Revisiting the growth mechanism of atomic layer deposition of Al₂O₃

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Revisiting the growth mechanism of atomic layer deposition of Al$_2$O$_3$: A vibrational sum-frequency generation study

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I. INTRODUCTION

In microelectronics and related fields, many key advances in dry etching and thin-film deposition have been the result of detailed insight into the underlying fundamental surface reactions. The pioneering work by Coburn and Winters has been exemplary for the approach used in mechanistic studies in semiconductor processing by etching and deposition. They introduced a methodology combining the systematic aspects of fundamental surface-science studies with the close-to-actual operation conditions and the nonideal surfaces used in the etch processes. On these nonideal surfaces, additional processes can occur that are critical for understanding the etching mechanism. The value of this approach was demonstrated by their seminal work on Si etching. Similar processes play a role in the growth of thin-films by methods such as atomic layer deposition (ALD).

ALD is an enabling technology for the fabrication of semiconductor devices because of its capability to uniformly and conformally cover complex 3D structures with thin films with subnanometer thickness control. The capabilities of ALD processes are inherent to their underlying growth mechanism. In essence, ALD consists of a sequence of self-limiting surface reactions which together deposit an “atomic layer” of material. The repeatable sequence of steps is called an ALD cycle and the number of cycles can be chosen to grow a film with a certain thickness.

Currently, there is a push toward even more demanding applications for ALD films. A good example of this trend is the deposition of ALD films on temperature sensitive substrates requiring the development of low temperature or even room temperature ALD processes. In order to meet these evermore demanding requirements in a systematic way, it is essential to gain a better understanding of the surface reactions governing the ALD process. This calls for an approach similar to that of Coburn and Winters, and the success of earlier mechanistic studies of ALD growth processes highlights the value of this approach.

This work focuses on the surface chemistry of the prototypical ALD process growing Al2O3 using trimethylaluminum [TMA, Al(CH3)3] as precursor and water as coreactant. This process serves as a model system for ALD of metal-oxides with metal-organic precursors. Moreover, it is one of the more ubiquitous ALD processes. Higashi and Fleming introduced the ALD process of Al2O3 and they reported on its key aspects as well as noteworthy properties...
of the resulting Al₂O₃ films. Ensuing, many details of this ALD process have been studied intensively, and as a result, the growth mechanism is fairly well understood as will be addressed in Sec. II. Nevertheless, new insights into some of the fundamental mechanisms of this ALD process can be gained. For example, in our previous work we reported on the fundamental mechanism causing the commonly observed decrease in growth-per-cycle (GPC) at low temperatures. It was demonstrated that this decrease in GPC was caused by persistent –CH₃ groups present on the surface at low temperatures. Basically, these persistent –CH₃ groups limit the TMA uptake and therefore result in a lower GPC. Ensuing, it was demonstrated by others that these persistent groups play a key role in other ALD processes as well.

For the Al₂O₃ ALD process, several open questions pertaining to the growth mechanism were identified and investigated here: First, the origin of the self-limiting behavior in the precursor half-cycle is still debated in the literature. The conclusions drawn from experiments have been contradictory, and recently, this topic has been studied using density functional theory (DFT) indicating the need for further experimental work. Second, how the TMA chemisorbs on the -OH terminated surface is of interest. So far, indirect measurements by quadrupole mass spectrometry (QMS) and quartz-crystal microbalance have shed some light on this topic; however, a more direct measurement is desirable. Third, in our previous work, the temperature dependence of the reaction kinetics was found to be relatively complex, and it was concluded that they should be studied in more detail. Finally, the apparent paradox between virtually carbon free Al₂O₃ films, as typically reported for ALD, and the presence of the persistent –CH₃ groups at low temperatures needs to be addressed.

