ABSTRACT: Metal fluorides generally demonstrate a wide band gap and a low refractive index, and they are commonly employed in optics and optoelectronics. Recently, an SF$_6$ plasma was introduced as a novel co-reactant for the atomic layer deposition (ALD) of metal fluorides. In this work, the reaction mechanisms underlying the ALD of fluorides using a fluorine-containing plasma are investigated, considering aluminum fluoride (AlF$_3$) ALD from Al(CH$_3$)$_3$ and an SF$_6$ plasma as a model system. Surface infrared spectroscopy studies indicated that Al(CH$_3$)$_3$ reacts with the surface in a ligand-exchange reaction by accepting F from the AlF$_3$ film and forming CH$_3$ surface groups. It was found that at low deposition temperatures Al(CH$_3$)$_3$ also reacts with HF surface species. These HF species are formed during the SF$_6$ plasma exposure and were detected both at the surface and in the gas phase using infrared spectroscopy and quadrupole mass spectrometry (QMS), respectively. Furthermore, QMS and optical emission spectroscopy (OES) measurements showed that CH$_4$ and CH$_x$ (x ≤ 3) species are the main reaction products during the SF$_6$ plasma exposure. The CH$_4$ release is explained by the reaction of CH$_3$ ligands with HF, while CH$_x$F$_{6−x}$ species originate from the interaction of the SF$_6$ plasma with CH$_3$ ligands. At high temperatures, a transition from AlF$_3$ deposition to Al$_2$O$_3$ etching was observed using infrared spectroscopy. The obtained insights indicate a reaction pathway where F radicals from the SF$_6$ plasma interact with Al$_2$O$_3$ and where F radicals are simultaneously responsible for the fluoration.

1. INTRODUCTION

Metal fluorides typically have a low refractive index (1.3–1.6) and a wide band gap (>10 eV), and due to these properties, they are widely used in optical devices. Recently, metal fluorides, AlF$_3$ and LiF in particular, have also received considerable attention for application in Li-ion batteries, either as a protective layer on the electrodes or as an active electrode catalyst for the synthesis of chloro-carbons and hydro-fluorocarbons and have been employed in photovoltaics, e.g., as an electron-selective contact. A variety of methods have been used for the deposition of metal fluorides, including evaporation, sputtering, and ion-assisted deposition, as well as atomic layer deposition (ALD). Since ALD is a chemical vapor deposition technique that relies on sequential and self-limiting surface reactions, it typically results in highly uniform and conformal ultrathin films. These characteristics are often relevant for the aforementioned applications of metal fluorides. ALD of metal fluorides has been reported using various co-reactants, such as NH$_3$, F, the volatile metal fluorides TaF$_5$ and TiF$_4$, and HF. Moreover, Lee et al. demonstrated the ALD of AlF$_3$, ZrF$_4$, MnF$_2$, HfF$_4$, MgF$_2$, and ZnF$_2$ using HF from a HF–pyridine solution. For the thermal ALD of AlF$_3$ using HF, it was proposed that the reaction occurs according to the following two reaction equations:

$$xHF_{(ads)} + Al(CH_3)_3(g) \rightarrow AlF_x(CH_3)_{3−x}(ads) + xCH_4(g) \quad (1.1)$$

$$AlF_x(CH_3)_{3−x}(ads) + 3HF(g) \rightarrow AlF_x(s) + xHF_{(ads)} + (3−x)CH_4(g) \quad (x = 1, 2) \quad (1.2)$$

In the precursor subcycle (eq 1.1), the Al(CH$_3$)$_3$ (trimethylaluminum, TMA) precursor reacts with HF that remained adsorbed to the surface after the preceding co-reactant subcycle. Upon this reaction with HF, one or more CH$_4$ would be released. The understanding of the reaction mechanisms during ALD of AlF$_3$ growth can help in developing ALD processes for other metal fluorides using a fluorine-containing plasma as the co-reactant as well as atomic layer etching (ALE) processes involving surface fluorination.
and C\textsubscript{2}F\textsubscript{6} are employed for etching of Si-based materials (e.g., an ALE process for Al\textsubscript{2}O\textsubscript{3}, using SF\textsubscript{6} plasma as an surface species. On the basis of quartz crystal microbalance explaining why this ALD process is strongly dependent on the high-purity fi. TMA and HF can also be used for atomic layer etching (ALE) reaction, where TMA accepts F and donates CH\textsubscript{3} to the eq 2.2 can be considered a ligand-exchange transmetalation surface.47,54 As mentioned, the volatility of AlF\textsubscript{3} layer is etched, resulting in AlCH\textsubscript{3} species on the dominant neutral species are reported to be F\textsubscript{2}, SF\textsubscript{6}, and of volatile AlF(CH\textsubscript{3})\textsubscript{2}, as described by eq 2.2. The reaction in eq 2.1, HF is responsible for the self-limiting of the Al\textsubscript{2}O\textsubscript{3} surface. Subsequently, the formed AlF\textsubscript{3} surface layer can be removed by dosing Al(CH\textsubscript{3})\textsubscript{3} leading to the formation of volatile AlF(CH\textsubscript{3})\textsubscript{3} as described by eq 2.2. The reaction in eq 2.2, can be considered a ligand-exchange transmetalation reaction, where TMA accepts F and donates CH\textsubscript{3} to the surface.47,54 As mentioned, the volatility of AlF(CH\textsubscript{3})\textsubscript{3} species is dependent on the temperature, and the desorption of these species at high temperatures enables ALE. In addition to the reaction of eq 2.2, Al(CH\textsubscript{3})\textsubscript{3} can react with Al\textsubscript{2}O\textsubscript{3} after the AlF\textsubscript{3} layer is etched, resulting in AlCH\textsubscript{3} species on the surface, which are responsible for the self-limiting behavior of the surface reactions.

