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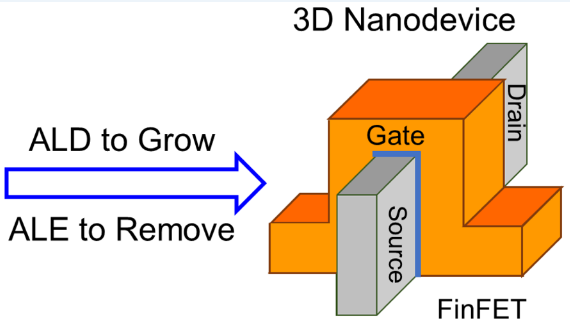
Prospects for Thermal Atomic Layer Etching Using Sequential, Self-Limiting Fluorination and Ligand-Exchange Reactions

Steven M. George*,[†,‡] and Younghee Lee[†]

[†]Department of Chemistry and Biochemistry and [‡]Department of Mechanical Engineering, University of Colorado at Boulder, Boulder, Colorado 80309, United States

ABSTRACT: **Thermal atomic layer etching (ALE) of Al_2O_3 and HfO_2 using sequential, self-limiting fluorination and ligand-exchange reactions was recently demonstrated using HF and tin acetylacetonate ($Sn(acac)_2$) as the reactants. This new thermal pathway for ALE represents the reverse of atomic layer deposition (ALD) and should lead to isotropic etching. Atomic layer deposition and ALE can together define the atomic layer growth and removal steps required for advanced semiconductor fabrication. The thermal ALE of many materials should be possible using fluorination and ligand-exchange reactions. The chemical details of ligand-exchange can lead to selective ALE between various materials. Thermal ALE could produce conformal etching in high-aspect-ratio structures. Thermal ALE could also yield ultrasmooth thin films based on deposit/etch-back methods. Enhancement of ALE rates and possible anisotropic ALE could be achieved using radicals or ions together with thermal ALE.**



Atomic layer etching (ALE) is a thin film removal technique based on sequential, self-limiting surface reactions that is needed for advanced semiconductor manufacturing.[1,2] Most previous ALE processes have obtained etching using ion-enhanced or energetic-noble-gas-atom-enhanced surface reactions after adsorbing halogens on the surface of the material.[1] In contrast, only a few thermal chemical processes have been demonstrated for ALE. Thermal ALE should be able to remove thin films isotropically with atomic layer control. Thermal ALE can be viewed as the reverse of atomic layer deposition (ALD).[3] Working together with ALD, thermal ALE will advance the toolset for atomic layer processing.

New pathways for thermal ALE have recently been discovered using sequential, self-limiting thermal reactions. Al_2O_3 ALE has been reported using HF and either tin acetylacetonate ($Sn(acac)_2$) or $Al(CH_3)_3$ as the reactants.[4−6] HfO_2 ALE has also been documented using HF and $Sn(acac)_2$ as the reactants.[7] Quartz crystal microbalance results for Al_2O_3 ALE using HF and $Al(CH_3)_3$ at 300 °C are shown in Figure 1.[6] The removal of Al_2O_3 is linear with the number of Al_2O_3 ALE reaction cycles. The mass change per cycle for Al_2O_3 ALE at 300 °C is -15.9 ng/(cm^2 cycle). This mass loss is equivalent to an etch rate of 0.51 Å/cycle.[6]

The chemistry of thermal ALE is based on fluorination and ligand-exchange reactions.[4−7] A schematic of the proposed reaction mechanism for Al_2O_3 ALE using $Al(CH_3)_3$ as the metal precursor is displayed in Figure 2. In the ligand-exchange reaction, the metal precursor accepts fluorine from a metal fluoride surface layer and concurrently transfers its ligand to the metal fluoride. This ligand-exchange can be characterized as a metal-exchange transmetalation reaction between adjacent metal centers.[8] Etching results if this reaction forms a stable and volatile reaction product.

