_3$ layer. For instance, $\Delta G_{\text{300°C}} = +4.3$ kJ/mol-CCl$_4$ for partial etching

$$100\% \text{ F-slab} + 12\text{CCl}_4(g) + 2/3\text{Al}_2\text{O}_3(s) \rightarrow 66\% \text{ Cl-slab} + 12\text{CFCI}_3(g) + 4/3\text{AlCl}_3(g)$$ (R11)

and $\Delta G_{\text{300°C}} = -58$ kJ/mol-CCl$_4$ for complete etching to a bare surface.

100% F-slab + 12CCl$_4$(g) + 2Al$_2$O$_3$(s) → 0%-slab + 12CFCI$_3$(g) + 4AlCl$_3$(g) (R13)

Similar results for the 166% F surface are displayed in Figure 11. As expected, these etch reactions are driven by entropy and thus become more favored at high temperatures. We cannot confidently state the exact temperature above which a given reaction becomes exoergic since this is affected by the pressure correction and thus by the arbitrary choice of the sticking coefficient $s$. Nevertheless, Figure 11 allows us to conclude that it is thermodynamically favored for CCl$_4$ to entirely etch away the aluminum fluoride layer and reveal bare alumina (0% surface).

Since CCl$_4$ may in principle etch bulk alumina (reaction R7), we need to consider whether the bare alumina surface is reactive with this precursor. Converting the bare surface to a 100%-chlorinated surface is found to be exoergic, with $\Delta E = -40$ kJ/mol-CCl$_4$ and $\Delta G_{\text{300°C}} = -51$ kJ/mol-CCl$_4$ (reaction R9) following a similar trend to the conversion of bulk alumina to bulk aluminum chloride (reaction R8). However, as noted above, the experimental result of no etching by CCl$_4$ alone indicates that this reaction pathway is not accessible. A bare alumina surface is therefore the thermodynamically favored outcome of the CCl$_4$ pulse.

In case fluorinated or chlorinated portions of the surface persist into the NbF$_5$ pulse of the next ALEt cycle, we include exemplary reactions of 100% F and 100% Cl surfaces with NbF$_5$ in Figure 10 (reactions R4–R6). In this case, halide-exchange to NbClF$_4$ is the most favorable reaction, but the addition of F and removal of O is also exoergic across the entire temperature range. Therefore, these reactions also lead to a fluorinated surface as the outcome of the NbF$_5$ pulse.

Having identified the saturated surfaces at the end of each precursor pulse, we are now able to combine half-reactions (R3 + R13 or R4 + R14) into the overall ALEt reaction

$$\text{Al}_2\text{O}_3(s) + 3\text{NbF}_5(g) + 6\text{CCl}_4(g) \rightarrow 2\text{AlCl}_3(g) + 3\text{NbOF}_3(g) + 6\text{CFCI}_3(g)$$ (R15)

The overall energies per ALEt cycle computed with DFT are $\Delta E = +421$ kJ/mol-Al$_2$O$_3$ and $\Delta G_{\text{300°C}} = -329$ kJ/mol-Al$_2$O$_3$. 

![Figure 9](https://doi.org/10.1021/acs.chemmater.1c00142)}
Table 1. Reaction Thermodynamics Computed with DFT for Potential Half-Reactions in the NbF₅ Pulse (Reactions R1−R6), CCl₄ Pulse (R7−R14), and the Overall ALEt Cycle (R15)\(^a\)