Recently, we presented an ALD process for AlF\textsubscript{3} as well as an ALE process for Al\textsubscript{2}O\textsubscript{3} using SF\textsubscript{6} plasma as an alternative, easy-to-handle, and readily available co-reactant. SF\textsubscript{6} is a stable and nontoxic gas, which is widely used in the industry. Notably, F-containing plasmas such as SF\textsubscript{6}, NF\textsubscript{3}, CF\textsubscript{4}, and C\textsubscript{2}F\textsubscript{6} are employed for etching of Si-based materials (e.g., Si, SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}). An SF\textsubscript{6} plasma is characterized by high concentrations of F radicals and F\textsuperscript{−} ions, which are known to be approximately 10\textsuperscript{5} times higher than the concentrations of S and S\textsuperscript{−}. SF\textsubscript{6} gas can form electronegative plasmas where significant concentrations of positive ions (mainly SF\textsubscript{6}\textsuperscript{+} and SF\textsubscript{5}\textsuperscript{+}) are balanced by negative ions (mainly F\textsuperscript{−} and SF\textsubscript{6}\textsuperscript{−}) and electrons. In an inductively coupled SF\textsubscript{6} plasma, the dominant neutral species are reported to be F\textsubscript{2}, SF\textsubscript{6}, and SF\textsubscript{4}\textsuperscript{−}–SF\textsubscript{6}\textsuperscript{−}. It is noted that F is very reactive due to a very high electronegativity and electron affinity. The high concentration of reactive F radicals makes SF\textsubscript{6} plasma a suitable co-reactant for ALD of metal fluorides.

The ALD process using SF\textsubscript{6} plasma as co-reactant yields high-purity films with material properties similar to those reported in the literature for AlF\textsubscript{3} films deposited using various methods. Since an SF\textsubscript{6} plasma etches Si or SiO\textsubscript{2} substrates, ALE-grown Al\textsubscript{2}O\textsubscript{3} was used as a protective coating. A decrease in the growth per cycle (GPC) was reported elsewhere. Brie
dy, a TMA dose of 80 ms, followed by a purge step of 6 s, an SF\textsubscript{6} plasma exposure of 10 s (300 W power), and a final purge step of 4 s were used. The TMA precursor (Sigma-Aldrich, >99.9999%) was contained in a stainless steel canister, kept at a temperature of 30 °C. The chamber pressure was set to 15 and 50 mTorr during the TMA dose and SF\textsubscript{6} plasma exposure, respectively. The substrate table and reactor walls were kept at temperatures of 200 and 120 °C, respectively. Since the surface area of the reactor wall is significantly larger than that of the substrate table, a large part of the QMS signal originates from reactions occurring on the wall at a temperature of 120 °C.

For the in situ infrared spectroscopy studies in the home-built reactor, an SF\textsubscript{6} plasma pressure of 15 mTorr and a plasma power of 100 W were used. Measurements were performed on Aerosil OX50 SiO\textsubscript{2} powders, pressed on a tungsten grid. As will be discussed in Sections 3.1 and 4, a transition from AlF\textsubscript{3} ALD to Al\textsubscript{2}O\textsubscript{3} ALE was observed in the infrared spectroscopy experiments, whereas this was not observed for the temperates studied in the FlexAL reactor. This difference can likely be attributed to the higher temperature of the SiO\textsubscript{2} powder as compared to the Si wafer coupons. For depositions on the SiO\textsubscript{2} powder, the tungsten grid was heated directly by resistive heating using DC current, and the temperature was monitored using a thermocouple. This method of heating is significantly different from the heating employed for the deposition on blanket wafers in the FlexAL reactor, where wafer coupons are placed on a carrier wafer, which is loaded onto a heated substrate table. Due to reduced thermal contact at low working pressure between the wafer coupons, the carrier wafer, and the table heater, the actual sample temperature is significantly lower than the substrate temperature. For instance, the sample temperature is estimated to be 200–220 °C for a table temperature of 300 °C. This is in contrast to the depositions on SiO\textsubscript{2} powder where the actual temperature of the powder surface is expected to be in agreement with the set
temperature. Moreover, it was found that the SF₆ plasma exposure resulted in slight heating (∼20–30 °C) of the tungsten grid, while this effect is expected to be less pronounced on wafer coupons.

