Thermal Atomic Layer Etching of ZnO by a “Conversion-Etch” Mechanism Using Sequential Exposures of Hydrogen Fluoride and Trimethylaluminum

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ABSTRACT: The atomic layer etching (ALE) of ZnO thin films was demonstrated using sequential, self-limiting thermal reactions with hydrogen fluoride (HF) and trimethylaluminum (TMA) as the reactants. The initial polycrystalline ZnO films were grown by atomic layer deposition (ALD) using diethylzinc (DEZ) and H2O as the precurors, such as SF6, and metal precursors, such as AlCl(CH3)2 and SiCl4, can also be employed for thermal ALE.20 The use of diethylzinc (DEZ) and diethylzinc (DEZ) as metal precursors provides pathways for selective thermal ALE.20 Although thermal ALE methods are promising, thermal ALE has been demonstrated for only a few metal compounds to date. In addition, most of these metal compounds have been grown using ALD methods and have been amorphous. In this

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paper, thermal ALE is examined for polycrystalline ZnO ALD films. ZnO is a wide-bandgap semiconductor that has many applications in various areas such as optoelectronics, surface acoustic wave devices, and transparent electronics.23–25 Etching is required to fabricate ZnO devices. Earlier approaches for the dry etching of ZnO have focused on plasma etching using chlorine and hydrocarbon-based chemistries.26–29 Thermal ZnO ALE methods can provide more control of the etching rates and also avoid plasma-induced damage during etching.28

ZnO ALE was studied by in situ quartz crystal microbalance (QCM) and ex situ spectroscopic ellipsometry (SE) measurements using HF and TMA as the reactants. The QCM and SE measurements examined the effect of various reaction conditions such as reactant exposure and temperature. The ZnO ALE etching rates were determined over the temperature range between 205 and 295 °C. The QCM investigations revealed large mass changes during the TMA exposures that were not consistent with only a ligand-exchange reaction. The large mass losses during the TMA exposures required an alternative etching mechanism based on both ligand-exchange and an additional conversion of ZnO to Al2O3. This new “conversion-etch” mechanism may occur frequently during metal precursor reactions and may allow a wide variety of additional materials to be etched using thermal ALE.

II. EXPERIMENTAL SECTION

II.A. Viscous Flow Hot-Wall Reactor with in Situ Quartz Crystal Microbalance. A hot-wall stainless steel reactor was utilized for the ALD growth and the subsequent ALE removal. The reactor was built-in-house and adjusted for optimal viscous flow conditions.30 The mass changes during ALD and ALE were monitored by an in situ quartz crystal microbalance.31 The QCM sensor was a quartz crystal (gold coated, 6 MHz, 285 °C optimized, Inficon) mounted inside of a customized bakeable sensor housing (modified BSH-150, Inficon). The sensor housing was sealed using a low-outgassing, high temperature epoxy (Epo-tek H212, Epoxy Technology, Inc.). All of the QCM measurements were recorded by a thin film deposition monitor (Maxtek TM-400, Inficon). The mass sensitivity of the Maxtek monitor was ~0.375 ng/cm².

The reactor temperature was held constant to ±0.1 °C by a proportional-integral-derivative (PID) temperature controller (2408, Eurotherm) and power controller (7100A, Eurotherm). These controllers operated two ceramic fiber heaters (VS102A06S, VS102A12S, Watlow) that encased the reactor body. The isothermal environment is important for high quality QCM measurements. After loading the QCM, or changing operation temperatures, the reactor was allowed to reach its new equilibration conditions over the course of 4 h.

The reactor was equipped with a corrosion-resistant, two-stage rotary vane pump (Pascal 2010C1, Pfeiffer). A bakeable capacitance manometer (Baratron 121A, MKS) was used to monitor the pressure inside the reactor. The pump was able to maintain a base pressure of ~20 mTorr without any N2 flow. Under experimental conditions, three mass flow controllers provided a constant flow of 170 sccm of ultrahigh purity (UHP) N2 gas (99.999%, Airgas) through the reactor. Two mass flow controllers (1179A, MKS) controlled the N2 flow through the metal and nonmetal precursor lines. Each line had a constant flow of 75 sccm that purged the precursor zones and subsequently entered the main chamber. An additional mass flow controller (1159B, MKS) provided a steady flow of 20 sccm through the QCM housing underneath the crystal to prevent backside deposition. The total N2 flow of 170 sccm maintained an experimental pressure of ~1.2 Torr in the chamber.

