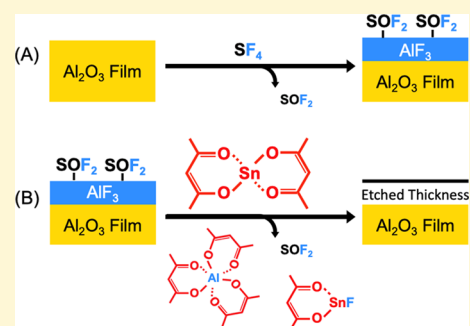


SF₄ as the Fluorination Reactant for Al₂O₃ and VO₂ Thermal Atomic Layer Etching

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ABSTRACT: Thermal atomic layer etching (ALE) is an important technique for the precise isotropic etching of nanostructures. Thermal ALE of many materials can be achieved using a two-step fluorination and ligand-exchange reaction mechanism. Most previous thermal ALE processes have used HF as the fluorination reactant. Alternative fluorination reactants may be needed because HF is a weak nucleophilic fluorination reactant. Stronger fluorination agents may be required for the fluorination of some materials. To demonstrate the usefulness of SF₄ as an alternative to HF, thermal Al₂O₃ ALE was compared using SF₄ or HF together with Sn(acac)₂ as the metal precursor for ligand exchange. SF₄ and HF were observed to behave similarly as fluorination reactants during Al₂O₃ atomic layer deposition (ALD) films at 200 °C were comparable at 35 and 38 ng/cm², respectively, using quartz crystal microbalance measurements. In addition, the etch rates were similar at 0.20 and 0.28 Å/cycle for Al₂O₃ ALE using SF₄ and HF, respectively, at 200 °C. Thermal VO₂ ALE was also performed for the first time using SF₄ or HF and Sn(acac)₂ as the reactants. There was evidence that SF₄ is a stronger fluorination reactant than HF for VO₂ fluorination. The mass gains during the initial SF₄ and HF exposures on VO₂ ALD films were 38 and 20 ng/cm², respectively, at 200 °C. Thermal VO₂ ALE also had a higher etch rate when fluorinating with SF₄ compared with HF. Etch rates of 0.30 and 0.11 Å/cycle were measured for VO₂ ALE using SF₄ and HF, respectively, together with Sn(acac)₂ at 200 °C. Fourier transform infrared experiments were also used to monitor fluorination of the Al₂O₃ and VO₂ ALD films by SF₄ or HF. FTIR difference spectroscopy was used to observe the increase of Al–F and V–F stretching vibrations and the loss of the Al–O and V–O/V=O stretching vibrations for Al₂O₃ and VO₂, respectively, versus SF₄ or HF exposure at 200 °C. Additional absorbance features after fluorination of the Al₂O₃ ALD films by SF₄ were consistent with SF_x surface species. SF₄ is a useful fluorination agent for thermal ALE processes and can be used as an alternative to HF. In addition, SF₄ may be necessary when fluorination requires a stronger fluorination reactant than HF.



I. INTRODUCTION

Atomic layer etching (ALE) is possible using sequential and self-limiting surface reactions.¹ ALE is becoming increasingly important for advanced semiconductor manufacturing.² ALE can be viewed as the reverse of atomic layer deposition (ALD).^{3,4} ALE can be accomplished using either plasma or thermal methods.^{1,5} The first reaction during ALE usually involves surface modification by the adsorption of a reactive species that activates the surface. The second reaction during ALE is a reaction that produces a volatile etch product. In plasma ALE, the second reaction is the removal of the activated layer by sputtering using an energetic ion or neutral species.¹ Plasma ALE leads to anisotropic etching.¹ In thermal ALE, the second reaction is a reaction between a gaseous reactant and the surface layer that produces stable and volatile etching products.⁵ Thermal ALE leads to isotropic etching.⁶

During thermal ALE, the main reaction that activates the surface has been fluorination. For example, thermal Al₂O₃ ALE was initially demonstrated using HF and Sn(acac)₂ as the reactants.^{5,7} The mechanism for thermal Al₂O₃ ALE is based on fluorination and ligand-exchange reactions.^{5,7} HF and Sn(acac)₂ have also been employed as the reactants for HfO₂

and AlN ALE.^{8,9} Other metal precursors such as Al(CH₃)₃, AlCl(CH₃)₂, SiCl₄, and TiCl₄ have also been effective for the ligand-exchange reaction following fluorination with HF.^{10–13} These reactants have led to Al₂O₃, HfO₂, and ZrO₂ ALE.^{10–13} HF and Al(CH₃)₃ have also been used for SiO₂ and ZnO ALE using a “conversion-etch” mechanism, where Al(CH₃)₃ both is involved in ligand-exchange after fluorination and also converts the surface of the remaining substrate to Al₂O₃.^{14,15}

Although HF has been useful as a fluorination reactant during thermal ALE, HF does have some drawbacks. HF is a highly corrosive gas.¹⁶ Upon contact with moisture, HF forms hydrofluoric acid, which is also corrosive and toxic. Anhydrous HF is particularly problematic because its vapor pressure at room temperature exceeds atmospheric pressure. HF-pyridine liquid sources of HF are safer because the vapor pressure of HF above the HF-pyridine solution is 90–100 Torr at room temperature.⁹ However, alternative fluorination reactants to

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replace HF are desirable because HF is a weak fluorination reactant.

HF is a nucleophilic fluorination reactant where the fluoride anion serves as the active reaction species. HF is a convenient fluorination reactant that can fluorinate most metal oxides or metal nitrides. HF produces metal fluorides and H₂O or NH₃ as the reaction products. However, HF is a relatively weak fluorination agent compared with other inorganic nucleophilic fluorination reactants, such as SF₄. Many electrophilic fluorinating agents also exist in which an electron-deficient fluorine serves as the active reaction species. The most widely used inorganic electrophilic fluorination reactant is F₂. Another common inorganic electrophilic fluorination reactant is XeF₂.

The standard free energy changes, ΔG° , for the fluorination of a variety of materials using HF, SF₄, F₂, and XeF₂ are given in Table 1.¹⁷ The ΔG° values are all reported at 200 °C. Most

Table 1. Fluorination Reactions for Various Metal Compounds Using HF, SF₄, F₂, and XeF₂^a

Al ₂ O ₃	
Al ₂ O ₃ + 6HF → 2AlF ₃ + 3H ₂ O	$\Delta G^\circ = -58$ kcal
Al ₂ O ₃ + 3SF ₄ → 2AlF ₃ + 3SOF ₂	$\Delta G^\circ = -199$ kcal
Al ₂ O ₃ + 3F ₂ → 2AlF ₃ + 3/2O ₂	$\Delta G^\circ = -297$ kcal
Al ₂ O ₃ + 3XeF ₂ → 2AlF ₃ + 3Xe + 3/2O ₂	$\Delta G^\circ = -258$ kcal
HfO ₂	
HfO ₂ + 4HF → HfF ₄ + 2H ₂ O	$\Delta G^\circ = -19$ kcal
HfO ₂ + 2SF ₄ → HfF ₄ + 2SOF ₂	$\Delta G^\circ = -113$ kcal
HfO ₂ + 2F ₂ → HfF ₄ + O ₂	$\Delta G^\circ = -178$ kcal
HfO ₂ + 4XeF ₂ → HfF ₄ + 4Xe + 3/2O ₂	$\Delta G^\circ = -152$ kcal
GaN	
GaN + 3HF → GaF ₃ + NH ₃	$\Delta G^\circ = -40$ kcal
GaN + 3/4SF ₄ → GaF ₃ + 1/2N ₂ + 3/16S ₈	$\Delta G^\circ = -114$ kcal
GaN + 3/2F ₂ → GaF ₃ + 1/2 N ₂	$\Delta G^\circ = -239$ kcal
GaN + 3/2XeF ₂ → GaF ₃ + 3/2Xe + 1/2N ₂	$\Delta G^\circ = -219$ kcal
ZnS	
ZnS + 2HF → ZnF ₂ + H ₂ S	$\Delta G^\circ = +6$ kcal
ZnS + 1/2SF ₄ → ZnF ₂ + 3/16S ₈	$\Delta G^\circ = -33$ kcal
ZnS + F ₂ → ZnF ₂ + 1/8S ₈	$\Delta G^\circ = -116$ kcal
ZnS + XeF ₂ → ZnF ₂ + Xe + 1/8S ₈	$\Delta G^\circ = -103$ kcal
VO ₂	
VO ₂ + 4HF → VF ₄ + 2H ₂ O	$\Delta G^\circ = +9$ kcal
VO ₂ + 2SF ₄ → VF ₄ + 2SOF ₂	$\Delta G^\circ = -85$ kcal
VO ₂ + 2F ₂ → VF ₄ + O ₂	$\Delta G^\circ = -150$ kcal
VO ₂ + 2XeF ₂ → VF ₄ + 2Xe + O ₂	$\Delta G^\circ = -124$ kcal

^a ΔG° values are reported at 200 °C.¹⁷

of the ΔG° values are negative except for HF fluorination of ZnS and VO₂, which have slightly positive ΔG° values. A comparison of the various ΔG° values reveals that SF₄, F₂, and XeF₂ have higher negative ΔG° values than HF for all the materials. SF₄, F₂, and XeF₂ are stronger fluorination reactants than HF and are all possible alternatives to HF.