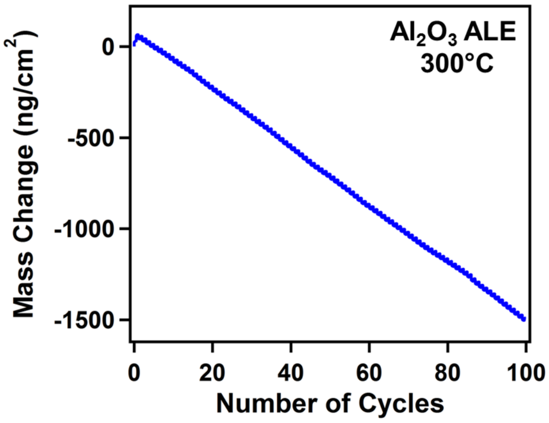


Figure 1. Mass change versus number of cycles for Al_2O_3 ALE using sequential HF and $Al(CH_3)_3$ exposures at 300 °C.

Published: May 24, 2016

DOI: 10.1021/acsnano.6b02991
ACS Nano 2016, 10, 4889−4894

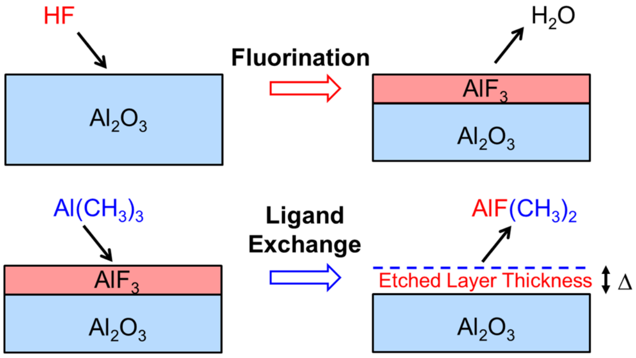


Figure 2. Schematic illustration showing the fluorination and ligand-exchange reactions during thermal Al_2O_3 ALE using HF and $Al(CH_3)_3$ as the reactants.

In this Perspective, we discuss the many prospects for thermal ALE that are on the horizon. Other materials besides metal oxides, such as metal nitrides, can be etched by the fluorination and ligand-exchange reactions that define thermal ALE. Selective ALE can be obtained with different metal precursors containing various ligands based on the stability and volatility of the possible metal etch products. Thermal ALE can also etch conformally in high-aspect-ratio structures. In addition, various new applications are envisioned for thermal ALE.

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THERMAL ALE OF VARIOUS MATERIALS

Thermal ALE is analogous to the reverse of ALD;[3,9] however, this is not quite accurate. Atomic layer deposition reactions are typically very exothermic, and are favorable thermochemical reactions.[9] These thermal reactions are spontaneous with negative Δ*G* values where *G* is the Gibbs free energy. Performing the same ALD reactions in reverse should not be possible because of thermodynamic considerations. Thermal ALE requires alternative, self-limiting reactions with different reactants that are exothermic and have negative Δ*G* values to ensure spontaneity.

Thermal ALE based on fluorination and ligand-exchange reactions represents a broad class of favorable reactions. These reactions should be applicable for etching a wide variety of materials such as metal oxides, nitrides, phosphides, sulfides, arsenides, selenides, and tellurides. Many fluorination sources may be used for the fluorination reactions, such as HF or XeF_2. Thermochemical calculations indicate that fluorination of metal compounds, including metal oxides, is thermochemically favorable. This may be surprising because metal oxides comprise many of the most stable compounds in the Earth's crust. However, these metal oxides would be metal fluorides if the Earth was covered with seas of HF. The thermochemical free energies for the reaction of fluorine-containing gases with Al_2O_3 at 200 °C are given in Table 1.[10]

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The ligand-exchange reactions during thermal ALE are metal-exchange transmetalation[8] or redistribution[11] reactions. Ligands are transferred between adjacent metal centers during the ligand-exchange reaction. The proposed transition state for ligand-exchange is a four-center ring. This four-center ring is formed by the metal in the metal precursor and the metal in the metal fluoride, with the fluorine and one ligand from the metal precursor serving as bridging species.[8] Fluorine easily forms bimetallic bridges and stabilizes the four-center ring transition state.[12] A schematic of the proposed four-center ring transition state during the ligand-exchange reaction between $Al(CH_3)_3$ (trimethylaluminum, TMA) and AlF_3 during Al_2O_3 ALE is shown in Figure 3.