2.2. Reaction Mechanism Studies. The in situ surface spectroscopy studies were done with a Bruker Vector Fourier transform infrared spectrometer, as described in previous work.⁶⁸ Prior to AlF₃ ALD, the SiO₂ powder was coated with Al₂O₃ using 50 thermal (TMA + H₂O) ALD cycles at ∼275 °C. Sets of five TMA–SF₆ plasma cycles were performed at temperatures between 100 and 250 °C, while collecting an infrared spectrum after each subcycle. After each set of the TMA–SF₆ plasma cycles, 10 Al₂O₃ ALD cycles were repeated at ∼275 °C to obtain the same starting surface. The TMA dose and SF₆ plasma exposure time for these experiments were 1.1 and 30 s, respectively, which was confirmed to be sufficient to reach saturation of the surface reactions on the Al₂O₃-coated SiO₂ powder. To correct for changes in surface area of the powder due to film growth, the absorbance spectra were normalized on the basis of the signal for Al(CH₃)₃ adsorption on Al₂O₃.⁶⁹ For this correction, the normalized integrated infrared absorbance corresponding to CH₃ stretching vibrations in the range of 3060–2800 cm⁻¹ was used. This absorbance peak can serve as a measure for the quantity of adsorbed Al(CH₃)₃ and was determined by calculating the difference spectrum using measurements before and after dosing Al(CH₃)₃ on the Al₂O₃-coated powder.

Quadrupole mass spectrometry (QMS) measurements were performed using a Pfeiffer Vacuum Prisma QME-200 (mass-to-charge ratio m/z = 1–200) connected to a flange on the side of the FlexAL reactor chamber. The selection of measured m/z ratios was based on initial screening and mostly corresponds to SF₆ and CH₃F⁺ species. The procedure for time-resolved QMS measurements was similar to a method described previously.⁷⁰ In short, six m/z ratios were measured simultaneously, of which one was always m/z = 40. This m/z value corresponds to Ar⁺ and is used as a reference. For each type of recipe, five cycles were performed and averaged. OES was done using a four-channel AvaSpec ULS2048 spectrometer from Avantes (200–1100 nm) as a line-of-sight measurement perpendicular to the substrate table (i.e., the fiber is installed vertically at the top of the plasma source). For the OES measurements, an SF₆ gas flow of 50 sccm was used instead of the standard 100 sccm to increase the residence time of the plasma species.

3. RESULTS

3.1. Surface Reactions. In situ surface infrared spectroscopy was performed to investigate the surface reactions taking place during the subcycles. Figure 1 shows absorbance spectra in the range of 4250 to 2500 cm⁻¹ for the TMA and the SF₆ plasma subcycles performed at temperatures between 100 and 250 °C. For all temperatures, an absorbance gain is observed in the spectrum for the TMA subcycle in the region of 3060–2800 cm⁻¹, which corresponds to the formation of CH₃ stretching vibrations.⁷¹–⁷⁴ The presence of CH₃ can be explained by AlF(CH₃)₂, AlF₂(CH₃), or AlCH₃ species formed upon the reaction of TMA with the surface.⁷⁵ With increasing temperature, the absorbance gain decreases, indicating less Al(CH₃)₃ adsorption at high temperatures, which is in line with the decrease of the GPC as a function of temperature.⁷⁶ This temperature dependence of the CH₃ stretching vibrations is similar to what was observed by DuMont and George for thermal ALD/ALE using HF.⁷⁷ Furthermore, an absorbance loss can be seen in the range of 3700–3060 cm⁻¹ in the spectra for 100 and 150 °C, which is attributed to the consumption of HF species on the AlF₃ surface.⁷⁷,⁷⁸ These HF species are formed during the SF₆ plasma exposure, as evidenced by the positive absorbance peaks in the spectra for the plasma subcycle at 100 and 150 °C. Note that HF was also detected as a gas-phase reaction product during the SF₆ plasma exposure using QMS, as will be addressed in Section 3.2. At temperatures of 200 and 250 °C, negligible peaks corresponding to HF are observed, which reveals that no significant amount of HF is consumed or adsorbed during the TMA or SF₆ plasma subcycle, respectively. Although the removal of HF surface species is only observed at 100 and 150 °C, the spectra for the TMA subcycle indicate the formation of CH₃ groups at all investigated temperatures. This implies that, at higher temperatures, Al(CH₃)₃ reacts directly with the AlF₃ film, likely by accepting F from the surface and forming CH₃ surface groups.⁷⁸