In this paper, SF₄ was examined as an alternative to HF. SF₄ is an effective fluorination reactant for organic carbonyl compounds and metal oxides.^{18,19} Previous work has also demonstrated that SF₄ can fluorinate γ -Al₂O₃.²⁰ The high SF₄ vapor pressure of ~10 atm at 25 °C also facilitates the implementation of SF₄.²¹ However, although SF₄ is considered a safer alternative to HF because SF₄ has a distinct sulfur odor, SF₄ also has issues because hydrolysis of SF₄ can produce HF via SF₄ + H₂O → SOF₂ + 2HF.²²

SF₄ was used as the fluorination reactant for the thermal ALE of Al₂O₃ and VO₂. Sn(acac)₂ was used as the metal precursor for the ligand-exchange reaction. Al₂O₃ ALE was studied to compare SF₄ with the previous results using HF as the fluorination reactant for thermal Al₂O₃ ALE.^{5,7,10,23} VO₂ ALE was also examined using HF or SF₄ and Sn(acac)₂ as the reactants. SF₄ may be needed as the fluorination agent for thermal VO₂ ALE. Thermochemical calculations indicate that the predicted ΔG° for the fluorination of VO₂ to VF₄ is slightly positive for HF at 200 °C.¹⁷ In contrast, fluorination of VO₂ to VF₄ has a large negative ΔG° using SF₄ at 200 °C.¹⁷

Thermal VO₂ ALE is reported for the first time in this paper. VO₂ is a semiconductor at room temperature and has a metal–insulator transition around 68 °C.^{24,25} This transition is accompanied by a large change in resistivity and optical transmittance. Consequently, VO₂ is a useful material for thermochromic films,^{25,26} bolometers,^{27,28} and switching devices.^{29,30} Thermal VO₂ ALE may be useful to produce thin VO₂ films with low thermal mass and high film stability. A low thermal mass is needed for larger thermal transients when using VO₂ as a thermal sensor. Thin films employed for their metal–insulator transition are also less susceptible to fracture from stress that can result from temperature cycling and structural changes around the metal–insulator transition.

II. EXPERIMENTAL SECTION

II.A. Growth and Etching of Al₂O₃ and VO₂ Films. The initial Al₂O₃ and VO₂ films were prepared using Al₂O₃ and VO₂ ALD. The Al₂O₃ ALD films were grown using Al(CH₃)₃ (trimethylaluminum (TMA)) (97%, Sigma-Aldrich) and DI H₂O as the reactants at deposition temperatures between 130 and 200 °C. TMA and H₂O are known to yield amorphous Al₂O₃ ALD films at these temperatures.³¹ The VO₂ ALD films were deposited using tetrakis(ethylmethylamino) vanadium (TEMAV) (Air Liquide) and DI H₂O as the reactants at 150 °C.³² TEMAV is a useful vanadium source for VO₂ ALD because vanadium is already in the +4 oxidation state. TEMAV and H₂O are known to yield vanadium(IV) oxide films.³³ TEMAV and H₂O also yield amorphous VO₂ ALD films at 150 °C.^{32,33}

ALD films were deposited and etched in a custom-built stainless steel viscous flow reactor. This reactor is similar in design to a previous viscous flow reactor built for quartz crystal microbalance (QCM) studies of ALD.³⁴ However, the flow tube was replaced with a circular puck-shaped chamber to accommodate 8" wafers. The reactants and the carrier gas flow across the samples in the chamber. The chamber had a 10" diameter and was equipped with a fast-entry load-lock door for sample loading. The QCM was positioned at the center of this chamber.

A total N₂ flow of 160 sccm was used as both a purge and inert carrier gas during the reactions and produced a reactor pressure of 1.0 Torr. The N₂ flow was controlled on each precursor line by mass flow controllers (Alicat Scientific). The N₂ flow was uniformly distributed inside the circular puck-shaped chamber using a baffle that served to limit the gas conductance. The reactor was pumped with a dual-stage mechanical pump (Alcatel Adixen Pascal 2010 C2). The pressure was monitored using a capacitance manometer (MKS Baratron 626A) on the reactor. The temperature of the reactor chamber was maintained using heaters regulated with proportional–integral–derivative (PID) control.

The stainless steel bubbler containing the TEMAV was heated to 60–65 °C to increase the vapor pressure. An N₂ flow of ~20 sccm over the headspace of the TEMAV source was also used to increase the precursor transport. The other growth reactants were maintained at room temperature. All lines were heated to define a temperature gradient between the reactant sources and the reactor. The temperature progressively increased to prevent condensation in the dosing lines in the reactor chamber.

Al_2O_3 ALE and VO_2 ALE were performed using sulfur tetrafluoride (SF_4 , >98.5%, SynQuest Laboratories), HF-pyridine (70 wt % HF, Sigma-Aldrich), and tin(II) acetylacetonate ($\text{Sn}(\text{acac})_2$, 99.9% trace metals basis, Sigma-Aldrich). SF_4 and HF-pyridine were maintained at room temperature. The $\text{Sn}(\text{acac})_2$ bubbler was heated to around 100 °C to obtain adequate vapor pressure.

II.B. QCM, XPS, SE, and FTIR Measurements. The reactor chamber was equipped with an in situ quartz crystal microbalance (QCM). The QCM was an SC-cut quartz crystal (Maxtek SC-101 gold coated, 6 MHz). The frequency of the QCM was recorded using an Inficon Q-pod quartz crystal monitor. The QCM housing was a modified Inficon Cool Drawer single sensor that used N_2 flow to provide a backside purge on the crystal.³⁴ The housing around the crystal was sealed using high temperature silver epoxy (Epo-Tek H21D, Epoxy Technology). The additional N_2 flow from the QCM purge exited downstream from the QCM crystal and raised the reactor pressure to 1.05 Torr when only N_2 was flowing.

The VO_2 films on Si coupons were analyzed with ex situ X-ray photoelectron spectroscopy (XPS, PHI 5600) after VO_2 ALD to verify the chemical state of the film. The films were loaded into the XPS chamber within 1 h of unloading from the deposition chamber to reduce surface oxidation effects. In addition, the Al_2O_3 ALD film thicknesses were investigated with ex situ spectroscopic ellipsometry (J. A. Woollam M-2000) both before and after etching at varying temperatures to determine the temperature dependence of Al_2O_3 ALE using SF_4 and $\text{Sn}(\text{acac})_2$ as the reactants.

In situ infrared spectroscopy was employed to monitor VO_2 ALD and the fluorination of the Al_2O_3 and VO_2 ALD films with SF_4 and HF. A description of this reactor, equipped for in situ FTIR transmission spectroscopy, has been presented earlier.³⁵ To increase the surface area for higher sensitivity to the surface species, the Al_2O_3 and VO_2 ALD films were deposited on silicon nanoparticles that were 30–50 nm in diameter (>98%, US Research Nanomaterials). The Si nanoparticles were initially pressed into tungsten grids.^{36,37} The tungsten grids have an area of $2 \times 3 \text{ cm}^2$ and were 50 μm thick and contained 100 grid lines per inch.

The tungsten grids were resistively heated to 150 °C for VO_2 ALD and 200 °C for SF_4 and HF fluorination of the Al_2O_3 and VO_2 ALD films. The heating was conducted using a DC power supply (6268B, 20 V/20 A, Hewlett-Packard). The voltage output of the DC power supply was controlled by a PID temperature controller (Love Controls 16B, Dwyer Instruments). The temperature was monitored with a K-type thermocouple. This thermocouple was fixed to the tungsten grid with epoxy (Ceramabond 571, Aremco). The epoxy also electrically isolated the thermocouple from the tungsten grid. The FTIR spectra were recorded at 150 °C during VO_2 ALD and at 200 °C for Al_2O_3 and VO_2 fluorination.

III. RESULTS AND DISCUSSION

III.A. Al_2O_3 ALE Using SF_4 and $\text{Sn}(\text{acac})_2$. Figure 1 displays the mass change versus time during 100 cycles of Al_2O_3 ALE at 200 °C using SF_4 and $\text{Sn}(\text{acac})_2$ as the reactants. The SF_4 exposures were performed at 500 mTorr for 2.5 s. The $\text{Sn}(\text{acac})_2$ exposures were conducted at 50 mTorr for 2.5 s. After each reactant exposure, the system was purged with a viscous flow of N_2 gas at 160 sccm for 55 s. This reaction sequence is designated as 2.5–55–2.5–55. The initial Al_2O_3 film was deposited on the QCM with trimethylaluminum (TMA) and H_2O as the reactants using 150 Al_2O_3 ALD cycles. The reaction sequence for Al_2O_3 ALD was 3–55–3–55. The purge times are longer than usual because of the design and larger volume of the reactor that could accommodate 8" silicon wafers.