Prior to each ALE experiment, fresh substrate films were grown on the in situ QCM crystal at 150 °C. An Al2O3 ALD layer with a thickness of ~5 nm was deposited initially to aid ZnO ALE nucleation. The Al2O3 was deposited using 50 cycles of TMA (97%, Sigma-Aldrich) and H2O (HPLC grade, submicron filtered, Fisher Scientific) as the reactants. Subsequently, a ZnO ALD layer with a thickness of ~80 nm was deposited using 400 cycles of diethylzinc (DEZ; S2 wt % Zn, Sigma-Aldrich) and H2O as the reactants. All ALD reagents were held at room temperature. ZnO ALD films were also deposited on Si(100) witness wafers. The thickness of these ZnO ALD films was measured using SE. In agreement with earlier studies,32 the ZnO ALD growth rate was 2.0 Å/cycle.

The ZnO ALE experiments using the QCM were performed at 265 °C. Controlled etching was accomplished by sequential exposures of HF, originating from HF-pyridine (70 wt % HF, Sigma-Aldrich), and TMA. HF-pyridine is a convenient liquid source of HF. The HF vapor pressure above this solution is 90–100 Torr at room temperature. There is negligible pyridine vapor pressure above the HF-pyridine solution.33 The HF-pyridine was transferred to a gold-coated stainless steel bubbler in a dry, N2 purged glovebag. The HF-pyridine underwent freeze–pump–thaw cycles to eliminate dissolved gases. Both the HF-pyridine and TMA doses were controlled by two pneumatically actuated valves in combination with a metering valve. The HF-pyridine and TMA precursor doses produced consistent pressure transients of ~60 and ~80 mTorr, respectively. Both ALE reagents were held at room temperature.

II.B. ALD and ALE on Silicon Wafers for ex Situ Film Analysis. The ex situ studies of ZnO deposition and etching were performed on boron-doped Si wafers (p-type, 100), Silicon Valley Microelectronics). The 125 mm Si wafers were cleaved into 2 cm by 2 cm squares and then rinsed with deionized water, acetone, and methanol. UHP N2 was used to blow dry the samples. The samples were loaded into the reactor and given a minimum of 2 h for thermal equilibration. After deposition of the Al2O3 ALD nucleation layer and the ZnO ALD film at 150 °C, the samples were removed from the reactor for the ex situ SE thickness measurements. The samples were then rinsed with methanol, blown dry with UHP N2, and reinserted into the reactor for the ALE experiments. ZnO ALE experiments were performed between 205 and 295 °C.

The crystallinity of the ZnO substrates was confirmed using a high resolution grazing-incidence X-ray diffractometer (XRD) (Bede D1, Jordan Valley Semiconductors) with Cu Kα radiation at 1.540 Å. Scans were performed from 20° to 80° with a step size of 0.05° and 50 s acquisition time. The filament voltage and current for the X-ray source were 40 kV and 35 mA, respectively. XRD software (QuickGraph 2.1.12, Jordan Valley Semiconductors) was used to analyze the data.

SE measurements were utilized to measure the thickness of the films after the ALD and ALE processes. A spectroscopic ellipsometer (M-2000UT, J.A. Woollam Co.) collected data between 245 and 1690 nm at angles of 65° and 75°. The CompleteEASE software, provided by J.A. Woollam Co., fitted the amplitude ratio (ψ) and phase difference (Δ) based on a custom model to determine the film thickness and index of refraction. The model accuracy was verified by thickness comparison with X-ray reflectometry measurements (Bede D1, Jordan Valley Microelectronics).

X-ray photoelectron spectroscopy (XPS) measurements were performed for elemental analysis of the sample surface. An X-ray photoelectron spectrometer (PHI 5600) recorded surface survey scans using monochromatic Al Kα radiation (E = 1486 eV). The XPS data were collected using AugerScan (RBD Instruments) and analyzed using CASA XPS software (Casa Software Ltd.). Atomic force microscopy (AFM) images were obtained using an easyScan 2 (Nanosurf) with a dynamic module. The data were collected using easyScan 2 AFM software (Nanosurf) and analyzed with Gwyddion.34 The instrument utilized 1 μm × 1 μm scans for RMS surface roughness analysis before and after ZnO ALE.