Atomic layer etching reactions for various representative metal compounds are given in Table 2. The thermochemical free energies for the fluorination reactions are given at 200 °C.[10] With the exception of the metal sulfides, selenides, and tellurides, Table 2 illustrates that the fluorination reactions using HF have negative Δ*G* values and are spontaneous. The fluorination of metal sulfides, selenides, and tellurides have large negative Δ*G* values and are spontaneous with XeF_2 as the fluorination reagent. The metal precursor in Table 2 is assumed to be $Sn(acac)_2$. The acac ligand forms volatile metal reaction products with a wide variety of metal elements.[13] Other metal precursors would provide different ligands that may be more selective toward particular metal elements.

PATHWAYS TO SELECTIVITY

In selective ALE, one material is etched preferentially in the presence of other materials. Selective ALE could occur in the fluorination process or the ligand-exchange process. The fluorine reactants could selectively fluorinate one particular material in a mixture of neighboring materials. Fluorination could also lead to partial selectivity based on different amounts of fluorination. More pronounced ALE selectivity can be achieved in the ligand-exchange process. When the metal precursor accepts fluorine from the metal fluoride layer, the metal precursor donates a ligand to the metal in the metal fluoride and forms a reaction product. Depending on the nature of the ligand, the reaction products formed after ligand-exchange have distinct stabilities and volatilities. Differences in stability and volatility of the reaction products may be used to achieve selective ALE.

Table 3 provides examples of various metal precursor families and the ligand-exchange process during their reaction with metal fluorides, MF_x. Selectivity could be obtained depending on the stability and volatility of the metal reaction product. For example, consider metal precursors for selectivity between Al_2O_3 and ZrO_2. Fluorination should initially form an AlF_3 layer on Al_2O_3 and a ZrF_4 layer on ZrO_2. The metal precursor $Al(CH_3)_3$ could remove AlF_3 during Al_2O_3 ALE because $Al(CH_3)_3$ or $AlF(CH_3)_2$ are stable and volatile metal reaction products.[14] In contrast, $Al(CH_3)_3$ is not expected to remove ZrF_4 to perform ZrO_2 ALE because $Zr(CH_3)_4$ or $ZrF(CH_3)_3$ are not stable metal reaction products.[15]

Recent experiments have revealed selectivity in thermal ALE.[16] Figure 4 shows results for ALE using sequential HF and TMA exposures on TiN, SiO_2, Si_3N_4, Al_2O_3, HfO_2, and ZrO_2 thin films at 300 °C. These films were all etched using identical conditions at the same time. The sequential HF and TMA exposures are able to etch Al_2O_3 and HfO_2. The etching rate

DOI: 10.1021/acsnano.6b02991
ACS Nano 2016, 10, 4889−4894

Table 1. Fluorination Reactions for Al_2O_3 and ΔG at 200 °C

$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O$	$\Delta G = -58$ kcal/mole
$Al_2O_3 + SF_6 \rightarrow 2AlF_3 + SO_3$	$\Delta G = -130$ kcal/mole
$Al_2O_3 + 3/2SF_4 \rightarrow 2AlF_3 + 3/2SO_2$	$\Delta G = -157$ kcal/mole
$Al_2O_3 + 2ClF_3 \rightarrow 2AlF_3 + Cl_2O + O_2$	$\Delta G = -224$ kcal/mole
$Al_2O_3 + 2NF_3 \rightarrow 2AlF_3 + NO + NO_2$	$\Delta G = -230$ kcal/mole
$Al_2O_3 + 3XeF_2 \rightarrow 2AlF_3 + 2Xe + 3/2O_2$	$\Delta G = -258$ kcal/mole
$Al_2O_3 + 3F_2 \rightarrow 2AlF_3 + 3/2O_2$	$\Delta G = -297$ kcal/mole