The loss of mass versus time is linear in Figure 1. The slight deviations from linearity are attributed to the effect of small temperature deviations on the QCM measurements over the course of the long experiments. The average mass change per

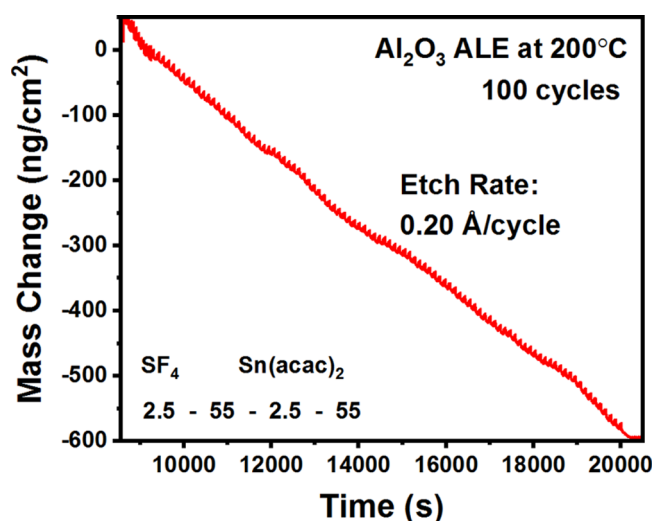


Figure 1. Mass change versus time during 100 cycles of Al_2O_3 ALE at 200 °C using SF_4 and $\text{Sn}(\text{acac})_2$ as the reactants. Etch rate is 0.20 Å/cycle.

cycle (MCPC) over the 100 cycles is -6.0 ng/cm^2 . This MCPC yields an etch rate of 0.20 Å/cycle. The conversion between mass and thickness used an Al_2O_3 ALD film density of 2.95 g/cm^3 determined by X-ray reflectivity (Bede D1 System). This etch rate for Al_2O_3 ALE using SF_4 and $\text{Sn}(\text{acac})_2$ at 200 °C is very comparable with the etch rate for Al_2O_3 ALE using HF and $\text{Sn}(\text{acac})_2$ at 200 °C. The etch rate for Al_2O_3 ALE employing HF and $\text{Sn}(\text{acac})_2$ at 200 °C was previously measured to be 0.28 Å/cycle.^{5,7}

An expanded view of three Al_2O_3 ALE cycles from Figure 1 is shown in Figure 2. The SF_4 exposure fluorinates the Al_2O_3

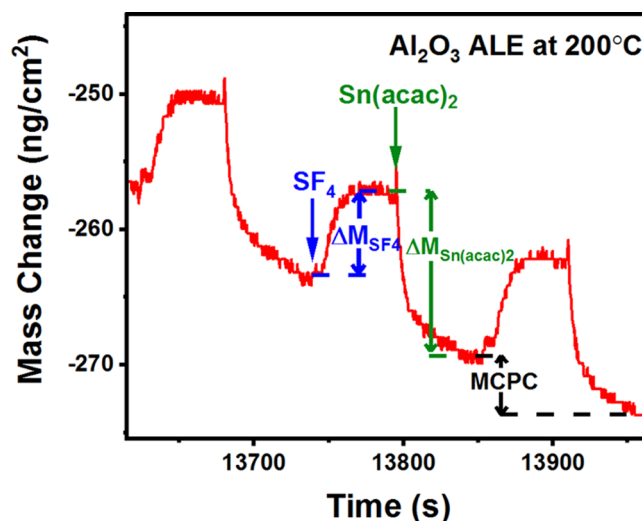


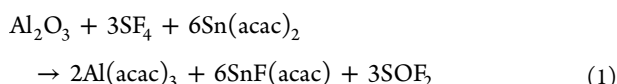
Figure 2. Expanded view of three Al_2O_3 ALE cycles from Figure 1 showing mass gain during the SF_4 exposure and mass loss during $\text{Sn}(\text{acac})_2$ exposure.

surface and may produce AlF_3 or AlF_xO_y surface species. AlF_3 is a stable fluoride with a melting temperature of 1290 °C and an extremely low vapor pressure at 200 °C.³⁸ In addition, SF_4 should remove oxygen from Al_2O_3 through SOF_2 desorption. SOF_2 is the main reaction product from the reaction of SF_4 with metal oxides, H_2O , or oxygen-containing organic compounds.^{18,19,22} SF_4 should also remove any possible acac

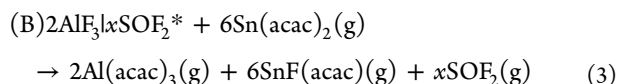
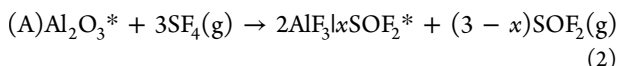
species on the surface from the previous $\text{Sn}(\text{acac})_2$ exposure. The SF_4 exposure leads to a mass gain $\Delta M_{\text{SF}_4} = 6.2 \text{ ng/cm}^2$.

$\text{Sn}(\text{acac})_2$ can then react with the fluorinated Al_2O_3 surface through ligand-exchange to form volatile $\text{SnF}(\text{acac})$ and $\text{Al}(\text{acac})_3$ or $\text{AlF}(\text{acac})_2$ species. $\text{Al}(\text{acac})_3$ has a vapor pressure of 3.3 Torr at 150 °C and ~ 7 Torr at 200 °C.^{39,40} The net result of the $\text{Sn}(\text{acac})_2$ exposure is a mass loss $\Delta M_{\text{Sn}(\text{acac})_2} = -12.2 \text{ ng/cm}^2$. The gradual mass reduction during the purge time of 55 s may be attributed to the slow desorption of acac species from the surface. Acac species were observed on Al_2O_3 surfaces during Al_2O_3 ALE using HF and $\text{Sn}(\text{acac})_2$.⁷ There was also an inverse correlation between the coverage of acac surface species and the Al_2O_3 etch rate in these previous studies that was consistent with more desorption of acac species at higher substrate temperatures.⁷

Assuming that the volatile etch products are $\text{Al}(\text{acac})_3$, $\text{SnF}(\text{acac})$, and SOF_2 , the overall reaction can be described as:



This overall reaction can be divided into the proposed SF_4 and $\text{Sn}(\text{acac})_2$ reactions occurring during Al_2O_3 ALE at steady state:



These reactions include the surface species that change during the SF_4 and $\text{Sn}(\text{acac})_2$ exposures. The asterisks indicate the surface species. The vertical lines separate the various surface species. To satisfy the overall reaction stoichiometry in eq 1, the ΔM_{SF_4} and $\Delta M_{\text{Sn}(\text{acac})_2}$ values require the presence of a surface intermediate that adds mass during reaction A and subtracts mass during reaction B. SOF_2^* is the most likely surface intermediate produced during the SF_4 exposure in reaction A. A schematic illustrating the proposed SF_4 and $\text{Sn}(\text{acac})_2$ reactions is shown in Figure 3.

Al_2O_3^* in eq 2 represents the amount of Al_2O_3 that is etched during the ALE reactions.⁷ x quantifies the amount of SOF_2^*

surface species after the SF_4 exposures relative to the amount of Al_2O_3 that is etched in one Al_2O_3 ALE cycle. The parameter x can be determined by the $\Delta M_{\text{Sn}(\text{acac})_2}$ and MCPC values using the equation:

$$x = [M_{\text{Al}_2\text{O}_3}(\Delta M_{\text{Sn}(\text{acac})_2}/\text{MCPC}) - 2M_{\text{AlF}_3}]/M_{\text{SOF}_2} \quad (4)$$

$$x = [102.0(-12.2/-6.0) - 2(84.0)]/86.1 \quad (5)$$

The values 84.0, 102.0, and 86.1 are the molecular weights in atomic mass units for AlF_3 , Al_2O_3 , and SOF_2 , respectively. Using $\Delta M_{\text{Sn}(\text{acac})_2} = -12.2 \text{ ng/cm}^2$ and $\text{MCPC} = -6.0 \text{ ng/cm}^2$, eq 5 yields $x = 0.46$. This x value indicates that there are 0.46 SOF_2^* species present on the surface after the SF_4 exposures for every Al_2O_3 unit etched during one Al_2O_3 ALE cycle.

The MCPC and etch rate during Al_2O_3 ALE at 200 °C using SF_4 and $\text{Sn}(\text{acac})_2$ are -6.0 ng/cm^2 and 0.20 \AA/cycle , respectively. This removal rate of Al_2O_3 is equivalent to $3.54 \times 10^{13} \text{ Al}_2\text{O}_3 \text{ units/cm}^2$. This removal rate is only $\sim 5\%$ of the number of Al_2O_3 units on the Al_2O_3 surface. An estimate for the number of Al_2O_3 units on the Al_2O_3 surface is obtained from the mass density of 3.0 g/cm^3 for Al_2O_3 ALD films. This mass density is equivalent to a number density $\rho = 1.77 \times 10^{22} \text{ Al}_2\text{O}_3 \text{ units/cm}^3$. $\rho^{2/3}$ then provides an estimate for the number of Al_2O_3 units on the Al_2O_3 surface of $6.8 \times 10^{14} \text{ Al}_2\text{O}_3 \text{ units/cm}^2$. Based on the x value of 0.46, the SOF_2^* coverage is determined to be $1.63 \times 10^{13} \text{ SOF}_2^* \text{ species/cm}^2$. This SOF_2^* coverage is only about 2.4% of the number of Al_2O_3 units on the Al_2O_3 surface.