<table>
<thead>
<tr>
<th>R. no.</th>
<th>reaction</th>
<th>(\Delta E)</th>
<th>(\Delta G^{100,^\circ,C})</th>
<th>(\Delta G^{200,^\circ,C})</th>
<th>(\Delta G^{300,^\circ,C})</th>
<th>(\Delta G^{600,^\circ,C})</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>(\text{Al}_2\text{O}_3(\text{s}) + 3\text{NbF}_5(\text{g}) \rightarrow 2\text{AlF}_3(\text{g}) + 3\text{NbOF}_3(\text{g})}) (R1)</td>
<td>139.9</td>
<td>-10.2</td>
<td>-54.6</td>
<td>-100.1</td>
<td>-241.4</td>
<td>kJ/mol (NbF₅)</td>
</tr>
<tr>
<td>R2</td>
<td>(\text{Al}_2\text{O}_3(\text{s}) + 3\text{NbF}_5(\text{g}) \rightarrow 2\text{AlF}_3(\text{g}) + 3\text{NbOF}_3(\text{g})}) (R2)</td>
<td>-24.1</td>
<td>-47.4</td>
<td>-52.5</td>
<td>-57.5</td>
<td>-71.7</td>
<td>kJ/mol (NbF₅)</td>
</tr>
<tr>
<td>R3</td>
<td>0%-slab + 6\text{NbF}_5(\text{g}) \rightarrow 100% F-slab + 6\text{NbOF}_3(\text{g}) (\text{(R3)})</td>
<td>-26.8</td>
<td>-50.1</td>
<td>-55.3</td>
<td>-60.3</td>
<td>-74.5</td>
<td>kJ/mol (NbF₅)</td>
</tr>
<tr>
<td>R4</td>
<td>100%-slab + 4\text{NbF}_5(\text{g}) \rightarrow 166% F-slab + 4\text{NbOF}_3(\text{g}) (\text{(R4)})</td>
<td>-4.5</td>
<td>-22.4</td>
<td>-27.6</td>
<td>-32.6</td>
<td>-46.8</td>
<td>kJ/mol (NbF₅)</td>
</tr>
<tr>
<td>R5</td>
<td>100% Cl-slab + 12\text{NbF}_5(\text{s}) \rightarrow 166% F-slab + 12\text{NbClF_4(g)} + 4\text{NbOF}_3(\text{g}) (\text{(R5)})</td>
<td>-44.9</td>
<td>-80.4</td>
<td>-91.1</td>
<td>-102.1</td>
<td>-136.0</td>
<td>kJ/mol (NbF₅)</td>
</tr>
<tr>
<td>R6</td>
<td>100% Cl-slab + 12\text{NbF}_5(\text{s}) \rightarrow 100% F-slab + 12\text{NbClF_4(g)} (\text{(R6)})</td>
<td>-60.1</td>
<td>-99.7</td>
<td>-112.3</td>
<td>-125.3</td>
<td>-165.7</td>
<td>kJ/mol (NbF₅)</td>
</tr>
<tr>
<td>R7</td>
<td>(\text{Al}_2\text{O}_3(\text{s}) + 3\text{CCl}_4(\text{g}) \rightarrow 2\text{AlCl}_3(\text{g}) + 3\text{COCl}_2(\text{g})}) (\text{(R7)})</td>
<td>-17.7</td>
<td>-164.1</td>
<td>-206.0</td>
<td>-248.4</td>
<td>-372.9</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R8</td>
<td>(\text{Al}_2\text{O}_3(\text{s}) + 3\text{CCl}_4(\text{g}) \rightarrow 2\text{AlCl}_3(\text{g}) + 3\text{COCl}_2(\text{g})}) (\text{(R8)})</td>
<td>-62.8</td>
<td>-74.2</td>
<td>-74.1</td>
<td>-73.4</td>
<td>-62.8</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R9</td>
<td>0%-slab + 6\text{CCl}_4(\text{g}) \rightarrow 100% Cl-slab + 6\text{COCl}_2(\text{g}) (\text{(R9)})</td>
<td>-40.1</td>
<td>-51.6</td>
<td>-51.5</td>
<td>-50.7</td>
<td>-40.2</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R10</td>
<td>100% F-slab + 12\text{CCl}_4(\text{g}) \rightarrow 100% Cl-slab + 12\text{AlCl}_3(\text{g}) (\text{(R10)})</td>
<td>72.5</td>
<td>51.4</td>
<td>46.2</td>
<td>41.0</td>
<td>25.7</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R11</td>
<td>100% F-slab + 12\text{CCl}_4(\text{g}) + (2/3)\text{Al}_2\text{O}_3(\text{s}) \rightarrow 66% Cl-slab + 12\text{AlCl}_3(\text{g}) + (4/3)\text{AlCl}_3(\text{g}) (\text{(R11)})</td>
<td>72.5</td>
<td>28.9</td>
<td>16.7</td>
<td>4.3</td>
<td>-33.5</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R12</td>
<td>166% F-slab + 20\text{CCl}_4(\text{g}) + (4/3)\text{Al}_2\text{O}_3(\text{s}) \rightarrow 100% Cl-slab + 20\text{AlCl}_3(\text{g}) + (8/3)\text{AlCl}_3(\text{g}) (\text{(R12)})</td>
<td>71.5</td>
<td>23.3</td>
<td>9.7</td>
<td>-4.1</td>
<td>-46.4</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R13</td>
<td>100% F-slab + 12\text{CCl}_4(\text{g}) + 2\text{Al}_2\text{O}_3(\text{g}) \rightarrow 0%-slab + 12\text{AlCl}_3(\text{g}) + 4\text{AlCl}_3(\text{g}) (\text{(R13)})</td>
<td>83.7</td>
<td>-4.9</td>
<td>-31.1</td>
<td>-57.9</td>
<td>-140.6</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R14</td>
<td>166% F-slab + 20\text{CCl}_4(\text{g}) + (10/3)\text{Al}_2\text{O}_3(\text{g}) \rightarrow 0%-slab + 20\text{AlCl}_3(\text{g}) + (20/3)\text{AlCl}_3(\text{g}) (\text{(R14)})</td>
<td>78.2</td>
<td>-10.4</td>
<td>-36.6</td>
<td>-63.4</td>
<td>-146.2</td>
<td>kJ/mol (CCl₄)</td>
</tr>
<tr>
<td>R15</td>
<td>(\text{Al}_2\text{O}_3(\text{s}) + 3\text{NbF}_5(\text{g}) + 6\text{CCl}_4(\text{g}) \rightarrow 2\text{AlCl}_3(\text{g}) + 3\text{NbOF}_3(\text{g}) + 6\text{AlCl}_3(\text{g}) (\text{(R15)})</td>
<td>421.8</td>
<td>-62.6</td>
<td>-194.2</td>
<td>-329.1</td>
<td>-747.6</td>
<td>kJ/mol (Al₂O₃)</td>
</tr>
</tbody>
</table>