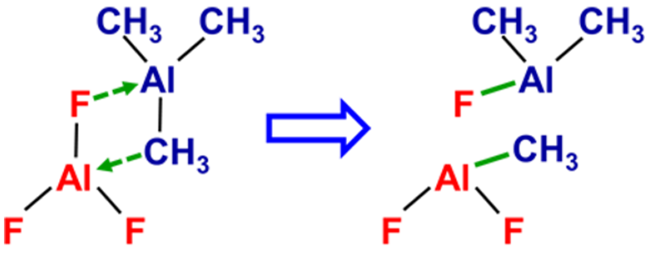

Figure 3. Schematic of the proposed four-center ring transition state during the ligand-exchange reaction between $Al(CH_3)_3$ and AlF_3 during Al_2O_3 ALE.

during Al_2O_3 ALE was 0.45 Å/cycle. The etching rate during HfO_2 ALE was 0.10 Å/cycle. No etching is observed for sequential HF and TMA exposures on TiN, SiO_2, Si_3N_4, or ZrO_2. As expected, HF and TMA can etch Al_2O_3 but not ZrO_2. The etching of HfO_2 and the lack of etching of TiN, SiO_2, and Si_3N_4 can also be understood in terms of the stability and volatility of the metal reaction products.

Besides selectivity in the fluorination or ligand-exchange reactions, there are also other pathways to selectivity. Additional selectivity may be obtained by tuning the substrate temperature.[16] The kinetics of the fluorination or ligand-exchange reactions can lead to different etching rates at different temperatures for various metal precursors. Temperature may also affect the volatility of the metal reaction products.

Selective ALE could also be achieved using molecular adsorbates that bind to one material and not to another material. These molecular adsorbates could act as surface blocking groups that would prevent the adsorption of the fluorine precursor or metal precursor. These "molecular masks" could lead to selective ALE. Similar surface blocking effects during ALD have been observed recently by studies of the effect of hfacH on Pt ALD on TiO_2.[17]

Table 2. Atomic Layer Etching Reactions for Various Materials and ΔG at 200 °C

Metal Oxide/HfO_2 ALE
overall: $HfO_2 + 4\ Sn(acac)_2 + 4\ HF \rightarrow Hf(acac)_4 + 4\ SnF(acac) + 2\ H_2O$
fluoride formation: $HfO_2 + 4\ HF \rightarrow HfF_4 + 2\ H_2O$ $\Delta G = -19$ kcal/mol
Metal Nitride/GaN ALE
overall: $GaN + 3\ Sn(acac)_2 + 3HF \rightarrow Ga(acac)_3 + 3\ SnF(acac) + NH_3$
fluoride formation: $GaN + 3\ HF \rightarrow GaF_3 + NH_3$ $\Delta G = -40$ kcal/mol
Metal Phosphide/InP ALE
overall: $InP+ 3\ Sn(acac)_2 + 3HF \rightarrow In(acac)_3 + 3\ SnF(acac) + PH_3$
fluoride formation: $InP+ 3HF \rightarrow InF_3 + PH_3$ $\Delta G = -39$ kcal/mol
Metal Sulfide/ZnS ALE
overall: $ZnS+ 2\ Sn(acac)_2 + 2HF \rightarrow Zn(acac)_2 + 2\ SnF(acac) + H_2S$
fluoride formation: $ZnS+ 2\ HF \rightarrow ZnF_2 + H_2S$ $\Delta G = +6$ kcal/mol
$ZnS+ 3\ XeF_2 \rightarrow ZnF_2 + SF_4 + 3Xe$ $\Delta G = -244$ kcal/mol
Metal Arsenide/GaAs ALE
overall: $GaAs+ 3\ Sn(acac)_2 + 3\ HF \rightarrow Ga(acac)_3 + 3\ SnF(acac) + AsH_3$
fluoride formation: $GaAs+ 3\ HF \rightarrow GaF_3 + AsH_3$ $\Delta G = -21$ kcal/mol
Metal Selenide/PbSe ALE
overall: $PbSe+ 2\ Sn(acac)_2 + 2\ HF \rightarrow Pb(acac)_2 + 2\ SnF(acac) + H_2Se$
fluoride formation: $PbSe+ 3\ HF \rightarrow PbF_2 + H_2Se$ $\Delta G = +14$ kcal/mol
$PbSe+ 3\ XeF_2 \rightarrow PbF_2 + SeF_4 + 3Xe$ $\Delta G = -258$ kcal/mol
Metal Telluride/CdTe ALE
overall: $CdTe+ 2\ Sn(acac)_2 + 2\ HF \rightarrow Cd(acac)_2 + 2\ SnF(acac) + H_2Te$
fluoride formation: $CdTe+ 2\ HF \rightarrow CdF_2 + H_2Te$ $\Delta G = +26$ kcal/mol
$CdTe+ 4\ XeF_2 \rightarrow CdF_2 + TeF_6 + 4Xe$ $\Delta G = -364$ kcal/mol