Figure 4 demonstrates the self-limiting nature of the SF_4 and $\text{Sn}(\text{acac})_2$ reactions during Al_2O_3 ALE. Each point represents the average mass change per cycle (MCPC) versus exposure time over 20 reaction cycles. In Figure 4a, the $\text{Sn}(\text{acac})_2$ exposure time was held constant at 2.5 s, and the SF_4 exposure time was varied from 0 to 3 s. The purge time after each reactant exposure was 55 s. This reactant pulse sequence is designated as X-55-2.5-55. Similarly, in Figure 4b, the SF_4 exposure time was held constant at 2.5 s, and the $\text{Sn}(\text{acac})_2$ exposure time was varied between 0 and 2.5 s. This reactant pulse sequence is denoted as 2.5-55-X-55. The MCPC levels off versus exposure time for both SF_4 and $\text{Sn}(\text{acac})_2$. In addition, neither reactant is capable of spontaneously etching the Al_2O_3 film.

Other experiments have recently explored the effect of both exposure and pressure on Al_2O_3 fluorination using HF as the fluorination reactant.⁴¹ These investigations have revealed that Al_2O_3 fluorination is self-limiting as a function of exposure. The fluoride thickness, y , changes according to $dy/dt = k/y$ where k is a constant that is dependent on HF pressure, $k = k_0P$. Integration of this rate equation yields the parabolic expressions $y^2(t) = 2kt$ or $y(t) = (2k_0Pt)^{1/2}$. The fluorination kinetics are restricted by the fluoride layer on the Al_2O_3 surface that acts as a diffusion barrier for further fluorination. The kinetics of Al_2O_3 fluorination are similar to the kinetics of Si oxidation that have been described by the Deal-Grove model.^{42,43} Similar behavior is expected for Al_2O_3 fluorination using SF_4 as the fluorination reactant.

Figure 5 shows the first three cycles of Al_2O_3 ALE using SF_4 and $\text{Sn}(\text{acac})_2$. The mass gain observed during the first SF_4 exposure represents the fluorination of an initial Al_2O_3 ALD film prior to any $\text{Sn}(\text{acac})_2$ exposures. The first SF_4 exposure leads to a mass gain $\Delta M_{\text{SF}_4} = 35.1 \text{ ng/cm}^2$. The SF_4 exposure is believed to fluorinate the Al_2O_3 film according to the reaction

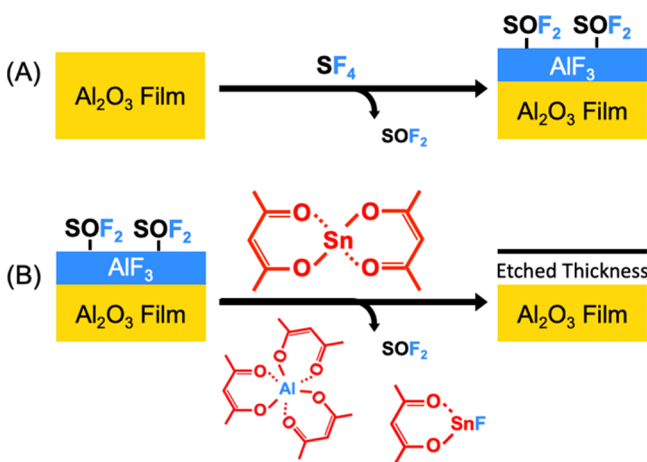


Figure 3. (A, B) Schematic of the sequential surface reactions during Al_2O_3 ALE using exposures of SF_4 and $\text{Sn}(\text{acac})_2$.

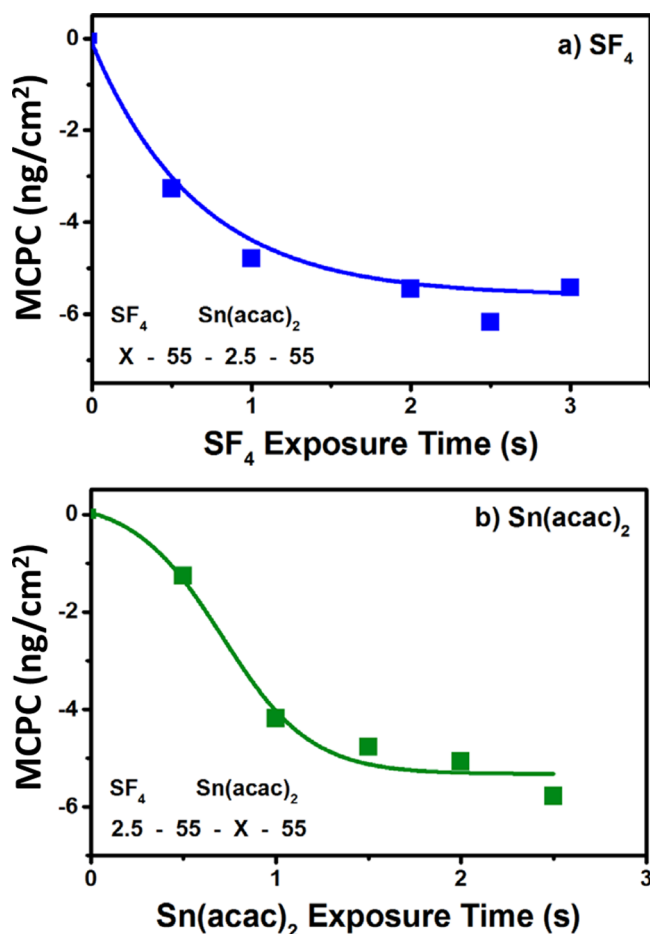


Figure 4. Mass change per cycle (MCPC) showing the self-limiting nature of the SF_4 and $\text{Sn}(\text{acac})_2$ reactions during Al_2O_3 ALE at 200 °C. (a) SF_4 exposure time, X , is varied as the $\text{Sn}(\text{acac})_2$ exposure time is held constant at 2.5 s. (b) $\text{Sn}(\text{acac})_2$ exposure time, X , is varied as the SF_4 exposure time is held constant at 2.5 s. Purge times after each reactant exposure are 55 s.

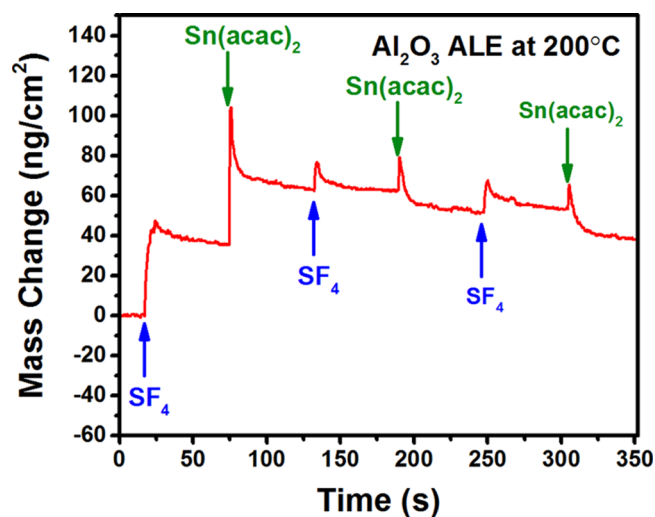


Figure 5. First three cycles of Al_2O_3 ALE using SF_4 and $\text{Sn}(\text{acac})_2$ at 200 °C showing initial fluorination mass gain during SF_4 exposure, subsequent mass changes during the first $\text{Sn}(\text{acac})_2$ exposure, and subsequent SF_4 and $\text{Sn}(\text{acac})_2$ exposures.

given in Table 1: $\text{Al}_2\text{O}_3 + 3\text{SF}_4 \rightarrow 2\text{AlF}_3 + 3\text{SOF}_2$. The mass gain can be used to calculate the Al_2O_3 thickness converted to an AlF_3 thickness by the SF_4 exposure. The mass change $\Delta M_{\text{SF}_4} = 35.1 \text{ ng}/\text{cm}^2$ is consistent with the conversion of $\sim 1.8 \text{ \AA}$ of Al_2O_3 to $\sim 3.1 \text{ \AA}$ of AlF_3 . These thicknesses are based on the change in mass of 66 g/mol during Al_2O_3 conversion to 2AlF_3 , an Al_2O_3 ALD film density of $2.95 \text{ g}/\text{cm}^3$ from XRR, and an AlF_3 density of $2.88 \text{ g}/\text{cm}^3$.

Figure 5 also shows that there is a mass gain $\Delta M_{\text{Sn}(\text{acac})_2} = 27.5 \text{ ng}/\text{cm}^2$ for the first $\text{Sn}(\text{acac})_2$ exposure after the initial SF_4 exposure. Although $\text{Sn}(\text{acac})_2$ can undergo ligand exchange with the fluorinated surface, the net mass gain indicates that acac species are added to the surface during the first $\text{Sn}(\text{acac})_2$ exposure. Subsequently, the SF_4 and $\text{Sn}(\text{acac})_2$ exposures for the second and third reaction cycles are evolving to the steady-state etching behavior observed in Figure 2. This nucleation period occurs over approximately six reaction cycles.