The nonlinear optical technique of broadband sum-frequency generation (BB-SFG) was used to study the surface chemistry during ALD of Al₂O₃. BB-SFG spectroscopy is a state of the art technique, predominantly used in the field of surface science, which is now utilized to study the surface chemistry of ALD in this work. BB-SFG spectroscopy is ideally suited for this task because of its submonolayer sensitivity, inherent surface selectivity, and fairly short acquisition times. In short, the BB-SFG signal is generated by simultaneously exposing the surface groups to a picosecond visible pulse and a femtosecond broadband mid-IR pulse. These two pulses mix, generating a new signal in the visible part of the spectrum. The mixing is resonantly enhanced for photon energies matching a vibrational transition of the surface groups. As a result, a part of the vibrational fingerprint of the surface groups is present in the visible BB-SFG signal. The surface groups can be identified by the unique spectral position of the resonances, and the density of the surface groups is proportional to the strength of those resonant signals. For example, the C-H stretch mode of –CH₃ groups at ~2900 cm⁻¹ can be used to identify the presence of these groups and to study their density on the surface. A key merit of BB-SFG spectroscopy is that the detected signals are proportional to the square of the absolute surface coverage. Moreover, because of its inherent surface selectivity, differential spectra are not required. This allows a more direct interpretation of the data and requires less prior knowledge of the system under investigation than a differential technique such as Fourier transform IR (FTIR) absorption spectroscopy.

Because BB-SFG spectroscopy is not yet established in the field of ALD, it is valuable to explore its capabilities and verify whether the –CH₃ and –OH surface groups resulting from TMA and H₂O exposure during ALD can be detected. For this purpose, an isotope study using H₂O, D₂O, Al(CH₃)₃, and Al(CD₃)₃ was performed. The aforementioned open questions were investigated with BB-SFG spectroscopy. The reaction kinetics during the H₂O half-cycle was studied by BB-SFG spectroscopy by measuring the –CH₃ density as a function of coreactant exposure, i.e., a type of saturation curve was established. To address the influence of temperature on the reaction kinetics, these experiments were performed at different temperatures ranging from 100 up to 300 °C. To gain more quantitative information about the surface chemistry, the absolute areal density of –CH₃ surface groups was determined after both half-cycles for ALD between 100 and 450 °C. This data yielded insights into the origin of the self-limiting nature of the ALD reactions and the chemisorption of TMA itself. A separate x-ray photo-emission spectroscopy (XPS) experiment was performed to study the possible incorporation of carbon into the film from –CH₃ groups remaining at the surface after the H₂O step.

The manuscript is organized as follows: A brief recapitulation of the growth mechanism of Al₂O₃ ALD is given in Sec. II. This provides the necessary background for the interpretation of the experimental results and puts the results in their proper perspective. In Sec. III, the experimental details are given. In Sec. IV, the results are presented and discussed. The section is divided into four parts: basic surface chemistry, reaction kinetics, quantification of the –CH₃ coverage, and carbon incorporation. In Sec. V, the main conclusions are given.

II. GROWTH MECHANISM OF ALD OF Al₂O₃

The growth of Al₂O₃ during steady-state ALD is ruled by surface chemistry involving predominantly –CH₃ and –OH groups. A schematic representation of the growth mechanism is shown in Fig. 1. At the beginning of the TMA half-cycle, the surface is –OH terminated. This surface is exposed to vapor phase TMA which chemisorbs on the –OH groups. Each chemisorbed TMA molecule reacts with one or two –OH groups. This ligand exchange reaction releases gas phase CH₄ as a volatile reaction product. After a sufficiently large precursor exposure, no more TMA can chemisorb on the surface. This is the self-limiting aspect of the chemistry, and the half-cycle is said to be “in saturation,” resulting in a –CH₃ terminated surface. At the end of the TMA half-cycle, the gas phase reaction products (CH₄) and excess precursor are removed from the reactor by purging and/or pumping. In the ensuing H₂O half-cycle, vapor phase H₂O reacts with the
In these equations, the “–” sign indicates a surface species –OH terminated while a layer of Al2O3 has been deposited, removed by purging and/or pumping. The surface is now molecules and gas phase reaction products are again observed involving the same surface groups: After the H2O exposure, the number of –CH3 groups decreased and the number of –OH groups increased. This indicates that vapor phase H2O reacted with –CH3 groups, removing the –CH3 groups from the surface and forming –OH groups. This observation is in line with Eq. (1b).