Table 3. Metal Precursors for Reaction with Metal Fluoride and Metal Reaction Products

metal precursor family	metal precursor example	ligand-exchange process	metal reaction product from MF_x
β-diketonate	$Sn(acac)_2$	accept fluorine, donate acac	$M(acac)_y$ or $MF_z(acac)_{y-z}$
alkyl	$Al(CH_3)_3$	accept fluorine, donate CH_3	$M(CH_3)_y$ or $MF_z(CH_3)_{y-z}$
halide	$SiCl_4$	accept fluorine, donate chloride	MCl_y or MF_zCl_{y-z}
cyclopentadienyl	$Ni(Cp)_2$	accept fluorine, donate Cp	$M(Cp)_y$ or $MF_z(Cp)_{y-z}$
silylamide	$Zn(N(SiMe_3)_2)_2$	accept fluorine, donate $N(SiMe_3)_2$	$M(N(SiMe_3)_2)_y$ or $MF_z(N(SiMe_3)_2)_{y-z}$
alkoxide	$Al(OCH_2CH_3)_3$	accept fluorine, donate OCH_2CH_3	$M(OCH_2CH_3)_y$ or $MF_z(OCH_2CH_3)_{y-z}$
amidinate (amd)	$Zn(amd)_2$	accept fluorine, donate amd	$M(amd)_y$ or $MF_z(amd)_{y-z}$

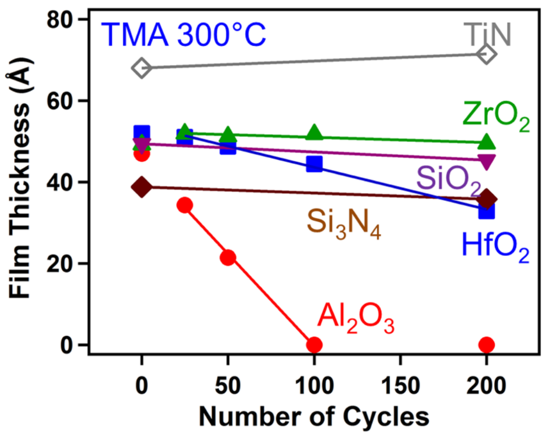

Figure 4. Film thickness versus number of cycles of HF and $Al(CH_3)_3$ (trimethylaluminum, TMA) exposures at 300 °C. Thin film materials were Al_2O_3, HfO_2, ZrO_2, SiO_2, Si_3N_4, and TiN.