Fluorination of the Al_2O_3 ALD film with SF_4 and HF was also monitored with in situ FTIR spectroscopy. Figure 6a

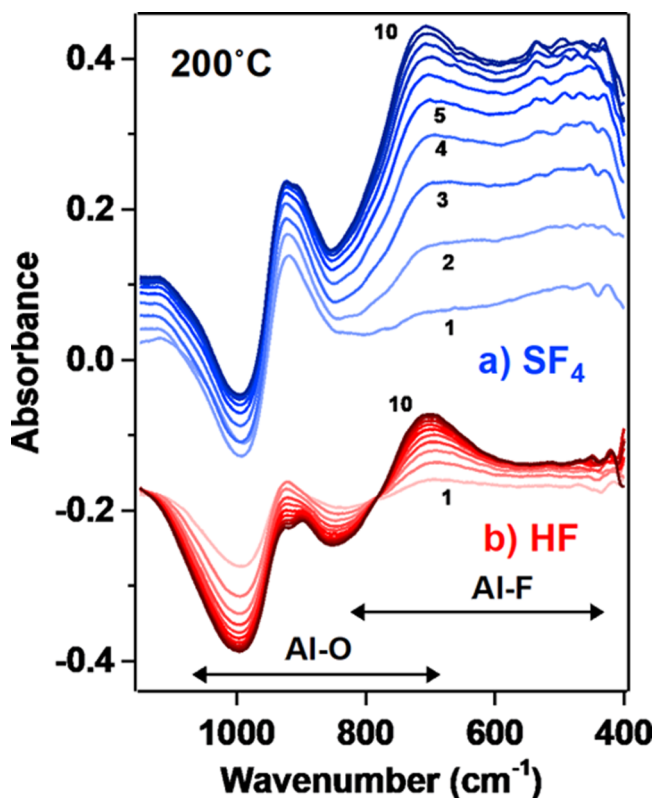


Figure 6. FTIR spectra recorded at 200 °C during fluorination of the Al_2O_3 ALD film at 200 °C. (a) Difference spectra for 10 SF_4 exposures on the Al_2O_3 ALD film. (b) Difference spectra for 10 HF exposures on the Al_2O_3 ALD film.

shows the difference spectra for 10 SF_4 exposures on the Al_2O_3 ALD film at 200 °C. Each SF_4 exposure was performed at 300 mTorr for 1 s. The difference spectra were obtained by subtracting the spectra after each SF_4 exposure from the spectrum for the initial Al_2O_3 ALD film. These difference spectra show the progressive fluorination of the Al_2O_3 ALD film by the SF_4 exposures according to the proposed reaction $\text{Al}_2\text{O}_3 + 3\text{SF}_4 \rightarrow 2\text{AlF}_3 + 3\text{SOF}_2$.

Figure 6a demonstrates that a broad absorbance peak becomes larger at $\sim 700\text{ cm}^{-1}$ with increasing SF_4 exposures. This absorbance peak is assigned to an Al–F stretching vibration.^{44,45} An additional absorbance peak is observed at $\sim 900\text{ cm}^{-1}$. A broad shoulder is also present at frequencies between 400 and 600 cm^{-1} that are less than the frequency of the Al–F stretching vibration. These absorbance features are attributed to the presence of SF_x species on the AlF_3 surface. SF_2 stretching vibrations are observed in SF_4 at ~ 890 and $\sim 860\text{ cm}^{-1}$.^{46,47} Additional stretching and deformation vibrational modes exist for SF_4 at ~ 560 and $\sim 530\text{ cm}^{-1}$.^{46,47} Likewise, a strong symmetric FSO deformation mode has been reported in SOF_2 at $\sim 530\text{ cm}^{-1}$.^{48,49}

Figure 6a also shows that a prominent absorbance loss occurs at $\sim 1000\text{ cm}^{-1}$. This absorbance loss is attributed to the reduction of absorbance from Al–O stretching vibrations in Al_2O_3 .¹³ In addition, there is an increase in the background absorbance during SF_4 fluorination. This baseline shift is larger than the progressive loss of Al–O stretching vibrations with increasing SF_4 exposures in Figure 6a. The origin of this increasing background absorbance with increasing SF_4 exposures is not understood at this time.

For comparison, Figure 6b shows difference spectra for 10 HF exposures on the Al_2O_3 ALD films at 200°C . These difference spectra have been displayed for clarity in presentation. Each HF exposure was conducted at 100 mTorr for 1 s. The difference spectra were obtained by subtracting the spectra after each HF exposure from the spectrum recorded for the initial Al_2O_3 ALD film. These difference spectra are consistent with the progressive fluorination of the Al_2O_3 ALD film by HF exposures according to the reaction $\text{Al}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O}$. The HF exposures may also fluorinate the Al_2O_3 ALD film to produce oxyfluorides by the reaction $\text{Al}_2\text{O}_3 + z\text{HF} \rightarrow 2\text{AlO}_{(6-z)/4}\text{F}_{z/2} + (z/2)\text{H}_2\text{O}$.⁵⁰

The absorbance peak from the Al–F stretching vibration in Figure 6b is located at $\sim 700\text{ cm}^{-1}$.^{13,44,45} This absorbance peak progressively becomes larger with increasing HF exposures. A prominent absorbance loss also occurs at $\sim 1000\text{ cm}^{-1}$ resulting from the progressive loss of Al–O stretching vibrations from Al_2O_3 with increasing HF exposure.¹³ In contrast to the results for SF_4 , absorbance gains at $\sim 900\text{ cm}^{-1}$ and between 400 and 600 cm^{-1} are not observed for HF fluorination of Al_2O_3 because there are no SF_x surface species. There is also no increase in the background absorbance during HF fluorination.

Figure 7 shows results for the temperature dependence of Al_2O_3 ALE using SF_4 and $\text{Sn}(\text{acac})_2$. These results were obtained using spectroscopic ellipsometry (SE) measurements with Al_2O_3 ALD films on Si wafers. A spectroscopic ellipsometer was used to measure film thicknesses both before and after etching. The samples were initially coated with Al_2O_3 ALD films at 130°C . The individual samples were then etched for various numbers of cycles at temperatures from 150 to 225°C prior to the SE measurements. The Al_2O_3 etch rates increased with temperature. The etch rates were 0.04 \AA/cycle at 150°C , 0.07 \AA/cycle at 175°C , 0.14 \AA/cycle at 200°C , and 0.25 \AA/cycle at 225°C . The etch rate of 0.14 \AA/cycle at 200°C from these SE measurements is less than the etch rate of 0.2 \AA/cycle from the QCM analysis in Figure 1. The SE measurements in Figure 7 provide the trends versus temperature but are not as accurate as the QCM analysis because they are based on only 2–3 data points.

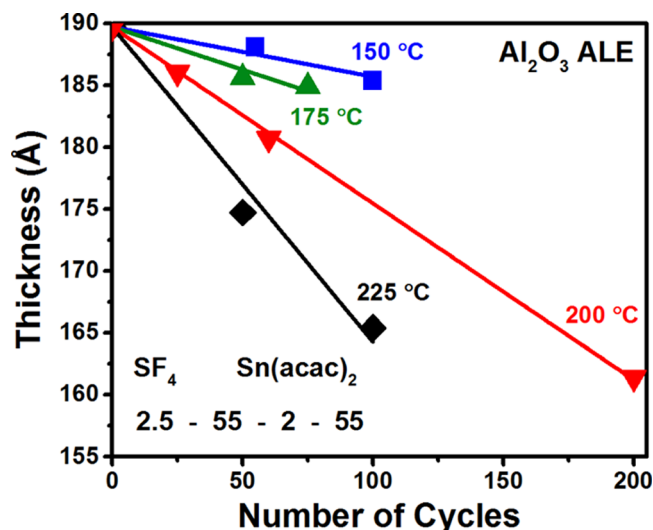


Figure 7. Temperature dependence of Al_2O_3 ALE using SF_4 and $\text{Sn}(\text{acac})_2$. Etch rate increases from 0.04 \AA/cycle at 150°C to 0.25 \AA/cycle at 225°C .

An Arrhenius plot of these temperature-dependent etch rates yields an activation barrier of 44 kcal/mol . This activation barrier of 44 kcal/mol could result from the temperature dependence of the fluorination reaction. Higher temperatures should produce progressively thicker fluoride layers on Al_2O_3 . If these fluoride layers are removed during the ligand-exchange reaction, then the Al_2O_3 etch rates would be expected to be temperature-dependent. The activation barrier may also be associated with the $\text{Sn}(\text{acac})_2$ ligand-exchange reaction. The ligand-exchange reaction may leave acac species on the Al_2O_3 surface that may block the etching.⁷ Removing these acac species would then increase the etching. The thermal desorption of these acac species may produce temperature-dependent Al_2O_3 etch rates.⁷

III.B. VO_2 ALD Using TEMAV and H_2O . VO_2 ALD films were grown using TEMAV and H_2O prior to the VO_2 ALE studies. Figure 8 shows the linear growth of VO_2 ALD films at

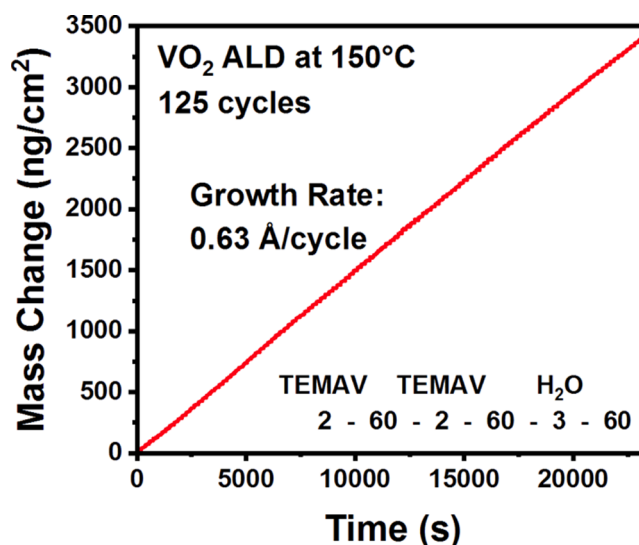


Figure 8. Mass change versus time during 125 cycles of VO_2 ALD at 150°C using TEMAV and H_2O as the reactants. Growth rate is 0.63 \AA/cycle .