Evidence for the gas phase reaction products can also be obtained with FTIR using an alternative measurement of Al atoms terminated by –CH3 groups. (a) In the TMA half-cycle, TMA chemisorbs on the –OH site as described in Eq. (1a). For the H2O half-cycle, the opposite trends are observed involving the same surface groups: After the H2O exposure, the number of –CH3 groups decreased and the number of –OH groups increased. This indicates that vapor phase H2O reacted with –CH3 groups, removing the –CH3 groups from the surface and forming –OH groups. This observation is in line with Eq. (1b).

Reciprocal interconversion of surface groups is observed when TMA and H2O adsorb on an Al2O3 surface. This ligand exchange reaction replaces the –CH3 groups with –OH groups and again releases gas phase CH4. This reaction is also self-limiting, and at the end of this half-cycle, the remaining coreactant molecules and gas phase reaction products are again removed by purging and/or pumping. The surface is now –OH terminated while a layer of Al2O3 has been deposited, and the cycle can be repeated. In their simplest form, these reactions can be summarized as follows:

\[ x \text{–OH} + \text{Al(\text{CH}_3)_3} \rightarrow \text{OA}(\text{CH}_3)_3 + (3-x)\text{CH}_4, \]  
\[ -\text{Al(\text{CH}_3)} + \text{H}_2\text{O} \rightarrow -\text{AlOH} + \text{CH}_4. \]

In these equations, the “–” sign indicates a surface species and \( x \) represents the number of –CH3 ligands bonded to Al remaining after chemisorption. There exist several secondary reaction pathways with, e.g., different reactive sites that might contribute to the ALD growth. For example, TMA chemisorption has been shown to occur on Al–O–Al bridges, carbonates, and formates. However, the growth via these secondary reaction paths is generally small compared to the growth via the reaction path in Eq. (1).

The surface chemistry of Al2O3 ALD has been studied extensively with FTIR absorption spectroscopy. These measurements confirmed that the surface chemistry was dominated by the –CH3 and –OH groups when employing TMA and H2O. It is insightful to provide some background information on FTIR spectroscopy before discussing a typical result. To study the surface chemistry of ALD with FTIR absorption spectroscopy, the absorption of infrared radiation by a monolayer of –CH3 or –OH groups needs to be detected. This contribution is small compared to other elements in the optical path absorbing infrared radiation such as the bulk of the substrate on which ALD is performed. To eliminate the contributions by other elements not related to the surface groups and to facilitate the interpretation of the data, it is convenient to work with so called “difference spectra.” Such a difference spectrum is calculated from spectra recorded directly before and after a half-cycle. The main difference between the two spectra is the absorption due to the change in surface groups; hence, the difference of the two spectra will emphasize these changes. A positive (negative) peak in a difference spectrum indicates the increase (decrease) of the presence a specific surface group. Note that this approach will only reveal species that are changing.

Ott et al. used this approach to study which surface groups are involved in the growth of Al2O3 by ALD. Figure 2 shows the FTIR difference spectra they reported in their work for both the TMA and H2O half-cycle. For the TMA half-cycle, an increased absorption in the C–H stretch region around 2900 cm\(^{-1}\) can be seen. This implies an increase in the number of –CH3 groups on the surface. The negative peak in the O–H stretch region around 3700 cm\(^{-1}\) indicates that the number of –OH groups has decreased after TMA exposure. From these observations, it can be inferred that TMA has chemisorbed on the –OH site as described in Eq. (1a). For the H2O half-cycle, the opposite trends are observed involving the same surface groups: After the H2O exposure, the number of –CH3 groups decreased and the number of –OH groups increased. This indicates that vapor phase H2O reacted with –CH3 groups, removing the –CH3 groups from the surface and forming –OH groups. This observation is in line with Eq. (1b).