\(^a\)Bulk solid is labeled (s), gas-phase molecules (g), and coverage is indicated as a percentage for surface slabs.
Consistent with the data in Figure 2, the EPC in this mechanism depends on the level of conversion that is achieved in the NbF₅ pulse. 100% F means the etching of 2 (Al₂O₃)/cycle in the 2 × 1 slab. Dividing by the cross-sectional area of the slab (84.5 Å²) and multiplying by the molar volume of θ-alumina (48.5 Å³/Al₂O₃) yields a theoretical EPC of 1.2 Å/cycle for this F-coverage. Converting a greater proportion of the surface zone to AlF₃ means a higher EPC—e.g., 166% F means etching 3.3 (Al₂O₃)/cycle per slab and an EPC of 1.9 Å/cycle.

**Proposed Reaction Mechanism.** Many reported thermal ALEt reactions undergo a two-step, conversion-etch mechanism,⁷⁻¹¹,¹³ with the conversion (or fluorination) step followed by an etch step. The experimental findings in this report also suggest a two-step etch mechanism.

The first step of the proposed reaction mechanism shown in Figure 12 is the conversion step. Figure 12a depicts the initial Al₂O₃ film on the silicon substrate, and Figure 12b shows the fluorinated Al₂O₃ layer after exposing to the NbF₅. As evident from Figures 3 and 7, the NbF₅ is believed to act like a fluorinating agent similar to HF²⁻ or WF₆¹³ and converts the Al₂O₃ surface into AlF₅[O]. The experimental findings suggest that the fluorination is not self-limiting, and therefore, with excessive fluorination, a thicker AlF₅[O] layer is formed, as depicted in Figure 12c.