150 °C for 125 reaction cycles. Each reaction cycle consisted of two 2 s TEMAV exposures, followed by a 60 s N₂ gas purge, a 3 s H₂O exposure, and then a 60 s purge. The TEMAV pressure was 25 mTorr. Two exposures of TEMAV were used for every reaction cycle to ensure that the surface reaction reached completion. The H₂O pressure was 100 mTorr. The mass gain per cycle is 27.4 ng/cm². This mass gain per cycle is consistent with a VO₂ growth rate of 0.63 Å/cycle. This growth rate is based on a film density of 4.36 g/cm³ measured by XRR. This growth rate is in agreement with the previously reported VO₂ ALD growth rate of 0.67 Å/cycle using TEMAV and H₂O at 150 °C.^{32,33}

X-ray photoelectron spectroscopy (XPS) was used to confirm the stoichiometry of the VO₂ films. Figure 9 shows

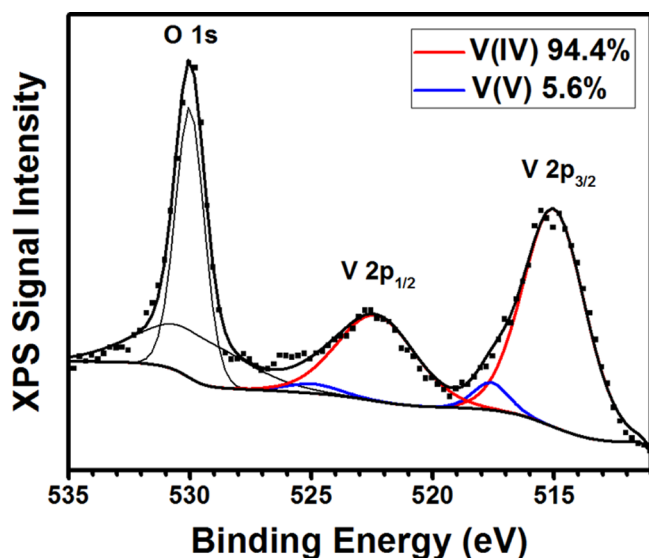


Figure 9. XPS spectrum of VO₂ ALD film in the O 1s and V 2p regions. Quantification of the V 2p_{3/2} peak indicates 94.4% VO₂ (V⁴⁺) and 5.6% V₂O₅ (V⁵⁺).

the XPS spectrum in the O 1s and V 2p regions. Curve fittings of the O 1s and V 2p regions are consistent with mostly a VO₂ film with a small component of V₂O₅. The percentages were 94.4% VO₂ and 5.6% V₂O₅. The peak position was calibrated using the O 1s binding energy set at 530 eV with a single Shirley background over the entire O 1s and V 2p areas. The vanadium(IV) oxide and vanadium(V) oxide V 2p_{1/2}–V 2p_{3/2} splitting was fixed at 7.33 eV and the 2p_{1/2} to 2p_{3/2} ratio was fixed at 2:1.^{51,52}

The growth of the VO₂ ALD films using TEMAV and H₂O at 150 °C was also investigated using in situ FTIR spectroscopy. The TEMAV exposure was performed at 10 mTorr for 2 s. The H₂O exposure was defined with a pressure of 100 mTorr for 1 s. A 60 s viscous flow N₂ purge at 1 Torr was employed after each reactant exposure. The FTIR spectra were also recorded after each reactant exposure.

Figure 10 shows the FTIR spectra at 150 °C after every 5 cycles of VO₂ ALD using TEMAV and H₂O for a total of 35 cycles. The spectra shown in Figure 10 were obtained after the H₂O exposures. There is a strong and broad absorbance that is centered at approximately 630 cm^{−1}. This absorbance peak progressively increases with the number of ALD cycles. This absorbance feature is attributed to V–O stretching vibrations.^{53,54} Earlier infrared vibrational spectroscopy studies of

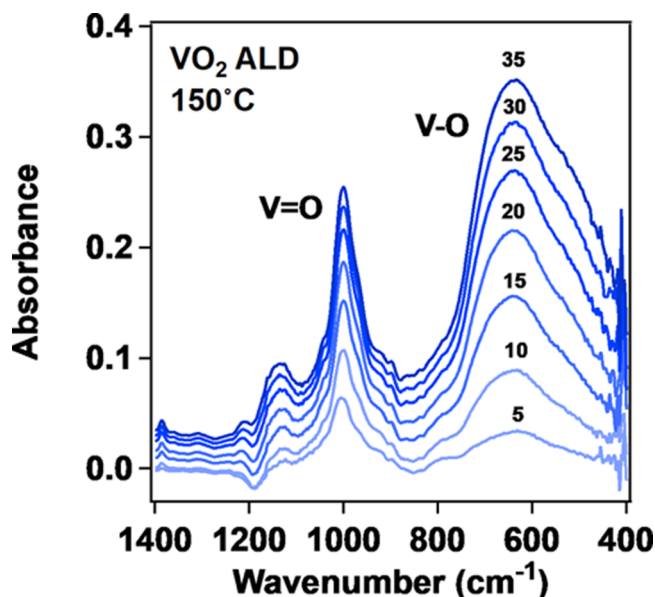


Figure 10. FTIR spectra recorded at 150 °C after every 5 cycles of VO₂ ALD for 35 cycles using TEMAV and H₂O as the reactants at 150 °C.

crystalline VO₂ demonstrated that the vibrational spectrum of VO₂ becomes featureless in the metallic state above the metal–insulator transition at 68 °C.⁵⁴ In contrast, vibrational features are observed in Figure 10 for the amorphous VO₂ films at 150 °C. However, evidence of an increase in the background absorbance was observed from 400 to 4000 cm^{−1} during VO₂ ALD.

Absorbance from another vibrational mode centered at ~996 cm^{−1} also increases mostly during the initial cycles of VO₂ ALD. This absorbance feature is attributed to V=O vibrations.^{53,55} The V=O vibration is associated with a terminal oxygen that is likely at the surface of the VO₂ ALD film.^{53,55} During the later cycles of VO₂ ALD, this absorbance is increasing more slowly because of some V=O vibrations in the VO₂ film and because of the increasing background absorbance. The frequency of the V=O vibration is also associated with the oxidation state of the vanadium.⁵³ The observation of the V=O vibrational feature at ~996 cm^{−1} may be an indicator for vanadium in the +4 oxidation state.⁵³

III.C. VO₂ ALE Using SF₄ or HF and Sn(acac)₂. Etching of the VO₂ ALD films was performed using SF₄ or HF and Sn(acac)₂ as the reactants. Figure 11 shows the mass change versus time during VO₂ ALE using SF₄ and Sn(acac)₂ as the reactants at 200 °C. The reactant exposure sequence was 3–55–3–55. The SF₄ pressure was 500 mTorr. The Sn(acac)₂ pressure was ~50 mTorr. Figure 11 reveals that a linear mass loss is observed during VO₂ ALE over 50 cycles. The average MCPC is −13.2 ng/cm² for the 50 cycles. Based on a VO₂ ALD film density of 4.36 g/cm³ from XRR measurements, the etch rate is 0.30 Å/cycle at 200 °C. Additional experiments revealed that the etch rates were in the self-limiting regime for SF₄ and Sn(acac)₂ exposures of 3 s.

An expanded view of three VO₂ ALE cycles from Figure 11 is shown in Figure 12. The SF₄ exposure leads to a mass gain ΔM_{SF₄} = 9.8 ng/cm². This mass gain is attributed to fluorination of the VO₂ surface to VF₄ or a VO_xF_y oxyfluoride. VF₄ is a fairly stable metal fluoride with a melting temperature at 325 °C. SF₄ may also leave SOF₂ on the surface similar to

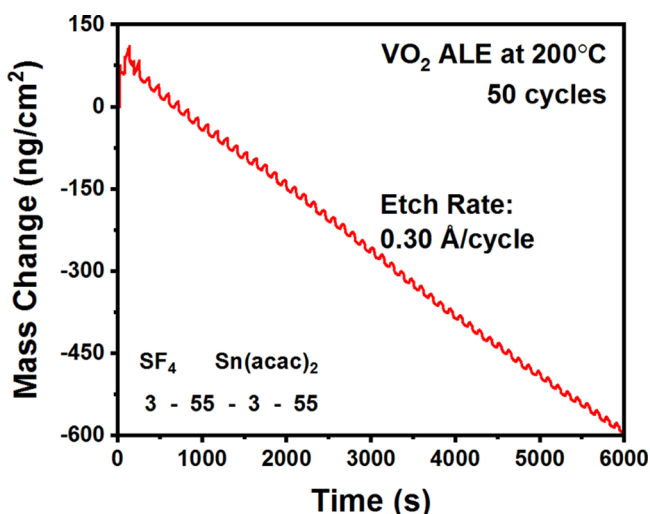


Figure 11. Mass change versus time during VO₂ ALE using SF₄ and Sn(acac)₂ as the reactants at 200 °C. Etch rate is 0.30 Å/cycle.