Evidence for the gas phase reaction products can also be obtained with FTIR using an alternative measurement approach.
scheme. In this scheme, the gas phase reaction products need to be present during the acquisition of one FTIR spectrum and absent during another acquisition. The difference spectrum now contains information about the gas phase species which were present. It is possible to follow the progress of the reactions during a half-cycle, by exposing the surface to multiple consecutive short exposures instead of a single long exposure. Figure 3 shows a set of FTIR spectra identifying the gas phase species formed during ALD. For the TMA half-cycle shown in Fig. 3(a), the first TMA exposure produces mainly CH\textsubscript{4} identified by its unique IR fingerprint.\textsuperscript{24} A trace of unreacted TMA can also be seen in the figure.\textsuperscript{24,27} Both the second and the third TMA exposure show less CH\textsubscript{4} production and the signature of (unreacted) TMA becomes more evident. During the H\textsubscript{2}O half-cycle shown in Fig. 3(b), both gas phase CH\textsubscript{4} and vapor phase H\textsubscript{2}O were seen after the first H\textsubscript{2}O exposure. Again less CH\textsubscript{4} was produced in the subsequent exposures. These results show that the observed gas phase reaction products are in line with Eq. (1). Moreover, the trends in the amount of gas phase reaction products and the consumption of the precursor and coreactant are in agreement with the self-limiting nature of the ALD reactions.

Complementary to FTIR spectroscopy, QMS is often used to identify and monitor the gas phase reaction products. In QMS, gas phase species are first ionized and subsequently filtered on the basis of their mass-to-charge ratio (m/z). Figure 4 shows the QMS signals recorded during ALD of m/z ratios of 15, 18, and 57 corresponding predominantly to CH\textsuperscript{+}, H\textsubscript{2}O\textsuperscript{+}, and Al(CH\textsubscript{3})\textsuperscript{+}\textsubscript{2}, respectively. In this case, the QMS signal strength scales with the partial pressure of the specific gas phase molecule. In the precursor half-cycle, TMA was dosed in five consecutive exposures of 40 ms each. The top panel in Fig. 4 shows the m/z = 57 signal corresponding to Al(CH\textsubscript{3})\textsuperscript{+}\textsubscript{2}, which is indicative of TMA. The first two exposures of TMA do not give rise to a peak in the m/z = 57 signal, indicating that all the TMA is consumed before it can reach the mass spectrometer. This is similar to the result in Fig. 3 where the majority of the TMA was also consumed in the first exposure. Each time the sample was exposed to TMA, an increase in the m/z = 15 signal was observed corresponding to CH\textsuperscript{+}. This ion can be produced by ionization of either gas phase CH\textsubscript{4} or gas phase TMA depending on their ionization cross section. For each TMA half-cycle, five consecutive TMA exposures were performed. Assuming that no TMA was consumed in the last exposure and thereby ascribing the entire signal to TMA yields an upper limit for the contribution of TMA to the CH\textsuperscript{+} signal. From Fig. 4, it can be seen that the TMA contribution to the CH\textsuperscript{+} signal is indeed small. In the coreactant half-cycle, H\textsubscript{2}O was dosed in five consecutive exposures of 100 ms each. The lower panel of Fig. 4 shows the m/z = 18 signal indicative of H\textsubscript{2}O. Again, gas phase CH\textsubscript{4} was observed as a reaction product. In this half-cycle, there is no

![Fig. 3](image-url)

**Fig. 3.** (Color online) Gas-phase reaction products during ALD of Al\textsubscript{2}O\textsubscript{3} measured with infrared absorption spectroscopy for three consecutive precursor and coreactant exposures labeled chronologically in (a) a TMA half-cycle and (b) a H\textsubscript{2}O half-cycle. The peak assignments are given in the figure. For both half-cycles, the produced amount of CH\textsubscript{4} decreased with each exposure as a result of the self-limiting nature of the reactions. These experiments were carried out in the home-built reactor ALD-I at 145°C (Ref. 27).

![Fig. 4](image-url)