From the DFT calculations for gas-bulk (R₁ and R₂) as well as gas–surface reactions R₃⁻R₅, it is proposed that niobium most likely forms the volatile NbOF₃ species. The existence of gaseous NbOF₃ has been previously reported, and its volatility has been studied.⁵³⁻⁵⁶ The reaction NbOF₃(s) → NbOF₃(g) is favorable ($ΔG < 0$) above 140 °C.²⁵ Moreover, thermogravimetric analysis of NbOF₃ showed mass loss above 80 °C.²⁵

During this conversion step, the oxygen from the Al₂O₃ layer is also removed at least partially if not completely and therefore the fluorinated layer is labeled as AlF₅[O]. Moreover, it is also possible that the fluorinated layer is AlF₃ which partially oxidizes in the air to form AlF₅[O]. Figure 12d depicts an outcome of the excess fluorination step and is supported by Figures 3 and 7.

In the second step, the AlF₅[O] layer can be etched as shown in Figure 12 (d−f). The etch step involves halide-exchange transmetalation to form volatile byproducts such as AlF₃Cl₃⁻a and CCl₃⁻aF₃⁻ where 0 ≤ a ≤ 2. The DFT computations reveal AlCl₃ and CFCl₃ as being the most favorable etch products from the various chlorination half-reactions R₁₀⁻R₁₄. In this fashion, an etching of Al₂O₃ can be achieved by alternating exposures of NbF₅ and CCl₄, which

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**Step 1:** Conversion/Fluorination - NbF₅(g) fluorinates the Al₂O₃ surface

```
Al₂O₃

Si (with native oxide)

a) Starting Al₂O₃ surface

Nbf₅

AlF₅[O]

Si (with native oxide)

b) Partial fluorination

Nbf₅

Al₂O₃

Si (with native oxide)

c) Excess fluorination
```

**Step 2:** Etch - CCl₄(g) reaction with AlF₅[O] surface

```
AlF₅[O]

Al₂O₃

Si (with native oxide)

d) AlF₅ surface

CCl₄

AlF₅[O]

Al₂O₃

Si (with native oxide)

e) CCl₄ interaction with AlF₅ surface

f) Removed converted AlF₅ layer
```

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Figure 10. Change in the Gibbs free energy with temperature for various fluorination ALEt-half-reactions.

Figure 11. Change in the Gibbs free energy with temperature for possible chlorination or halide-exchange reactions.

Figure 12. Proposed ALEt mechanism consists of a conversion step followed by an etch step: (a) starting Al₂O₃ surface, (b) after partial fluorination by NbF₅, (c) upon excess NbF₅ exposure, a thick AlF₅[O] is formed, (d) AlF₅[O] surface with Al–F bonds, (f) possible halide-exchange interaction between CCl₄ and the AlF₅[O] surface, and (g) converted AlF₅[O] layer removed and the underlying Al₂O₃ surface revealed.
may follow the described conversion-etch mechanism by the overall reaction R15.

Discussion of Etch Rate. According to the overall etch reaction R15, the theoretical EPC of 1.2 Å/cycle for 100% F-slab coverage is evaluated. For prolonged fluorination as per reactions R4 and R5, where 166% F-slab is used, an EPC of 1.9 Å/cycle is obtained. An EPC of 1.4 Å/cycle is recorded for 3 s NbF5 and CCl4 pulse lengths (as shown in Figure 2), which is therefore consistent with a coverage of 120% F during etching by R15. Moreover, both the experiment and the DFT calculations indicate that the EPC is not self-limiting for NbF5 pulse time variation and strongly depends on the fluorination step.

Another parameter that largely impacts the EPC is the etch temperature. Higher EPC values are observed at higher temperatures (≥380 °C). At temperatures below 380 °C, no etching was observed. However, DFT thermodynamic calculations did not show any evidence for this behavior. Therefore, this temperature dependence probably reflects the kinetics of diffusion and structural reorganization at the Al2O3-AlF3 interface. Based on our examination of the DFT-computed structures, it may be that atoms near the interface have to reorganize so that aluminum takes a low coordination number (i.e., 4 rather than 6) as the prerequisite for the fluoride to form and hence for the etching to take place.