Multiple cycles were performed, and the collected spectra for each cycle were referenced to the first cycle to gain insight into the progression of the film with the number of cycles. From these measurements, the data collected after two and after five cycles are displayed in Figure 2 for temperatures between 100 and 250 °C. The spectra for 100 and 150 °C show a small positive absorbance peak starting around 775 cm⁻¹, which can be attributed to the Al–F stretching vibrations in AlF₃.⁷⁵,⁷₆ Unfortunately, the end of the detector range lies at ∼700 cm⁻¹, meaning that only a part of the peak corresponding to the Al–F stretching vibrations could accurately be measured. However, the positive absorbance between ∼775 and ∼750 cm⁻¹ increases when additional cycles are performed, in line with the growth of the AlF₃ film.
Interestingly, an absorbance loss can be observed in the region below 950 cm\(^{-1}\) for temperatures of 200 and 250 °C. The region around ~1030 to 550 cm\(^{-1}\) corresponds to the Al–O stretching vibrations in amorphous Al\(_2\)O\(_3\) and the absorbance loss therefore suggests the removal of Al\(_2\)O\(_3\). For a temperature of 250 °C, the absorbance loss is larger than for 200 °C, indicating that more Al\(_2\)O\(_3\) is etched, in agreement with what was found that exposing Al\(_2\)O\(_3\) to SF\(_6\) plasma leads to a small increase in thickness and a decrease in refractive index, due to self-limiting fluorination of the top surface. Furthermore, XPS results presented in Figures S2 and S3 demonstrate that most of the F is located in the top layer of the Al\(_2\)O\(_3\) and that AlO\(_x\)F\(_{y}\) bonds are present in addition to Al\(_2\)O\(_3\). Similar self-limiting behavior can be expected for fluorination of MgO, HfO\(_2\), and ZnO films, since their fluorides are nonvolatile and have been deposited by ALD using HF.\(^{46}\)

### 3.2. Gas-Phase Reaction Products

QMS was employed to study the formation of gas-phase reaction products during Al\(_2\)O\(_3\) ALD. Figure 3 shows time-resolved QMS data for selected mass-to-charge (m/z) ratios 15, 16, 19, and 89, which correspond to CH\(_4\) and key plasma species (F and SF\(_6\)). In addition, Table 1 lists the most relevant m/z ratios and the assignment of these m/z ratios to corresponding parent species. The increase in signals for m/z = 15 (CH\(_4^+\)) and 16 (CH\(_3^+\)) upon TMA dosing (at t = 0 s) in Figure 3 can be explained by the release of CH\(_4\) as a reaction product as well as by dissociation of the precursor in the QMS detector. The small increase in ion current for m/z = 89 (SF\(_6^+\)) is likely due to an increase in chamber pressure after TMA dosing. Subsequently, at the start of the SF\(_6\) gas flow around t = 6 s, the chamber pressure increases from 15 to 50 mTorr, leading to an increase in ion current for all m/z ratios. After ignition of the SF\(_6\) plasma (at t ~ 12.5 s), the ion currents for F\(^+\) (m/z = 19) and SF\(_6^+\) (m/z = 89) decrease slightly, attributed to consumption and dissociation of F radicals and SF\(_6\), respectively. Meanwhile, the signals for m/z = 15 (CH\(_4^+\)) and 16 (CH\(_3^+\)) go up, indicating the formation of CH\(_4\) as the reaction product. After the initial increase, ion currents for m/z = 15 and 16 decrease quickly, which suggests that CH\(_4\) is being evacuated from the reactor or dissociated in the plasma.

![Figure 2](https://dx.doi.org/10.1021/acs.jpcc.0c10695)

**Figure 2.** Absorbance spectra collected after performing two and five TMA–SF\(_6\) plasma cycles, both referenced to the spectrum collected after performing one TMA–SF\(_6\) plasma cycle on Al\(_2\)O\(_3\)-coated SiO\(_2\) at the corresponding temperature. The pairs of spectra were given an offset on the vertical axis for clarity.

![Figure 3](https://dx.doi.org/10.1021/acs.jpcc.0c10695)

**Figure 3.** Time-resolved QMS signals for selected m/z ratios 15, 19, 16, and 89. Five Al\(_2\)O\(_3\) ALD cycles were averaged to improve the signal-to-noise ratio. The pressure in the reactor increases from 15 to 50 mTorr when the SF\(_6\) gas flow is started (at t ≈ 6 s), leading to an increase in ion currents.

| m/z   | assigned ion(s) | assigned parent species |
|-------|-----------------|-------------------------|
| 15    | CH\(_4^+\) | CH\(_4\), CH\(_3\), Al(Al(CH\(_3\))\(_3\)) |
| 16    | CH\(_3^+\) | CH\(_3\), Ar |
| 19    | F\(^+\) | SF\(_6\), F\(_3\), CH\(_2\)F\(_2\), CHF\(_3\), CF\(_4\) |
| 20    | HF\(^+\), Ar\(^{2+}\) | HF, Ar |
| 26    | C\(_2\)H\(_4^+\) | CH\(_2\), CH\(_3\), CH\(_4\) |
| 31    | CF\(^+\) | CH\(_2\), CH\(_3\), CH\(_4\), CF |
| 32    | S\(^+\), CHF\(^+\) | SF\(_6\), CH\(_2\)F, CH\(_3\)F, CF \(_2\), CHF \(_3\), CHF \(_4\) |
| 33    | CH\(_2\)F\(^+\) | CH\(_2\)F\(_2\), CHF \(_3\) |
| 40    | Ar\(^+\) | Ar |
| 50    | CF\(_2^+\) | CF\(_3\), CF\(_2\), CHF \(_3\) |
| 51    | SF\(_2^+\), CHF\(_3^+\) | SF\(_6\), CHF \(_3\), CHF \(_2\), CHF \(_4\) |
| 69    | CF\(_3^+\) | CF\(_3\), CHF \(_3\) |
| 70    | SF\(_2^+\), CHF\(_3^+\) | SF\(_6\), CHF \(_3\) |
| 89    | SF\(_6^+\) | SF\(_6\) |