**Fig. 4.** (Color online) Gas phase species measured with QMS as a function of time for ALD using consecutive exposures of TMA and H\textsubscript{2}O. (a) For the TMA half-cycle, the first two TMA exposures (out of five) was fully consumed by the reaction with surface groups, as can be seen from the m/z = 57 signal due to Al(CH\textsubscript{3})\textsuperscript{+}\textsubscript{2} indicative of TMA. (b) For both the TMA and H\textsubscript{2}O exposures, a peak was observed in the m/z = 15 signal that is mainly due to CH\textsuperscript{+} indicative of CH\textsubscript{4} as a gas phase reaction product. (c) For the H\textsubscript{2}O half-cycle, all H\textsubscript{2}O exposures resulted in a clear peak in the m/z = 18 signal that is mainly due to H\textsubscript{2}O\textsuperscript{+} and indicative of H\textsubscript{2}O. These experiments were carried out in an Oxford Instruments FlexAL reactor with a sample and wall temperature of 100°C.
ambiguity in the assignment of the \( m/z = 15 \) signal as no TMA was present. The \( m/z = 18 \) signal shows \( \text{H}_2\text{O} \) molecules reaching the QMS apparatus even in the first exposure. This is different from the TMA half-cycle, where no TMA reached the detector in the first two exposures. This difference is caused in part by the lower reactivity of \( \text{H}_2\text{O} \) toward \(-\text{CH}_3\) groups than TMA to \(-\text{OH}\) groups. To recapitulate, the gas phase reaction products measured with both FTIR and QMS are in line with the reactions given in Eq. (1).

A key step in the characterization of an ALD process is to verify that the surface chemistry is indeed self-limiting. This is often done by measuring the influence of the precursor and co-reactant exposure on the GPC. If the ALD process is well behaved, the GPC approaches a horizontal asymptotic value for sufficiently long exposures and purge steps, i.e., the GPC shows saturation. Figure 5 shows the variation in the GPC as a function of precursor exposure, co-reactant exposure, and purge time measured with spectroscopic ellipsometry (SE). To study the influence of a single parameter in these experiments, all other steps were made sufficiently long to ensure their saturation. The GPC showed saturation for a precursor exposure of \( \gtrsim 20 \) ms and a co-reactant exposure of \( \gtrsim 10 \) ms. For the purge steps, saturation was observed for purges of \( \gtrsim 1 \) s. The GPC for the optimized ALD cycle was \( \sim 1.0 \) Å, a typical value for \( \text{Al}_2\text{O}_3 \) ALD at a deposition temperature of 250°C.

The deposition temperature has a significant influence on the ALD process. The lowest practical temperature for thermal \( \text{Al}_2\text{O}_3 \) ALD is \( \sim 150 \) °C. At lower temperatures, the ALD cycle becomes quite long because \( \text{H}_2\text{O} \) is difficult to remove at low temperatures resulting in extremely long purge steps. Also the mass density of the deposited \( \text{Al}_2\text{O}_3 \) decreases significantly for deposition temperatures below 150°C. For example, Groner et al. showed that a deposition at 33°C requires a cycle time of \( \sim 200 \) s (compared to, e.g., 4 s) and the mass density of the film is \( \sim 20\% \) less than for films grown at high temperatures. Temperature also has an impact on the GPC of the \( \text{Al}_2\text{O}_3 \) ALD process. The GPC in Fig. 5 was expressed in thickness, labeled here as GPC(nm), which is a suitable parameter if, e.g., a certain thickness is required for an application. Moreover, it can be measured by, e.g. in situ SE. Alternatively, the GPC can be expressed as the number of atoms deposited per surface area, labeled as GPC(at). This quantity is more closely related to, e.g., the number of precursor molecules chemisorbing on the surface per cycle. For mechanistic studies, the GPC(at) is therefore more suited. Basically, the GPC(at) can be calculated from the GPC(nm) if the atomic density (atoms/m³) and the stoichiometry of the film are known. A direct method of determining the GPC(at) is Rutherford backscattering spectrometry (RBS). In RBS, the areal density of a specific atom is measured. Dividing the areal density by the number of ALD cycles used to prepare the film results in the GPC(at). On the other hand, as stated before, the GPC(at) is given by the atomic density multiplied by the GPC(nm). Both the atomic density and the GPC(nm) can be measured with x-ray reflectivity (XRR), or more indirectly with SE using the Lorentz–Lorenz relation. The temperature trend in the GPC(at) for the thermal process shows an increase with temperature up to \( \sim 200 \) °C. For temperatures above \( \sim 250 \) °C, the GPC(at) decreases steadily with temperature. For the PE-ALD process, the GPC(at) decreases monotonically with temperature. The cause of these trends will be discussed later. General consensus is lacking on the exact upper temperature limit at which it is no longer possible to achieve self-liminating growth and hence ALD. However, it has been reported that the precursor starts to decompose above \( \sim 450 \) °C.