SURFACE CLEANING BY REMOVAL OF METAL IMPURITIES

Thermal ALE may also be useful in semiconductor fabrication for surface cleaning to remove metal impurities. The gas phase nature of thermal ALE will be particularly important for cleaning nanostructures that are mechanically fragile and can be easily damaged by wet cleaning. The removal of a metal impurity requires that the metal impurity produce a stable and volatile reaction product during the fluorination and ligand-exchange reactions. In contrast, the main surface material does not produce etch products under the same reaction conditions. Surface cleaning is related to selectivity during thermal ALE and should be accomplished with only one or two ALE reaction cycles.

Removal of metal impurities could occur during either the fluorination or ligand-exchange reactions. The fluorination reaction may remove the metal impurity if the metal fluoride is volatile. Volatile metal fluorides include MoF_6 and WF_6. The ligand-exchange reaction could also remove the metal impurities based on the stability and volatility of the metal reaction products. For example, $Al(CH_3)_3$ could remove Al or Hf impurities on SiO_2 or Si_3N_4 surfaces based on the selectivity results presented in Figure 4. The AlF_3 and HfF_4 species produced by fluorination could be removed as volatile $AlF(CH_3)_2$ or $HfF(CH_3)_3$ reaction products during ligand-exchange. In comparison, the SiO_2 and Si_3N_4 surfaces do not etch, presumably because the Si−F surface species are too stable to undergo ligand-exchange.

CONFORMAL ETCHING IN HIGH-ASPECT-RATIO STRUCTURES

The self-limiting nature of the sequential fluorination and ligand-exchange reactions that define thermal ALE should lead to isotropic etching. If the gas exposures are sufficient to allow the surface reactions to reach completion, then thermal ALE should be able to etch conformally in high-aspect-ratio structures. Conformal etching would complement the ability of ALD to perform conformal deposition in high-aspect-ratio structures.[18] The previous ALE methods based on bombardment by ions or energetic atoms are able to provide anisotopic etching.[1] However, they cannot etch conformally in high-aspect-ratio structures because the ions or energetic atoms require line-of-sight to the surface.

In analogy to ALD in high-aspect-ratio structures, the reactant exposure times during thermal ALE should increase according to the square of the aspect ratio.[18,19] The purge times to remove unreacted reactant and products will also increase by a similar factor. Another factor influencing the exposure or purge times is the "stickiness" of the reactant. Molecular precursors with large dipole moments, like HF, have long surface residence times and are difficult to purge from the reaction chamber. If they are not removed before introducing the second precursor, then the etching rate could increase rapidly because of chemical vapor etching (CVE).

SMOOTHING AND DEPOSIT/ETCH-BACK METHODS

Thermal ALE provides a novel method for smoothing the surface of a solid substrate. Recent X-ray reflectivity (XRR) studies of Al_2O_3 ALE and HfO_2 ALE were consistent with surface smoothing occurring during ALE.[4,7] Smoothing of surfaces is important in the semiconductor industry to obtain flat and damage-free layers. Sputtering with ions or energetic atoms to remove material can leave a rough, damaged surface. Atomic layer etching can be used to remove the damaged layer and smooth the surface.

Surface smoothing can also be used to obtain high quality ultrathin films. For example, these continuous and smooth ultrathin films can be produced by depositing a thicker film and then etching back to obtain a thinner film. This possibility for "deposition/etch-back" is important when nucleation effects lead to roughness in the ultrathin deposited film. As the initial islands formed during nucleation grow and then merge together, they can form a continuous and pinhole-free film at higher thicknesses. Atomic layer etching can then etch this film back and obtain a smoother continuous film than would have been produced by growing to this ultrathin thickness. A schematic illustrating the "deposition/etch-back" method is shown in Figure 5.