*Most m/z ratios correspond to SF\(_6\) or CH\(_2\)F\(_2\) species (ν ≤ 4). The assignments for CH\(_2\)F\(_2\) species are based on cracking patterns taken from the NIST database.*
the SF$_6$ plasma exposure, the signals for $m/z$ ratios 16, 31, 33, 50, and 69 increase, all of which correspond to CH$_3$F$_{4-x}$ (hydrofluorocarbon) species. See Figure S4 for the cracking patterns of the CH$_3$F$_{4-x}$ species. In addition, the signal for $m/z = 26$ indicates the production of C$_2$H$_2$ (or possibly C$_3$H$_4$ or C$_4$H$_8$), which can be explained by the reactions of, for instance, CH$_4$ ($m/z = 16$) in the plasma (in the literature, it is reported that C$_3$H$_2$ forms in CH$_4$ plasmas). Several other $m/z$ ratios (18, 28, 32, 34, 35, 48, and 52) were also investigated, but their ion currents were found not to be affected by TMA dosing. Upon closer inspection of Figure 4, it can be seen that the temporal behavior is not the same for all of the investigated species. Signals related to CH$_4$ and C$_2$H$_2$ in Figure 4a show the highest ion currents at the beginning of the plasma exposure ($t \approx 14$ s) and a rapid decrease, while others (especially in Figure 4b) show the highest intensity later on. More specifically, the higher the concentration of F atoms in the species, the later the maximum intensity occurs. This suggests that the F concentration of surface species increases due to the interaction with F radicals from the plasma before they are released from the surface or that CH$_4$ and CH$_3$F$_{4-x}$ plasma species react with F in the plasma. The signal for $m/z = 20$ is also displayed in Figure 4a and corresponds to Ar (Ar$^+$ in this case) as well as HF. Between $t \approx 8$ and 12 s, the ion current for $m/z = 20$ decreases, which can be attributed to Ar being evacuated from the chamber (Ar is used as the background gas during the TMA dose). At the start of the SF$_6$ plasma (t $\approx 12$ s), the ion current quickly rises, indicating the formation of HF, after which the ion current stabilizes (at $t \approx 17$ s). The formation of HF can be explained by the recombination of H and F radicals (likely at the surface) and can lead to an additional thermal component in the reaction mechanism (see eq 1.2). This reaction between HF and CH$_3$ higher for the ALD cycle as compared to the signals for only SF$_6$ plasma. The higher ion currents prove that all these species are formed due to the interaction of the SF$_6$ plasma with the precursor ligands remaining after the precursor dose or due to interaction of the SF$_6$ plasma with formed reaction products. For instance, CH$_4$ species can be formed in a surface reaction and subsequently undergo dissociation reactions in the plasma. Certain signals (e.g., $m/z = 32$, 51, and 70) simultaneously correspond to hydrofluorocarbons and SF$_6$ and do not show a higher current for the ALD cycle than for the SF$_6$ plasma without TMA dosing. Probably, the production of CH$_3$F$_{4-x}$ species does not affect the currents for those $m/z$ ratios due to the high background signal from SF$_6$. It is noted that the ion currents for $m/z = 15$–16 (CH$_4^+$, CH$_3^+$), $m/z = 25$–29 (C$_2$H$_4^+$, x = 1–5), and $m/z = 31$, 50, and 69 (CF$_3^+$) also increased slightly during the SF$_6$ plasma exposure without preceding TMA dosing, which indicates that some C-containing species were present on the reactor wall due to previously performed ALD cycles. The excited species present in the plasma were analyzed using OES to corroborate the findings from the QMS measurements. Figure 6a shows OES spectra for an SF$_6$ plasma during an ALD cycle (after TMA dosing) and an SF$_6$ plasma (without preceding TMA dosing). Various key excited species can be identified in both spectra, including F, S, H$_2$, and H$_2$O. Emission related to F and S can be attributed to dissociation of SF$_6$ in the plasma, whereas H and H$_2$ are likely related to residual background species (e.g., H$_2$O). For the plasma during an ALD cycle, additional emission peaks corresponding to C$_2$H$_2$ and CF$_2$ are detected at wavelengths higher for the ALD cycle as compared to the signals for only SF$_6$ plasma. The higher ion currents prove that all these species are formed due to the interaction of the SF$_6$ plasma with the precursor ligands remaining after the precursor dose or due to interaction of the SF$_6$ plasma with formed reaction products. For instance, CH$_4$ species can be formed in a surface reaction and subsequently undergo dissociation reactions in the plasma. 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Figure 4. Time-resolved QMS signals collected during the plasma subcycle corresponding to (a) CH$_4$, HF, and C$_2$H$_2$ ($m/z = 16$, 20, 26) and (b) hydrofluorocarbons ($m/z = 31$, 33, 50, 51, and 69). Note that the time for which the species reach the maximum intensity correlates to the F-content and that signals corresponding to species with a higher F-content in (b) ($m/z = 31$, 50, and 69) reach the maximum later than H-rich species in (a). The data for $m/z = 16$ is also shown in Figure 3.