III. RESULTS AND DISCUSSION

III.A. Initial ZnO ALD Film and in Situ Quartz Crystal Microbalance Studies. The initial ZnO ALD films on the silicon wafers were analyzed using XRD. Figure 1a shows an XRD scan of a ZnO film grown on a Si(100) wafer using 400 cycles of DEZ and H2O exposures at 150 °C. This ZnO ALD...
film had a thickness of $\sim 80$ nm. The XRD peaks reveal the film as polycrystalline ZnO. Figure 1b shows the hexagonal wurtzite ZnO reference spectrum (ICDD-PDF Card # 89-1397). The intensities of the (002) and (101) peaks, at $34.65^\circ$ and $36.30^\circ$, respectively, differ from the reference spectrum. This difference is characteristic of ZnO ALD films grown at $150^\circ$C using DEZ and H$_2$O.

The crystalline ZnO ALD films were then employed for the ZnO ALE experiments. Figure 2 shows the QCM mass change versus time for 100 ALE cycles of sequential HF and TMA exposures on the ZnO ALD film at $265^\circ$C. The mass change for the individual HF and TMA exposures are denoted $\Delta M_{HF}$ and $\Delta M_{TMA}$, respectively. Figure 4 shows the $\Delta M_{HF}$ and $\Delta M_{TMA}$ mass changes and the mass change per cycle (MCPC) versus cycle number for the 100 ALE cycles in Figure 2. The MCPC is defined as MCPC = $\Delta M_{HF} + \Delta M_{TMA}$. The $\Delta M_{HF}$ and $\Delta M_{TMA}$ mass changes and the MCPC are constant throughout the 100 ALE cycles at $+53$, $-172$, and $-119$ ng/cm$^2$, respectively. The mass changes for the first ZnO ALE cycle are different from the subsequent cycles. For the first cycle, the mass changes are $\Delta M_{HF} = +7.5$ ng/cm$^2$ and $\Delta M_{TMA} = -221$ ng/cm$^2$. This MCPC is consistent with an etch rate of 2.11 Å/cycle using the ZnO ALD film density of 5.62 g/cm$^3$ determined by XRR analysis.

Figure 3 shows an expansion of the QCM results in Figure 2 for three cycles of HF and TMA exposures at $265^\circ$C. The mass change versus time for 100 ALE cycles of sequential HF and TMA exposures on the ZnO ALD film at $265^\circ$C. The mass change for the individual HF and TMA exposures are denoted $\Delta M_{HF}$ and $\Delta M_{TMA}$, respectively. Figure 4 shows the $\Delta M_{HF}$ and $\Delta M_{TMA}$ mass changes and the total mass change per cycle (MCPC) for ZnO ALE at $265^\circ$C.
The mass gain of $\Delta M_{TMA} = +7.5$ ng/cm$^2$ on the first HF exposure is attributed to fluorination of the ZnO surface given by

$$\text{ZnO} + 2\text{HF} \rightarrow \text{ZnF}_2 + \text{H}_2\text{O} \quad (1)$$

This fluorination reaction is favorable at 265 $^\circ$C with $\Delta G = -9.6$ kcal/mol.$^{35}$ ZnF$_2$ is a stable solid with a melting point of 872 $^\circ$C.$^{35}$ The mass gain of $+7.5$ ng/cm$^2$ is possible by the fluorination of 2.05 $\times$ 10$^{14}$ ZnO units/cm$^2$ to 2.05 $\times$ 10$^{14}$ ZnF$_2$ units/cm$^2$ on the surface. The 2.05 $\times$ 10$^{14}$ ZnF$_2$ units/cm$^2$ represents a thickness of 0.71 Å assuming a continuous and conformal ZnF$_2$ surface layer with a ZnF$_2$ density of 4.95 g/cm$^3$.

The first TMA exposure is then believed to lead to a ligand-exchange transmetalation reaction between TMA and ZnF$_2$. This ligand-exchange reaction would form volatile AlF(CH$_3$)$_2$ and Zn(CH$_3$)$_2$ reaction products.$^{3,17,18}$ The ligand-exchange reaction can be written as

$$\text{ZnF}_2 + 2\text{Al}(\text{CH}_3)\text{Al}(\text{CH}_3)(g) \rightarrow 2\text{AlF}(\text{CH}_3)\text{Al}(\text{CH}_3)(g) + \text{Zn}(\text{CH}_3)\text{Al}(\text{CH}_3)(g) \quad (2)$$

Zn(CH$_3$)$_2$ is a highly volatile compound with a vapor pressure of 15 Torr at 20 $^\circ$C.$^{36}$ Assuming that this ligand-exchange reaction removes the entire ZnF$_2$ surface layer of 2.05 $\times$ 10$^{14}$ ZnF$_2$ units/cm$^2$, the ligand-exchange reaction would only produce a small mass loss of $-35.2$ ng/cm$^2$. However, the mass loss during the first TMA reaction is much larger at $\Delta M_{TMA} = -221$ ng/cm$^2$. This large mass loss suggests that an additional reaction must be occurring after the removal of the ZnF$_2$ surface layer.