Conclusions

ALEt of amorphous Al2O3 is demonstrated using cyclic exposures of NbF5 and CCl4 etchants. The Al2O3 ALEt is found to follow a two-step etch mechanism. In the first step, NbF5 converts part of the Al2O3 layer into AlF3[O], or more evidently AlF3, which is described as a conversion or fluorination step. The most likely volatile byproduct is found to be NbOF3. In the second step, the chlorine atoms from CCl4 undergo halide-exchange with the converted AlF3[O] surface. As a result of such an interaction, various volatile byproducts such as AlF3Cl, AlFCl3, AlCl3, and several chlorofluorocarbon molecules can be produced. Of these, AlCl3 and CFCls are found by DFT to be the most favorable, which leads to the overall etching reaction

\[
\text{Al}_2\text{O}_3(\text{s}) + 3\text{NbF}_5(\text{g}) + 6\text{CCl}_4(\text{g}) \rightarrow 2\text{AlCl}_3(\text{g}) + 3\text{NbOF}_3(\text{g}) + 6\text{CFCl}_3(\text{g})
\]

Similar reactions can be written for the other possible byproducts.

In this manner, the converted AlF3[O] layer is volatilized from the surface by CCl4 and hence the desired etching takes place. The feasibility of the proposed reaction mechanism was confirmed with thermodynamic calculations based on DFT. In addition, XPS and XRD analyses confirmed the formation as well as the removal of the fluorinated AlF3[O] layer.

The dependence of the EPC on NbF5 pulse time shows soft self-limiting characteristics, which can be due to slow kinetics, diffusion-limited gas–solid reaction, high residence time of NbF5, low concentration or partial pressure of NbF5, or slow sublimation of volatile NbOF3 surface species. The CCl4 reaction is found to be more self-limiting than that of NbF5.

Aluminum oxide ALEt is observed between 380 and 460 °C. From its onset (removing just 0.08 Å/cycle at 380 °C), the etch rate tends to increase with etch temperature. We tentatively link this temperature-dependence to the kinetics of diffusion across the oxide–fluoride interface. The linear removal of Al2O3 with cycles is observed with an etch rate of about 1.1 Å/cycle at 460 °C. An etch rate of about 1.4 Å/cycle is measured when the exposure time for each precursor is set to 3 s, separated by 6 s N2 purges. This etch rate is consistent with fluorination that extends partly into the subsurface layer. As revealed by TEM analysis, the surface of the post-etch Al2O3 film was rougher than the unetched film, again pointing to diffusion at the interface.

It is proposed that the thermal NbF5 + CCl4 ALEt process reported here could etch other metal oxides in a similar two-step etch mechanism with selectivity against SiO2 and Si3N4.

Associated Content

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.1c00142.

Details on DFT calculations; bulk calculations; optimized unit cells of bulk structures of θ-Al2O3 and AlF3; slab calculations; entropy estimation; computed structural and energetic data of the surface slabs; optimized surface slabs; grazing-incidence XRD (GIXRD) analysis of aluminum fluoride and the formed aluminum fluoride layer after prolonged fluorination at 460°C; and surface morphology determination by AFM (PDF)

Computed bare slabs in crystallographic information file (.cif) format (ZIP)

Author Information

Corresponding Authors

Varun Sharma — ASM Microchemistry Oy, Helsinki, Uusimaa 00560, Finland; Department of Chemistry, University of Helsinki, Helsinki, Uusimaa 00014, Finland; orcid.org/0000-0003-0079-2434; Email: varun.sharma@asm.com, varun.sharma@helsinki.fi

Mikko Ritala — Department of Chemistry, University of Helsinki, Helsinki, Uusimaa 00014, Finland; orcid.org/0000-0002-6210-2980; Email: mikko.ritala@helsinki.fi

Authors

Simon D. Elliott — Schrödinger, New York 10036-4041, United States; orcid.org/0000-0001-5573-5694

Tom Blomberg — Department of Chemistry and Materials Science, Aalto University, Espoo, Uusimaa 02150, Finland

Suvi Haukka — ASM Microchemistry Oy, Helsinki, Uusimaa 00560, Finland

Michael E. Givens — ASM Microchemistry Oy, Helsinki, Uusimaa 00560, Finland

Marko Tuominen — ASM Microchemistry Oy, Helsinki, Uusimaa 00560, Finland

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.chemmater.1c00142

Notes

The authors declare no competing financial interest.

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