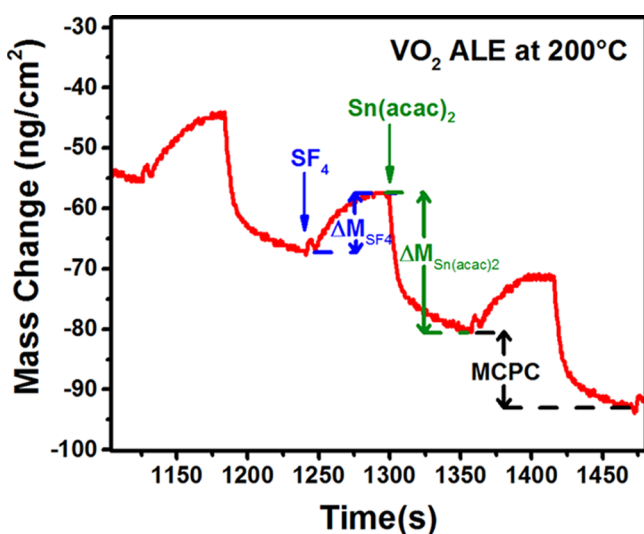
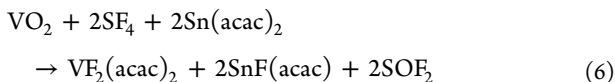


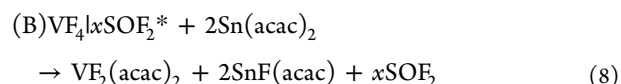
Figure 12. Expanded view of three VO₂ ALE cycles from Figure 11 showing mass gain during the SF₄ exposure and mass loss during Sn(acac)₂ exposure.

the proposed reactions for Al₂O₃ ALE using SF₄ and Sn(acac)₂. The subsequent Sn(acac)₂ exposure then produces a mass loss $\Delta M_{\text{Sn(acac)}_2} = -23.1 \text{ ng/cm}^2$. This mass loss is consistent with Sn(acac)₂ removing the VF₄ surface layer by a ligand-exchange reaction along with any SOF₂ surface species to produce volatile products such as VF₂(acac)₂, SnF(acac), and SOF₂. There is very little information on VF₂(acac)₂ in the literature. However, VCl₂(acac)₂ is used in the synthesis of other vanadium compounds.^{56,57} The Sn(acac)₂ exposure may also lead to SnF(acac) species adsorbed on the VO₂ surface.

If the volatile etch products are VF₂(acac)₂, SnF(acac), and SOF₂, the overall reaction can be written as



This overall reaction can then be divided into the proposed SF₄ and Sn(acac)₂ reactions occurring during VO₂ ALE at steady state



These reactions include the surface species that are believed to change during the SF₄ and Sn(acac)₂ exposures. The asterisks again indicate the surface species, and the vertical lines separate the various surface species. Assuming the reaction stoichiometry given in eq 6, the ΔM_{SF_4} and $\Delta M_{\text{Sn(acac)}_2}$ values require a surface intermediate that adds mass during reaction A and subtracts mass during reaction B. Therefore, SOF₂* is included as a surface intermediate in eqs 7 and 8.

VO₂* shown in eq 7 is the amount of VO₂ that is etched during the ALE reactions.⁷ *x* quantifies the amount of SOF₂* species on the surface after the SF₄ exposure relative to the amount of VO₂ that is etched in one VO₂ ALE cycle. The parameter *x* can be determined by the $\Delta M_{\text{Sn(acac)}_2}$ and MCPC values using the equation:

$$x = [M_{\text{VO}_2}(\Delta M_{\text{Sn(acac)}_2}/\text{MCPC}) - M_{\text{VO}_2}]/M_{\text{SOF}_2} \quad (9)$$

$$x = [82.9(-23.1/-13.2) - 126.9]/86.1 \quad (10)$$

The values 126.9, 82.9, and 86.1 are the molecular weights for VF₄, VO₂, and SOF₂, respectively. Using $\Delta M_{\text{Sn(acac)}_2} = -23.1 \text{ ng/cm}^2$ and MCPC = -13.2 ng/cm², eq 10 yields *x* = 0.21. This *x* value reveals that there are 0.21 SOF₂* species present on the surface after the SF₄ exposures for every VO₂ unit etched during one VO₂ ALE cycle.

The MCPC and etch rate during VO₂ ALE at 200 °C using SF₄ and Sn(acac)₂ are -13.2 ng/cm² and 0.30 Å/cycle, respectively. This removal rate of VO₂ is equivalent to $9.58 \times 10^{13} \text{ VO}_2 \text{ units/cm}^2$. The density of the VO₂ ALD films is 4.36 g/cm³ from XRR measurements. This density yields an estimate of $1.00 \times 10^{15} \text{ VO}_2 \text{ units/cm}^2$ for the number of VO₂ units on the VO₂ surface. The VO₂ removal rate is about 9.6% of the number of VO₂ units on the VO₂ surface. Based on the *x* value of 0.21, the SOF₂* coverage is determined to be $2.01 \times 10^{13} \text{ SOF}_2^* \text{ species/cm}^2$. This SOF₂* coverage is about 2.0% of the number of VO₂ units on the VO₂ surface.

The mass changes during the SF₄ and Sn(acac)₂ exposures decrease slightly as the etching proceeds. However, the MCPC stays nearly constant at -13.2 ng/cm² averaged over the 50 cycles in Figure 11. The slight decrease in the mass changes during the SF₄ and Sn(acac)₂ exposures may result from slow changes in the surface composition. There is a possibility that the Sn(acac)₂ reactant may be able to remove some vanadium species from the VO₂ film as vanadyl acetylacetonate (VO(acac)₂). The removal of VO(acac)₂ would change the V/O ratio on the surface and perhaps slowly affect the etch rate.

III.D. Fluorination of VO₂ Using SF₄ or HF. QCM experiments explored the effect of SF₄ exposure on an initial VO₂ ALD film independent of any acac surface species. Figure 13 shows the first three VO₂ ALE cycles on an initial VO₂ ALD film using SF₄ and Sn(acac)₂ as the reactants. The first SF₄ exposure leads to a mass gain $\Delta M_{\text{SF}_4} = 38.5 \text{ ng/cm}^2$ at 200 °C. The SF₄ exposure was conducted at 500 mTorr for 3 s. The SF₄ exposure is believed to fluorinate the VO₂ film according to the reaction given in Table 1: $\text{VO}_2 + 2\text{SF}_4 \rightarrow \text{VF}_4 + 2\text{SOF}_2$. The mass gain can be used to calculate the VO₂ thickness

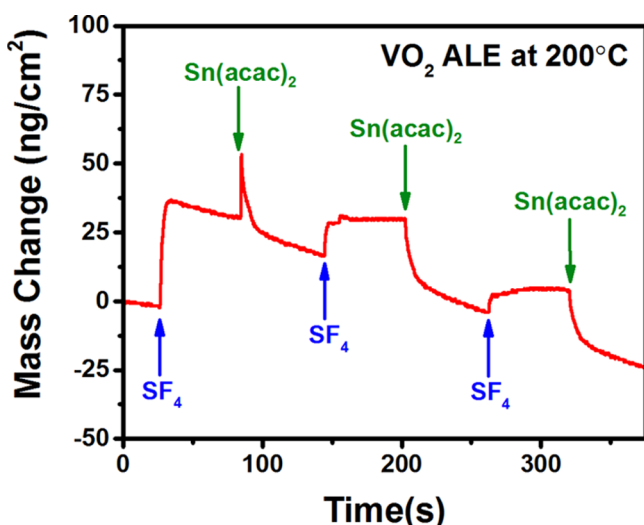


Figure 13. First three cycles of VO₂ ALE using SF₄ and Sn(acac)₂ at 200 °C showing initial mass gain from fluorination during SF₄ exposure and mass changes during the first Sn(acac)₂ exposure and subsequent SF₄ and Sn(acac)₂ exposures.

converted to VF₄ by the SF₄ exposure. The mass change of $\Delta M_{\text{SF}_4} = 38.5 \text{ ng/cm}^2$ is consistent with the conversion of $\sim 1.6 \text{ \AA}$ of VO₂ to $\sim 3.7 \text{ \AA}$ of VF₄. These thicknesses are based on the change in mass of 44 g/mol during VO₂ conversion to VF₄, a VO₂ ALD film density of 4.36 g/cm³ from XRR, and a VF₄ density of 2.98 g/cm³.