The large mass loss is believed to occur by reaction between TMA and the underlying ZnO film. This reaction converts ZnO to Al$_2$O$_3$ according to

$$3\text{ZnO} + 2\text{Al}(\text{CH}_3)\text{Al}(\text{CH}_3) \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Zn}(\text{CH}_3)\text{Al}(\text{CH}_3) \quad (3)$$

This conversion reaction is thermochemically favorable with a Gibbs free energy change of $\Delta G = -166.8$ kcal/mol at 265 $^\circ$C.$^{34}$ The amount of ZnO converted to Al$_2$O$_3$ can be determined by assuming that the conversion reaction accounts for the difference between $-221$ and $-35.2$ ng/cm$^2$. The difference of $-185.8$ ng/cm$^2$ is consistent with the conversion of 23.6 $\times$ 10$^{14}$ ZnO units/cm$^2$ to 7.86 $\times$ 10$^{14}$ Al$_2$O$_3$ units/cm$^2$ on the surface. The 7.86 $\times$ 10$^{14}$ Al$_2$O$_3$ units/cm$^2$ represents a thickness of 3.37 Å assuming a continuous and conformal Al$_2$O$_3$ surface layer with an Al$_2$O$_3$ density of 3.95 g/cm$^3$.

Evidence for the conversion of ZnO to Al$_2$O$_3$ was observed earlier during the growth of ZnO/Al$_2$O$_3$ alloy films using DEZ, TMA, and H$_2$O at 177 $^\circ$C.$^{29}$ In these studies, QCM studies observed large mass losses during the first TMA exposure after ZnO ALD. This mass loss was interpreted as resulting in part from the surface reaction:

$$\text{ZnOH}^\ast + \text{Al}(\text{CH}_3)\text{Al}(\text{CH}_3) \rightarrow \text{Al}(\text{OH})(\text{CH}_3)^\ast + \text{Zn}(\text{CH}_3)\text{Al}(\text{CH}_3) \quad (4)$$

where the asterisks indicate the surface species.$^{29}$ Mass spectrometry studies subsequently confirmed the production of Zn(CH$_3$)$_3$ during TMA exposures that followed DEZ exposures during the growth of ZnO striped structures in porous substrates.$^{37}$ More recent QCM experiments have also documented the mass loss caused by the TMA exposure after DEZ exposures during the growth of Al-doped ZnO.$^{38}$

After the first ALE cycle, Figure 4 shows that the next HF exposure and subsequent HF exposures yield a mass gain of $\Delta M_{HF} = +53$ ng/cm$^2$. This mass gain is attributed to the fluorination of the Al$_2$O$_3$ surface layer to AlF$_3$. The next TMA exposure and subsequent TMA exposures then produce a mass loss of $-172$ ng/cm$^2$. This mass loss can be explained by the removal of the AlF$_3$ layer by the ligand-exchange reaction and an additional conversion reaction of ZnO to Al$_2$O$_3$. A complete discussion of these mass changes and comparison with the measured ZnO etch rates will be given later in Section III.C.

The self-limiting nature of the ZnO ALE process is characterized in Figure 5. The MCPC for ZnO ALE is examined while changing the exposure time of one precursor and holding the exposure time of the other precursor constant. In Figure 5a, the HF exposure is varied while the TMA exposure is fixed at 2 s. This sequence is denoted as $x=60-2-60$, where a N$_2$ purge of 60 s is used after each exposure. As the HF exposure is increased, the MCPC decreases and then levels off at $-119$ ng/(cm$^2$ cycle). This leveling off is an indication that the fluorination reaction exhibits self-limiting behavior. Figure 5a indicates that a HF exposure of 1 s is sufficient for the saturation of the HF reaction.

Figure 5b analyzes the self-limiting nature of the TMA reaction during ZnO ALE. The TMA exposure is varied while the HF exposure is held at 1 s. This sequence is designated as $1-60-x-60$ sequence. The MCPC displays nearly self-limiting behavior. The MCPC drops slightly from $-119$ ng/(cm$^2$ cycle) at a 2 s TMA exposure to $-138$ ng/(cm$^2$ cycle) at a 3 s TMA exposure. This additional mass loss may be associated with the conversion of additional ZnO to Al$_2$O$_3$ at larger TMA
exposures. More converted ZnO to Al₂O₃ could in turn lead to thicker AlF₃ layers after fluorination and then more etching during the ligand-exchange reaction.