Figure 5. QMS mass spectra showing selected masses during the SF$_6$ plasma exposure of an ALD cycle and during an SF$_6$ plasma exposure (without TMA dosing). The spectra were collected at $t \approx 13.5$ s, which is approximately 1.5 s after igniting the plasma.
At the end of the plasma exposure, the emission signal at 623.9 nm approaches the same intensity as in an SF$_6$ plasma (Figure 6c), which can be explained by the saturation of the surface reactions between CH$_3$ ligands and F radicals. Emission peaks at other wavelengths related to F (e.g., 712.8, 720.2, and 733.1 nm) were found to show a similar behavior as function time, corroborating saturation. When comparing Figure 6b,c, it becomes clear that signals assigned to reaction products (257.7, 259.2, and 656.2 nm) demonstrate a quick rise and subsequent decrease during the ALD cycle, while they are not observed for the reference measurement of the SF$_6$ plasma (without TMA dosing). The additional emission in Figure 6b can be explained by the formation of reaction products (i.e., CH$_3$F$_{4-y}$ and HF species) due to the reaction of plasma species, most likely F radicals, with the surface groups. The gradual decrease in emission from these reaction products reveals the elimination of precursor ligands by F radicals and their removal from the reactor chamber. Note that a small amount of excited Ar is observed for the ALD cycle, which is apparently still present in the reactor after the precursor purge step but decreases soon after plasma ignition. Overall, the OES results are in line with the QMS data, indicating the consumption of F radicals and the formation of CH$_3$F$_{4-y}$ species as reaction products.

4. DISCUSSION

The insights obtained from the infrared, QMS, and OES data of Section 3 help one to understand the reaction mechanism of AlF$_3$ growth using Al(CH$_3$)$_3$ and SF$_6$ plasma. Before the reaction mechanisms are discussed, the main results can be summarized as follows:

i. Al(CH$_3$)$_3$ dosing in the precursor subcycle results in CH$_3$ groups on the surface, which are removed in the co-reactant subcycle.

ii. At low temperatures ($\leq$150 °C), adsorbed HF is consumed during the TMA dose and formed during the SF$_6$ plasma exposure, while it does not play a role in the surface reactions at higher temperatures. The presence of HF in the gas phase was observed during the SF$_6$ plasma exposure (at a temperature of 120 °C).

iii. CH$_4$ and CH$_3$F$_{4-y}$ gas-phase species are formed during the SF$_6$ plasma exposure, indicating the reactions of CH$_3$ groups with plasma species and HF.

iv. During the SF$_6$ plasma step, F radicals are consumed in surface reactions with CH$_3$ groups (and possibly other surface species) and lead to the fluorination of the surface.

The role of HF in the reaction mechanism requires some more discussion before the complete mechanism can be postulated. QMS measurements revealed that HF is produced as a reaction product during the SF$_6$ plasma, which can adsorb to the AlF$_3$ surface. The surface infrared spectroscopy data presented in Figure 1 show the adsorption of HF surface species during the SF$_6$ plasma exposure subcycle and the consumption of HF in the TMA subcycle (for 100 and 150 °C). Since the GPC for the plasma process is similar to the GPC for the thermal process, it is possible to compare the relative absorbance values for the two processes. For the thermal ALD process, DuMont and George also reported the consumption of HF, as indicated by a negative absorbance peak in the range of $\sim$3700−3000 cm$^{-1}$ (corresponding to HF), which was similar in intensity to the absorbance peak in the region of $\sim$3000−2800 cm$^{-1}$ of 247.8, 257.7, and 259.2 nm (see the inset of Figure 6a).$^{81-84}$

The OES spectrum for the ALD cycle thus corroborates the presence of CH$_3$F$_{4-y}$ species as reaction products.

Intensities corresponding to relevant species were followed as a function of time during an SF$_6$ plasma exposure of an ALD cycle (Figure 6b) and during the SF$_6$ plasma exposure without TMA (Figure 6c). Figure 6b shows that the signal corresponding to F radicals (623.9 nm) increases gradually after the plasma is started. As compared to the reference signals (Figure 6c), there is initially less emission related to excited F species, indicating that F is consumed in the surface reactions.

$^{81}$ https://dx.doi.org/10.1021/acs.jpcc.0c10695
$^{82}$ J. Phys. Chem. C 2021, 125, 3913–3923
corresponding to AlCH₃ species. However, when comparing the data shown in Figure 1 with the data reported by DuMont and George, it becomes clear that the relative absorbance corresponding to adsorbed HF is much smaller for the SF₆ plasma process than for the thermal process using HF as the co-reactant. Although some HF is produced during the SF₆ plasma of the co-reactant subcycle, the HF exposure and resulting surface coverage is likely much lower than when dosing HF directly as the co-reactant. The smaller relative absorbance corresponding to HF therefore suggests that Al(CH₃)₃ also reacts directly with the AlF₃ in a ligand-exchange reaction during the plasma process (forming AlF(CH₃)₃; see the discussion of eq 2.2).