Figure 14 shows additional QCM measurements that compare the mass gain during the fluorination of the initial

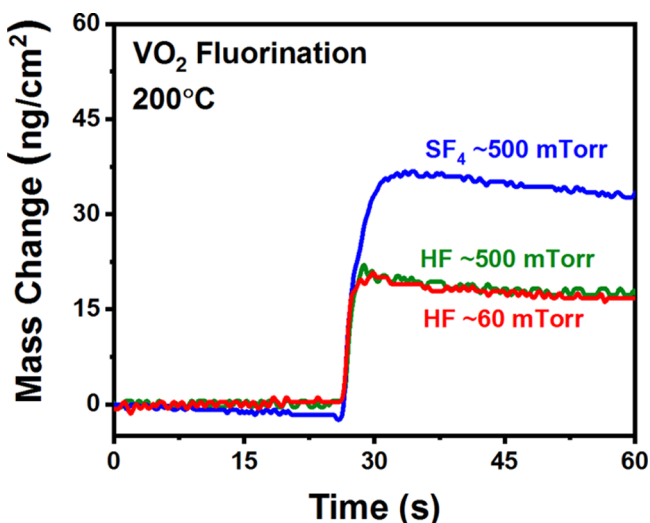


Figure 14. Mass gains during fluorination of the initial VO₂ ALD film with either SF₄ or HF. SF₄ exposure at 500 mTorr leads to a higher mass gain than HF exposures at either 60 or 500 mTorr.

VO₂ ALD film using either SF₄ or HF. The SF₄ exposure at 500 mTorr leads to a much higher mass gain than the HF exposures at either 60 or 500 mTorr. The mass gain resulting from the SF₄ exposures is 38.5 ng/cm². The mass gain from the HF exposures is 20.5 ng/cm² and is independent of the HF pressure. The higher mass gain from the SF₄ exposures probably cannot be explained solely by the presence of SOF₂* species on the VO₂ surface. The SOF₂* coverage of $2.01 \times$

$10^{13} \text{ SOF}_2^* \text{ species/cm}^2$ present after the SF₄ exposures during steady state VO₂ ALE using SF₄ and Sn(acac)₂ is equivalent to a mass of 2.9 ng/cm².

The ability of the HF to fluorinate the VO₂ ALD film was initially questioned because the ΔG° value for the VO₂ + 4HF → VF₄ + 2H₂O reaction is positive at $\Delta G^\circ = +9 \text{ kcal}$. The mass gain with HF exposure suggests that other fluorination reactions may be possible. For example, a subfluoride of vanadium may be formed from the reaction VO₂ + HF → VOF₂ + H₂O. This reaction has a negative standard free energy value $\Delta G^\circ = -1.58 \text{ kcal/mol}$ at 200 °C.

To explore further the VO₂ fluorination, in situ FTIR spectroscopy studies were used to monitor the fluorination of VO₂ ALD films with SF₄ and HF at 200 °C. Figure 15 displays

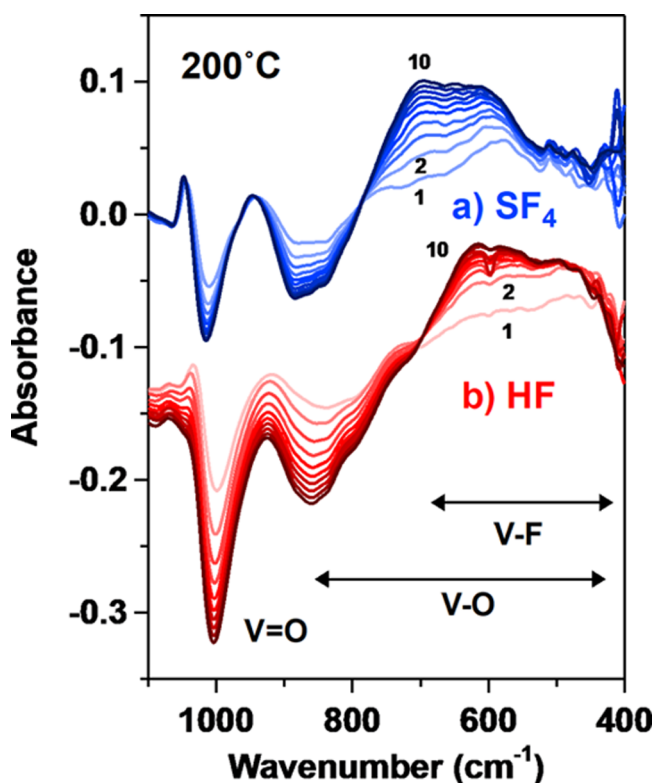


Figure 15. FTIR spectra recorded at 200 °C during fluorination of the VO₂ ALD film at 200 °C. (a) Difference spectra for 10 SF₄ exposures on the VO₂ ALD film. (b) Difference spectra for 10 HF exposures on the VO₂ ALD film.

the fluorination of the VO₂ ALD film using either SF₄ or HF exposures. Figure 15a shows the difference spectra for the fluorination using 10 consecutive SF₄ exposures. Each SF₄ exposure was defined by a pressure of 300 mTorr for 1 s. Figure 15b shows the difference spectra for the progressive fluorination using 10 consecutive HF exposures. These difference spectra have been displaced for clarity in presentation. Each HF exposure was defined by a pressure of 100 mTorr for 1 s. The reference spectrum for the difference spectra in Figures 15a and 15b was the spectrum of the initial VO₂ ALD film.

Broad absorbance gains centered at ~ 650 and $\sim 590 \text{ cm}^{-1}$ are observed for both SF₄ and HF exposures, respectively. This absorbance gain is consistent with V–F stretching vibrations. Previous investigations have observed the V–F stretching vibration at 530 cm^{−1} in VF₄ and at 540 cm^{−1} in VF₃.⁵⁸ The

slightly higher frequencies observed during the fluorination of VO₂ ALD films may be attributed to the presence of oxyfluorides and the higher V–F frequencies in vanadium oxyfluorides.⁵⁹ In comparison with the results for SF₄ on Al₂O₃ ALD films displayed in Figure 6a, no prominent absorbance gains are observed at ~900 cm⁻¹ or 530–560 cm⁻¹ in Figure 15a that would be consistent with an abundance of SF_x surface species.^{46–49} The absence of these absorbance gains is consistent with the lower *x* value for VO₂ ALE using SF₄ and Sn(acac)₂.

Another prominent absorbance feature in Figure 15 is the absorbance loss at ~1000 cm⁻¹ after both SF₄ and HF exposures. The loss of this V=O stretching vibration would be expected during fluorination if the V=O vibrational modes are primarily on the surface of the VO₂ ALD film. Fluorination with SF₄ also produces a small absorbance gain in the difference spectrum in Figure 15a at ~1045 cm⁻¹. This absorbance gain may again be indicative of vanadium oxyfluorides with vanadium atoms bonded to both oxygen and fluorine atoms.⁵⁹

IV. CONCLUSIONS

Fluorination and ligand-exchange reactions can be employed for thermal ALE. HF has been the most common fluorination reactant. However, HF is a fairly weak nucleophilic fluorination reactant. Stronger fluorination reactants may be useful as an alternative to HF. One possible option is SF₄. The thermal ALE of Al₂O₃ and VO₂ was explored using both SF₄ and HF as fluorination reactants together with Sn(acac)₂ as the metal precursor for ligand-exchange.

SF₄ and HF were very comparable as fluorination reactants during Al₂O₃ ALE. The mass gains during the initial fluorination of Al₂O₃ ALD films at 200 °C were 35 and 38 ng/cm² using SF₄ and HF, respectively. In addition, the etch rates for Al₂O₃ ALD films using SF₄ and HF, together with Sn(acac)₂, were 0.20 and 0.28 Å/cycle, respectively, at 200 °C. SF₄ is an effective alternative to HF for Al₂O₃ thermal ALE.

SF₄ was also compared to HF for VO₂ ALE. The mass gains during the initial SF₄ and HF exposures on VO₂ ALD films were 38 and 20 ng/cm², respectively. The larger fluorination when using SF₄ also led to higher VO₂ etch rates. Etch rates of 0.30 and 0.11 Å/cycle were measured for VO₂ ALE using SF₄ and HF, respectively, together with Sn(acac)₂ at 200 °C. The more favorable thermochemistry for VO₂ fluorination by SF₄ leads to a larger etch rate.

Additional FTIR experiments were also conducted to observe the fluorination of the Al₂O₃ and VO₂ ALD films by SF₄ or HF. These studies revealed that SF₄ and HF were comparable as fluorination reactants. The FTIR difference spectra were used to monitor the growth of Al–F and V–F stretching vibrations and the loss of Al–O and V=O stretching vibrations for Al₂O₃ and VO₂, respectively, versus SF₄ or HF exposure. The FTIR difference spectra also suggested that S–F stretching vibrations from SF_x surface species were present on Al₂O₃ after SF₄ exposures. SF₄ is a useful fluorination reactant for thermal ALE. SF₄ is also a stronger fluorination reactant that may be needed for etching some materials.

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Notes

The authors declare no competing financial interest.

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