The self-limiting nature of the fluorination reaction can be explained by the formation of a passivating fluoride layer during the HF exposure. The passivating surface layer can be understood if the fluoride layer forms a diffusion barrier on the metal oxide analogous to metal oxides on metals or SiO₂ layers on silicon. The self-limiting nature of the TMA ligand-exchange and conversion reaction may also result from the Al₂O₃ layer forming a diffusion barrier on ZnO. The Al₂O₃ layer may impede the diffusion kinetics required for additional conversion of ZnO to Al₂O₃.

The passivating fluoride layer can also be explained using the Pilling-Bedworth ratio (R_PB). R_PB is defined as the ratio of the molar volume, V, of the top layer to the molar volume of the underlying material. Systems with R_PB > 1 can form passivating top layers because of compressive stress in the top layer. The molar volume for AlF₃ is V_{AlF₃} = 28.96 cm³/mol based on M_{AlF₃} = 83.98 g/mol and ρ_{AlF₃} = 2.9 g/cm³. The molar volume for Al₂O₃ is V_{Al₂O₃} = 32.89 cm³/mol based on M_{Al₂O₃} = 101.96 g/mol and ρ_{Al₂O₃} = 3.1 g/cm³. The fluorination of Al₂O₃ to AlF₃ is expected to self-passivate because R_PB = (2 × V_{AlF₃})/V_{Al₂O₃} = 1.76. The coefficient of 2 is added for proper reaction stoichiometry.

QCM results for pulse sequences with exposures that have not reached completion for both reactants can also display a linear mass loss versus HF and TMA exposures. Figure 6 displays mass change versus time obtained during a 1−60 pulse sequence at 265 °C. In these experiments, the TMA reaction does not go to completion according to Figure 5b. The HF exposure of 1 s is sufficient for the HF reaction to reach completion. Although the TMA reaction does not reach completion, these results still exhibit a linear mass loss versus HF and TMA exposures. This behavior indicates that the etch rate for ZnO ALE could be lowered by operating the reactions in the subsaturation regime. However, the resulting etched ZnO films may not be as smooth as the ZnO films etched using reactive exposures that are self-limiting.

III.B. SE, AFM, and XPS Measurements. SE measurements examined the thickness change after various numbers of ZnO ALE cycles on ZnO ALD films. The ZnO films were grown by 400 cycles of ZnO ALD on Si(100) wafers at 150 °C. Figure 7 shows thickness change versus number of ALE cycles for ZnO films at 265 °C. Thickness changes of −103, −211, −306, and −409 Å were observed after 50, 100, 150, and 200 cycles of ZnO ALE, respectively. These measurements yield an etch rate of 2.05 Å/cycle at 265 °C. This etch rate is in excellent agreement with the etch rate of 2.11 Å/cycle at 265 °C obtained from the QCM measurements.

Atomic force microscopy (AFM) imaging was used to analyze the effect of ALE on the surface roughness. AFM measurements over 1 μm × 1 μm areas were performed first on the as-deposited ZnO ALD film and then again after 200 cycles of ZnO ALD at 265 °C. The polycrystalline ZnO ALD films have a surface roughness that increases with the number of ZnO ALD cycles used to deposit the film. Prior to etching, the polycrystalline ZnO films had an RMS roughness of 11 Å. After 200 cycles of ZnO ALE, the RMS roughness was reduced to 5.8 Å. These results indicate the surface of the ZnO ALD film is smoothed by ZnO ALE. The smoothing of Al₂O₃ and HfO₂ substrates has also been observed for Al₂O₃ and HfO₂ ALE.

Figure 8 displays the thickness change versus number of ZnO ALE cycles for temperatures between 205 and 295 °C. The reduction of the film thickness is linear versus number of ALE cycles at the various temperatures. The ZnO etch rates were 0.01, 1.07, 1.82, 2.05, and 2.19 Å/cycle for ALE temperatures 205, 220, 235, 265, and 295 °C, respectively. These results indicate that the ZnO etch rates can be tuned by adjusting the temperature.

Figure 9 displays the etch rate for ZnO ALE versus ALE temperature. The ZnO etch rates increase as the ALE temperature increases. The etch rates range from 0.01 Å/ cycle at 205 °C to 2.19 Å/cycle at 295 °C. The leveling off of the ZnO etch rate at higher temperatures is believed to result from the TMA reaction. Fluorination of Al₂O₃ may not be dependent on temperature as shown earlier in the study of Al₂O₃ ALE using HF and TMA. The increase in the ZnO etch rate from 205 to 235 °C is probably caused by the increasing efficiency for TMA reacting with AlF₃ and then...
converting ZnO to Al2O3. From 235 to 295 °C, there is a very slow increase in etch rate. This behavior would be expected if the TMA conversion reaction becomes limited by the Al2O3 passivation layer on ZnO.