On the basis of the results, it can be concluded that, during AlF₃ ALD using Al(CH₃)₃ and SF₆ plasma, Al(CH₃)₃ reacts with AlF₃ as well as with HF adsorbed on the surface and that part of the CH₃ ligands are released as CH₄. This is illustrated in Figure 7 and described by eqs 3.1 and 3.2. Al(CH₃)₃ reacts with HF and AlF₃, resulting in AlF(CH₃)₂ surface species. During the plasma subcycle ("B"), F radicals from the plasma remove the CH₃ ligands and fluorinate the film to AlF₃, HF, which is formed during the SF₆ plasma exposure, can adsorb to the surface, serving as an additional reactive site at low deposition temperatures. The formed reaction products can undergo dissociation and recombination reactions in the SF₆ plasma and at the reactor wall. Note that the reaction between AlF₃ and Al(CH₃)₃ results in three AlF₃(CH₃)₃ groups, although only two are displayed. For simplicity, only AlF(CH₃)₂ species are drawn after TMA dosing, whereas AlF₃(CH₃) can also be present.

with the AlF₃ film in a ligand-exchange reaction, forming AlF₃(CH₃) or AlF₃(CH₃)₂ (eq 3.1). In addition, at low temperatures (≤150 °C), adsorbed HF serves as a reactive site for Al(CH₃)₃ to bind (eq 3.2). HF is formed during the preceding co-reactant subcycle and partly remains adsorbed on the surface. Saturation of the reactions between Al(CH₃)₃ and the surface likely occurs due to steric hindrance effects between CH₃ groups. It is noted that in QCM measurements for thermal ALD using HF it was found that mainly AlF(CH₃)₃ is formed upon dosing Al(CH₃)₃. Equations 3.1 and 3.2 therefore describe the formation of AlF(CH₃)₂, although AlF₃(CH₃) surface species might probably also be present.

\[
\text{AlF}_3(s) + 2\text{Al(CH}_3)_3(g) \rightarrow 3\text{AlF(CH}_3)_2(ads) \tag{3.1}
\]

The CH₃ ligands remaining after the precursor subcycle are eliminated by F radicals during the following SF₆ plasma exposure, resulting in the formation of CH₄F₄⁺⁺ species (see eq 4.1 and Figure 7). These CH₄F₄⁺⁺ species can be formed either in surface reactions or in the plasma. Furthermore, HF is produced as a reaction product in eq 4.1, leading to an additional thermal component, which results in the production of CH₄ as described by eq 4.2. It was found that at low temperatures (≤150 °C) a small part of the formed HF remains adsorbed on the surface after the SF₆ plasma, providing reactive sites for the next TMA dose (eq 3.2).

\[
\begin{align*}
\text{AlF}_3(ads) + \text{Al(CH}_3)_3(g) & \xrightarrow{T \leq 150^\circ C} \text{AlF(CH}_3)_2(ads) + \text{CH}_4(g) \\
\text{AlF}_3(ads) + 4(4-y)\text{F}_2(g) & \rightarrow \text{AlF}_3(s) + 2\text{CH}_4(ads) + 2(3-y)\text{HF}(ads,g) (y \leq 3) \\
\text{AlF}_3(ads) + 2HF(ads,g) & \rightarrow \text{AlF}_3(s) + 2\text{CH}_4(g) \\
\text{(thermal component, } T \leq 150^\circ C) \tag{4.1}
\end{align*}
\]

The combination of the reactions described by eqs 3.1, 3.2, 4.1, and 4.2 results in the following overall reaction equation for the complete AlF₃ ALD cycle:

\[
\begin{align*}
\text{Al(CH}_3)_3(g) + 6(4-y)\text{F}_2(g) & \rightarrow \text{AlF}_3(s) + 3(3-y)\text{HF}(ads,g) + 3\text{CH}_4(ads) (y \leq 3) \\
\text{AlF}_3(ads) + \text{Al(CH}_3)_3(g) & \rightarrow \text{AlF(CH}_3)_2(ads) + \text{CH}_4(g) \tag{3.2}
\end{align*}
\]

In the mechanism described by eq 5 and Figure 7, Al(CH₃)₃ reacts with both AlF₃ and HF species, while F radicals play the dominant role in the ligand removal and the fluorination reaction. These mechanisms differ from the thermal ALD process on two aspects. During the thermal ALD process, Al(CH₃)₃ is believed to only react with HF, resulting in the formation of CH₄. For the plasma-based process, the main pathway is likely the ligand-exchange reaction between Al(CH₃)₃ and AlF₃ due to the lower coverage of adsorbed HF. The second difference between the two processes is which products are formed in the co-reactant subcycle. Whereas only CH₄ is released in the thermal process, the SF₆ plasma process is characterized by the formation of CH₄F₄⁺⁺ species due to the interaction of F radicals from the SF₆ plasma with CH₃ surface groups. Furthermore, the reaction products released from the surface can undergo a wide range of reactions in the plasma.