DOI: 10.1021/acsnano.6b02991
ACS Nano 2016, 10, 4889−4894

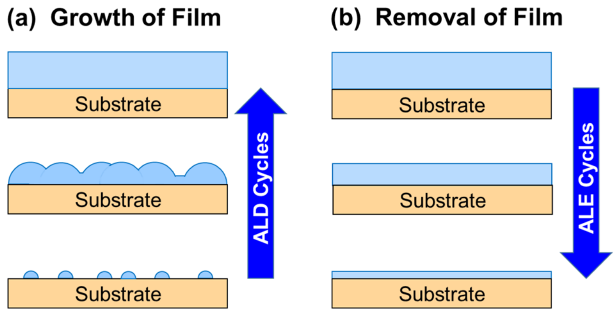

Figure 5. Illustration of "deposition/etch-back" strategy showing (a) ALD growth of film that nucleates by forming islands and (b) ALE removal that produces ultrathin conformal film.

STRATEGIES FOR ANISOTOPIC ETCHING AND ENHANCED THERMAL ALE

Thermal ALE may be combined with low energy, directional ion bombardment to obtain anisotropic etching. With hybrid etching approaches using thermal ALE and directional ion bombardment, new processing procedures may be defined that could exploit the advantages of both thermal ALE and ion-induced surface processes. The ion energies during ion-induced ALE are typically 25−50 eV.[1,20] These energies are above the threshold energy of ~20 eV that will yield ion sputtering of silicon.[20]

In the hybrid approach, the ion energies may be <20 eV because the ions are not required to remove surface material. Much lower energy ions may be effective because these ions can desorb more weakly bound surface species that may be limiting the thermal ALE.[21] For example, acac surface species are present during Al_2O_3 ALE after the HF and $Sn(acac)_2$ exposures.[5] The etching rates vary inversely with the acac surface coverage.[5] By desorbing the acac species with low energy ions, the etching rates may be increased substantially at lower temperatures at the highest acac surface coverages.

Figure 6 illustrates the ion desorption of surface species that can be impacted by directional ions. Surface species on the side walls of the high-aspect-ratio feature are not desorbed by the directional ions, but they limit the thermal ALE and produce anisotropic etching. In addition, radicals may also be able to enhance thermal ALE. Radicals from plasma sources are known to facilitate ALD reactions.[22] The expected effect of radicals would be alteration or removal of the surface species, such as acac, that are present during thermal ALE, and limiting the thermal etching rate. Radicals could also provide a limited amount of anisotopic etching depending on their directionality and radical recombination rates.

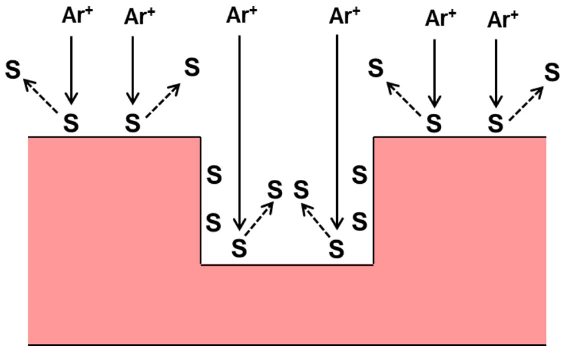

Figure 6. Directional ion removal of surface species, S, that act to limit the thermal ALE. Surface species on the trench wall are not removed and produce anisotropy during thermal ALE.

CONCLUSIONS AND PROSPECTS

In this Perspective, we highlighted some of the promising prospects for thermal ALE using sequential, self-limiting fluorination and ligand-exchange reactions. Thermal ALE can complement ALD to provide new capabilities for atomic layer processing based on selective ALE, conformal etching in high-aspect-ratio structures, novel smoothing methods, and possible anisotropic etching with ion or radical enhancement. These new processing capabilities will be important for the construction of nanoscale three-dimensional devices. Many areas should benefit from thermal ALE such as semiconductor and microelectromechanical systems (MEMS) fabrication. We eagerly anticipate the future developments and applications of thermal ALE.

AUTHOR INFORMATION

Corresponding Author

*E-mail: steven.george@colorado.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the National Science Foundation (CHE-1306131) and Intel Corporation through a Member Specific Research Project administered by the Semiconductor Research Corporation (SRC). Additional support was provided by the Defense Advanced Research Project Agency (DARPA).

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