X-ray photoelectron spectroscopy (XPS) measurements analyzed the elemental composition of the films before and after the ALE process. The samples were exposed to atmosphere while transferring to the XPS instrument. Prior to ZnO ALE, the XPS spectra from the ZnO ALD films monitored photoelectrons from Zn, O, and adventitious carbon. After 200 cycles of ALE at 265 °C ending with an HF exposure, the XPS results measured Al concentrations of 6.8 at% and F concentrations of 3.4 at%. These concentrations were quantified with adventitious carbon included in the list of elements summing to 100 at%. The XPS measurements confirm the presence of Al in the ZnO films.

The SE measurements also obtained the index of refraction, n, for the ZnO films before and after the ZnO ALE. For the as-prepared ZnO ALD films, the refractive index, n, was 1.96. For the Al2O3 ALD films grown in the same reactor at 150 °C, the refractive index, n, was 1.65. These refractive index values are consistent with earlier reported values. In contrast, the refractive index for the ZnO films after 200 ALE cycles was 1.92. This lower refractive index is consistent with the incorporation of a lower refractive index material, such as Al2O3, in the ZnO film.

III.C. Proposed Mechanism of ZnO ALE. In the proposed reaction mechanism for ZnO ALE, the first HF exposure fluorinates the ZnO surface and produces a ZnF2 surface layer as defined by eq 1. The first exposure of TMA then undergoes a ligand-exchange reaction with the ZnF2 surface layer according to eq 2. The large mass change during the TMA exposure also indicates that TMA can continue to react with ZnO to form AlF3, as described by eq 3. After the AlF3 layer is established on the ZnO film, the etching reaction can occur as

$$\text{Al}_2\text{O}_3 + 6\text{HF}(g) + 4\text{Al(CH}_3)_3(g) \rightarrow 6\text{AlF(CH}_3)_2 + \text{H}_2\text{O}$$

(5)

The etching reaction given in eq 5 can be broken into fluorination and ligand-exchange reactions as follows:

$$\text{Al}_2\text{O}_3 |\text{Al}_2\text{O}_3^* + 6\text{HF}(g) \rightarrow \text{Al}_2\text{O}_3 |2\text{AlF}^* + 3\text{H}_2\text{O}(g)$$

(6)

$$\text{Al}_2\text{O}_3 |2\text{AlF}^* + 4\text{Al(CH}_3)_3(g) \rightarrow \text{Al}_2\text{O}_3^* + 6\text{AlF(CH}_3)_2(g)$$

(7)

In eq 6, the Al2O3 surface layer is fluorinated by HF to form AlF3 as illustrated in Figure 10a. This reaction is highly favorable with $\Delta G = -52.4$ kcal/mol at 265 °C. This reaction also releases H2O as a reaction product. HF reacting with any methylated surface species, AlCH3*, also forms AlF3 and releases CH4 as a reaction product. The AlF3 surface layer should be stable because AlF3 has a high melting point of 1291 °C.

In eq 7, the AlF3 surface layer is removed by TMA through a ligand-exchange reaction as shown in Figure 10b. Previous studies have observed the spontaneous etching of AlF3 films by Al(CH3)3 exposures at 300 °C. This reaction would release AlF(CH3)2 as a volatile reaction product. The volatility of AlF(CH3)2 leads to mass loss and reduction of the film thickness. Loss of the AlF3 layer also allows TMA to convert more ZnO to Al2O3 as illustrated in Figure 10c. The reaction of TMA with the Al2O3 surface also produces AlCH3* surface species.

Figure 4 shows that the $\Delta M_{HF}$ and $\Delta M_{TMA}$ mass changes and the MCPC are constant throughout the 100 ALE cycles at 265 °C after the first ALE cycle. $\Delta M_{HF}$, $\Delta M_{TMA}$, and MCPC are +53, −172, and −119 ng/cm², respectively. The MCPC of −119 ng/cm² is consistent with a ZnO etch rate of 2.11 Å/cycle. The SE measurements independently yielded an etch rate of 2.05 Å/cycle at 265 °C. These mass changes and the ZnO etch rate can be employed to quantify the reactions during ZnO ALE after the first ALE cycle.