Note that some analogies can be identified between the reaction mechanism described by eq 5 and plasma ALD of Al₂O₃ using Al(CH₃)₃, where the formation of H₂O, CH₄, and C₂H₂ species is reported. During plasma ALD of Al₂O₃, H₂O is formed due to interaction of O radicals with CH₃ surface groups, which triggers a thermal component in the reaction mechanism, resulting in the formation of CH₄. The formed CH₄ can subsequently be dissociated in the plasma and lead to the formation of C₂H₂ species. Furthermore, the OH group serves as the reactive surface site, which can be seen in analogy with adsorbed HF during AlF₃ ALD.

On the basis of the reaction mechanisms that were found, it can be speculated that SF₆ plasma as co-reactant can be combined with metal organic precursors containing carbohydrate-based ligands (i.e., metal alkyls) for the growth of metal fluorides. Similar to AlF₃ ALD, this would lead to the release of CH₃ groups in the precursor subcycle. The reaction with F...
radicals during the plasma exposure would result in the elimination of the remaining ligands and the formation of \( \text{CH}_x\text{F}_{2x-y} \) species. Note that Lee et al. demonstrated ALD of MnF\(_2\), MgF\(_2\), ZnF\(_2\), and AlF\(_3\) using metal organic compounds with carbohydrate-containing ligands as the precursors and HF as the co-reactant.\(^{46}\) In addition, they employed precursors containing alkyamide and alkoxide groups, suggesting that also these types of precursors might be combined with SF\(_6\) plasma.

Interestingly, the chemistry based on fluorination and TMA dosing can also be used for ALE of Al\(_2\)O\(_3\) at higher substrate temperatures,\(^{48}\) which was demonstrated using an SF\(_6\) plasma as the reactant in our previous work.\(^{35}\) The transition between AlF\(_3\) ALD and Al\(_2\)O\(_3\) ALE is governed by the substrate temperature and is believed to depend on the desorption temperature of AlF\(_x\)(CH\(_3\))\(_{2-x}\) species.\(^{47}\) At low sample temperatures, AlF\(_x\)(CH\(_3\))\(_{2-x}\) species remain adsorbed to the surface, leading to growth, while at higher temperatures, they desorb from the surface; hence, etching is obtained. As described by eqs 2.1 and 2.2, two steps are essential for the ALE mechanism. The top surface of Al\(_2\)O\(_3\) should be fluorinated, followed by the formation of volatile AlF\(_x\)(CH\(_3\))\(_{2-x}\) species upon TMA dosing. The data on the fluorination of Al\(_2\)O\(_3\) using SF\(_6\) plasma in Figures S1–S3 showed that an SF\(_6\) plasma converts the top surface to AlO\(_x\)F\(_y\) in a self-limiting manner, similar to when HF is used as the F-source for ALE. Furthermore, the results in Figure 2 showed negative absorbance peaks in the region below \(\sim 950\) cm\(^{-1}\) at temperatures \(\geq 200\, ^\circ\text{C}\), indicating the removal of Al\(_2\)O\(_3\). As discussed in the Experimental Section, the actual sample temperature during the experiments on the wafer coupons deviates from the sample temperature during infrared spectroscopy experiments. In our previous work, ALE was already observed at a substrate temperature of \(155\, ^\circ\text{C}\) by employing a high TMA dose of 0.5 s.\(^{35}\) This indicates that, besides the temperature, the TMA dose has an influence on the competition between deposition and etching.

5. CONCLUSIONS

Following up on previous work where the use of an SF\(_6\) plasma was demonstrated, the reaction mechanisms during AlF\(_3\) ALD using TMA and SF\(_6\) plasma were studied. On the basis of the infrared spectroscopy results and the information on gas-phase reaction products from QMS and OES, a pathway for AlF\(_3\) ALD was proposed where Al(CH\(_3\))\(_3\) reacts with AlF\(_3\) and HF surface species during the precursor subcycle. During the subsequent SF\(_6\) plasma exposure, F species fluorinate the surface and eliminate the CH\(_3\) surface groups, resulting in CH\(_x\)F\(_{2x-y}\) species as well as HF. The infrared spectroscopy data showed the growth of AlF\(_3\) at low temperatures (\(\leq 150\, ^\circ\text{C}\)) and etching of Al\(_2\)O\(_3\) at high temperatures (\(\geq 200\, ^\circ\text{C}\)), which is explained by the desorption of AlF\(_x\)(CH\(_3\))\(_{2-x}\) species at high temperatures. The postulated reaction mechanisms can be generalized to plasma ALD of metal fluorides using metal alkyl compounds as the precursor. It can be speculated that C\(_x\)H\(_y\) species are released upon adsorption of such precursors on the metal fluoride surface and that F radicals from the SF\(_6\) plasma exposure result in the elimination of the remaining ligands and the formation of CH\(_x\)F\(_{2x-y}\) species. Furthermore, it is also expected that an SF\(_6\) plasma can be employed for self-limiting fluorination of a variety of metal oxides. The understanding provided in this work can thus help to develop ALD processes for other metal fluorides as well as ALE processes for metal oxides using a fluorine-containing plasma as the F-source.
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