![Fig. 5](image1.png)  
**Fig. 5.** (Color online) So-called saturation curves for thermal ALD of \( \text{Al}_2\text{O}_3 \) at 250°C. The growth-per-cycle [GPC(nm)] as a function of (a) the TMA and (c) the \( \text{H}_2\text{O} \) dose and (b) and (d) their corresponding purge steps. The lines serve as a guide to the eye. The experiments were carried out in an Oxford Instruments OpAL reactor, and the data were taken from Dingemans and Kessels (Ref. 29).

![Fig. 6](image2.png)  
**Fig. 6.** (Color online) Growth per cycle in terms of \( \text{Al} \) atoms per surface area [GPC(at)] for (a) thermal and (b) PE-ALD as reported in the literature. For the data obtained with RBS and XRR, the data was used as reported. For works reporting the GPC determined with SE, the GPC(at) was calculated from the reported refractive index and the GPC(nm). The data were taken from Matero et al., van Hemmen et al., Groner et al., and Potts et al. (Refs. 6, 7, 21, and 30). The solid line serves as a guide to the eye.
The deposition temperature also influences the density and stoichiometry of the ALD Al₂O₃ films to a certain extent. The Al₂O₃ films deposited by ALD, i.e., typically below 450 °C, are all amorphous. The structure of this amorphous material changes with temperature, going from a local structure similar to that of x-Al₂O₃ at high temperatures to a structure closer to amorphous aluminium oxide hydroxide [AlO(OH)] for deposition at low temperatures.³⁶ This trend is also reflected in the stoichiometry of the films which are slightly O rich at high temperatures.⁶,7,2¹,3²,3⁶,3⁷ At lower temperatures, the films become even more O rich,⁶,7,2¹,3²,3⁶,3⁷ in line with the AlO(OH) structure. The films prepared with thermal ALD are generally carbon free, even when deposited at low temperatures.²¹ Furthermore, an increasing amount of thermal ALD are generally carbon free, even when deposited at low temperatures.²¹ The mass density of the Al₂O₃ prepared at low temperatures is also reflected in the stoichiometry of the films which are slightly O rich at high temperatures.⁶,7,2¹,3²,3⁶,3⁷ At lower temperatures, the films are even more O rich.⁶,7,2¹,3²,3⁶,3⁷ For comparison, the density of crystalline x-Al₂O₃ and γ-Al₂O₃ are 3.99 and 3.97 g/cm³, respectively.³⁸

III. EXPERIMENTAL DETAILS
A. ALD setup and sample preparation

The growth mechanism of ALD was studied using BB-SFG spectroscopy in a purpose-built ALD reactor (see also Fig. 7). The reactor chamber consisted of two parts; both were equipped with a turbomolecular pump (Pfeiffer TMU 261P) with an individual backing pump. Both parts reached a base pressure of <1 × 10⁻⁶ mbar. The backing pumps were also used as roughing pumps. The ALD precursors [Al(CH₃)₃ and Al(CD₃)₃] and coreactants (H₂O and D₂O) were dosed into the ALD Gasses reactor with fast ALD valves (Swagelok). The ALD reactor, the laser system, and the key optical components used for BB-SFG spectroscopy, the surface groups are simultaneously irradiated with a spectrally narrow visible pulse and a broadband mid-IR pulse. The visible laser pulses were generated using a regenerative amplifier (Spectra-Physics Spitfire) producing pulses with a duration of ~90 fs at a repetition rate of 1 kHz. This amplifier was seeded with a mode-locked oscillator (Spectra-Physics Tsunami) and pumped with intracavity doubled, diode-pumped Nd doped yttrium lithium fluoride laser (Spectra-Physics Evolution 30). The average output power of Spitfire was 1.5 W. From this output beam, 30% of this light was used as the visible pulse in the BB-SFG experiment. To get the desired spectral and temporal shape, the visible light was passed through an etalon (CVI F1.1–800). The mid-IR laser pulse was generated from the remaining ~70% of the visible light using an optical parametric amplifier (Spectra-Physics TOPAS-C) with an additional difference-frequency mixer. The mid-IR beam and the visible beams were directed toward the ALD reactor, synchronized with a delay line, and focused noncollinearly onto the sample. A separate set of optics was used for each of the two beams. For the mid-IR beam a combination of a positive and a negative CaF₂ lens were used. This combination of lenses improved the numerical aperture and allowed a tighter focus (effective focal length 750 mm). The visible beam, which was much larger in diameter than the mid-IR beam, was focused on the sample with a single lens (focal length 750 mm). A CaF₂ window was used to admit the two laser beams. The two pulses impinged on the sample in a reflection geometry at an angle of incidence ~30° from the surface normal.