The constant mass gain of $\Delta M_{HF}$ = +53 ng/cm² resulting from the HF exposure is in agreement with the fluorination of $4.84 \times 10^{14}$ Al2O3 units/cm² to 9.67 × 1014 AlF units/cm² on the surface. Assuming continuous and conformal layers, the $4.84 \times 10^{14}$ Al2O3 units/cm² represents an Al2O3 thickness of 2.07 Å based on an Al2O3 density of 3.95 g/cm³. Likewise, the 9.67 × 1014 AlF units/cm² represents an AlF3 thickness of 2.07 Å based on an AlF3 density of 2.88 g/cm³.

Eq 3 can be employed to determine the number of ZnO units/cm² that are necessary to produce the $4.84 \times 10^{14}$ Al2O3 units/cm². Given the reaction stoichiometry, $14.52 \times 10^{14}$ ZnO units/cm² that are necessary to produce the $4.84 \times 10^{14}$ Al2O3 units/cm². Given the reaction stoichiometry, $14.52 \times 10^{14}$ ZnO units/cm² that are necessary to produce the $4.84 \times 10^{14}$ Al2O3 units/cm².
units/cm² are required to form the $4.84 \times 10^{14}$ Al₂O₃ units/cm². However, $14.52 \times 10^{14}$ ZnO units/cm² is more than the ZnO etch rate of 2.11 Å/cycle. The ZnO etch rate of 2.11 Å/cycle represents only $8.77 \times 10^{14}$ ZnO units/cm² using a ZnO density of 5.62 g/cm³. The conversion of $8.77 \times 10^{14}$ ZnO units/cm² would form $2.92 \times 10^{14}$ Al₂O₃ units/cm². Assuming a continuous and conformal Al₂O₃ layer, this Al₂O₃ coverage represents an Al₂O₃ layer thickness of 1.25 Å.

To resolve this discrepancy between the ZnO etch rate and number of Al₂O₃ units/cm² needed to be converted to AlF₃ and produce the mass change of +53 ng/cm², more Al₂O₃ is required from another source in addition to the ZnO conversion reaction. This extra Al₂O₃ may result from the reaction of TMA with residual H₂O or surface hydroxyl groups. The residual H₂O may be produced by the previous HF exposure. To obtain $4.84 \times 10^{14}$ Al₂O₃ units/cm², the extra Al₂O₃ from TMA reactions with H₂O or hydroxyl groups is $1.92 \times 10^{14}$ Al₂O₃ units/cm². This extra Al₂O₃ represents an Al₂O₃ layer thickness of 0.82 Å assuming a continuous and conformal Al₂O₃ layer.

To present a visual representation of the “conversion-etch” mechanism, Figure 11 summarizes the surface reactions and film thicknesses during ZnO ALE for the first ALE cycle and subsequent ALE cycles at 265 °C. The first HF exposure on ZnO is shown in Figure 11a. This HF exposure produces a ZnF₂ surface layer with a thickness of 0.71 Å. The first TMA exposure is given in Figure 11b. This TMA exposure removes the ZnF₂ layer. In addition, the TMA exposure converts ZnO to Al₂O₃ and produces an Al₂O₃ layer thickness of 3.37 Å.

The next and subsequent HF exposures on Al₂O₃ are displayed in Figure 11c. These HF exposures yield AlF₃ layers with a thickness of 4.68 Å. The remaining Al₂O₃ underneath this AlF₃ layer would have a thickness of 1.30 Å. This Al₂O₃ ALD thickness assumes that the TMA exposures from subsequent cycles produce Al₂O₃ thicknesses equivalent to the first ALE cycle. The next and subsequent TMA exposures illustrated in Figure 11d would then remove the AlF₃ layer and add an Al₂O₃ layer thickness of 2.07 Å by the conversion of ZnO to Al₂O₃ and reaction with residual H₂O or hydroxyl groups. The resulting Al₂O₃ layer thickness is 3.37 Å to agree with the Al₂O₃ layer thickness produced in the first ALE cycle.

III.D. Generality of Conversion-Etch Mechanism. The conversion of ZnO to Al₂O₃ in the reaction mechanism for ZnO ALE may be a fairly general phenomena. The conversion
reaction is driven by the stability of the product metal oxide. The conversion reaction can be expected when the metal precursor can form a metal oxide that is more stable than the initial metal oxide. When using TMA as the metal precursor, the conversion reaction is very likely because Al₂O₃ is one of the most stable metal oxides. There are similarities between the conversion reactions using TMA and thermite reactions. TMA assumes the role of metallic aluminum that is commonly employed in thermite reactions.⁴⁸

The conversion-etch mechanism may be very useful in thermal ALE. For example, the conversion reaction with TMA can convert metal oxides that may not have accessible etching pathways to Al₂O₃. The conversion reaction with TMA may also convert metal oxides that have volatile fluorides and would not display self-limiting fluorination, to Al₂O₃. Al₂O₃ can then be etched by a variety of fluorine precursors, such as HF and SF₆, and metal precursors, such as Sn(acac)₂, Al(CH₃)₃, and AlCl(CH₃)₂.¹⁶ Other metal precursors could also convert metal oxides to different metal oxides in addition to Al₂O₃. Moreover, metal precursors can also convert metal nitrides to more stable metal nitrides. The conversion reaction with TMA can convert metal nitrides that may not have etching pathways to AlN. AlN can be etched using sequential HF and Sn(acac)₂ exposures.²¹

The utility of the conversion-etch mechanism can be illustrated by examining the predicted thermochemistry of TMA reactions with a variety of metal compounds. Table 1 lists ∆G values at 200 °C for possible conversion reactions between TMA and a range of metal oxides and one metal nitride.⁴⁴ These conversion reactions depend on the existence of stable metal alkyl reaction products. A wider range of conversion reactions is possible using AlCl₃ instead of TMA because many metal chlorides are stable. However, the ∆G values for the AlCl₃ reactions are not as favorable as the ∆G values for the TMA reactions.⁴⁴

### IV. CONCLUSIONS

The atomic layer etching (ALE) of crystalline ZnO was demonstrated between 205 and 295 °C using sequential HF and TMA exposures. In situ quartz crystal microbalance (QCM) measurements on ZnO ALD films determined that the sequential exposures produced a linear mass loss versus time. At 265 °C, the mass changes during the HF and TMA exposures were ∆M_{HF} = +53 ng/cm² and ∆M_{TMA} = −172 ng/cm². The mass change during the TMA exposures was much larger than expected and indicated that alternative reaction pathways were occurring in addition to the ligand-exchange reaction. The average mass change per cycle (MPCP) was −119 ng/cm². The QCM measurements also determined that the HF and TMA reactions were self-limiting versus precursor exposure time. Ex situ SE measurements examined ZnO ALE for ZnO ALD films on Si(100) wafers. The ZnO ALE etch rates varied from 0.01 Å/cycle at 205 °C to 2.19 Å/cycle at 295 °C. Atomic force microscopy (AFM) measurements determined that the ZnO ALD films were smoothed by ZnO ALE.

The large mass changes during the TMA exposures suggested that the reaction mechanism of ZnO ALD follows a "conversion-etch" mechanism where a ZnO surface layer is converted to Al₂O₃ by reaction with TMA. This reaction proceeds as 3ZnO + 2Al(CH₃)₃ → Al₂O₃ + 3Zn(CH₃)₂. The Al₂O₃ then undergoes fluorination and ligand-exchange according to the reaction Al₂O₃ + 4Al(CH₃)₃ + 6HF → 6AlF(CH₃)₂ + 3H₂O. HF fluorinates the Al₂O₃ layer to produce AlF₃. The TMA ligand-exchange transmetalation reaction then removes the AlF₃ by forming volatile AlF(CH₃)₂. After the AlF₃ removal, TMA then reacts with additional ZnO to regenerate the Al₂O₃ surface layer. Conversion reactions may occur frequently during the thermal ALE of other materials. The conversion-etch mechanism may enlarge the spectrum of metal compounds that can be etched using thermal ALE techniques.

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![Table 1. ∆G Values at 200°C for Various Conversion Reactions with Al(CH₃)₃](image-url)

<table>
<thead>
<tr>
<th>Conversion reaction</th>
<th>∆G (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3ZnO + 2Al(CH₃)₃ → Al₂O₃ + 3Zn(CH₃)₂</td>
<td>−164.7</td>
</tr>
<tr>
<td>1.5SiO₂ + 2Al(CH₃)₃ → Al₂O₃ + 1.5Si(CH₃)₄</td>
<td>−200.0</td>
</tr>
<tr>
<td>1.5SnO₂ + 2Al(CH₃)₃ → Al₂O₃ + 1.5Sn(CH₃)₄</td>
<td>−229.2</td>
</tr>
<tr>
<td>In₂O₃ + 2Al(CH₃)₃ → Al₂O₃ + 2In(CH₃)₃</td>
<td>−317.6</td>
</tr>
<tr>
<td>Si₃N₄ + 4Al(CH₃)₃ → 4AlN + 3Si(CH₃)₄</td>
<td>−362.6</td>
</tr>
</tbody>
</table>
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