The BB-SFG signal exited the reactor through a fused silica window and was filtered spatially (using two irises of ~4 mm) and spectrally (using four Thorlabs FES0750 filters each with an optical density >5). The S-polarized component of the BB-SFG beam was selected with a polarizer and focused on the slit of the spectrometer. The BB-SFG signal was detected with an Acton Research SP2500 spectrometer and Princeton Instruments 100B CCD camera. The polarization combination of the BB-SFG signal recorded in this

![Fig. 7.](https://example.com/fig7.png)
work is $S_p$ (S-polarized SFG, $x$-polarized visible, and $p$-polarized mid-IR light).

The relative surface coverage $\rho$ of the measured groups was determined from the BB-SFG spectra. The resonant contribution caused by a vibrational mode of a surface group, e.g., the C-H stretch mode of a $-\text{CH}_3$ group, was modeled using a Lorentzian line shape. Furthermore, a small nonresonant contribution $I_{NR}$ had to be included. The spectral shape of the BB-SFG signal $I(\omega)$ for a single resonance was described by

$$I(\omega) \propto |I_{NR} + \rho \frac{A e^{-i\phi}}{\omega^2 + \omega_{res}^2 + \Gamma} I_{vis}I_{ir}|^2,$$

with $I_{vis}$ and $I_{ir}$ the intensity of the visible and mid-IR beams exciting the surface groups. The resonant contribution was described by: $A$ the cross section of the SFG process for the specific resonance, $\phi$ the phase of the resonance, $\omega_{res}$ the resonance frequency, and $\Gamma$ the broadening of the resonance. The spectra were modeled by fitting this equation to the data using a least-squares algorithm.

IV. RESULTS AND DISCUSSION

A. Basic surface chemistry

The C-H stretch region of the BB-SFG response was probed after the TMA and H$_2$O half-cycle during steady-state ALD growth of Al$_2$O$_3$ at 250°C. To ensure steady-state growth, five ALD cycles were performed before recording a BB-SFG spectrum. After this preparation, an ALD cycle was performed and a BB-SFG spectrum was recorded after each half-cycle with the mid-IR laser tuned to 2850 cm$^{-1}$ (see Fig. 8). After the TMA half-cycle, the C-H stretch mode of the $-\text{CH}_3$ surface groups was indeed observed at 2890 cm$^{-1}$. After the $\text{H}_2\text{O}$ cycle, a flat spectral response was recorded in this region, indicating that all the $-\text{CH}_3$ groups were removed by the H$_2$O exposure. The O-H stretch mode of the $-\text{OH}$ surface groups (3690 cm$^{-1}$) falls outside of the spectral region probed with the mid-IR laser tuned to 2850 cm$^{-1}$. In principle it was possible to tune the laser to a different wavelength and probe the O-H stretch region. However, for such a measurement, the beam path ($\sim$10 m) would need to be purged with, e.g., dry nitrogen to remove ambient H$_2$O. More importantly, it is preferable to probe both $-\text{CH}_3$ and $-\text{OH}$ groups with the same laser pulses without tuning the laser system, allowing a comparison of the relative $-\text{CH}_3$ and $-\text{OH}$ peak height eliminating a laborious and error prone calibration procedure. Replacing H$_2$O with D$_2$O conveniently shifts the vibrational frequency of the O-H stretch mode into the spectral range probed with the laser tuned to 2850 cm$^{-1}$. This shift is related to the heavier mass of D compared to H which should shift the stretch mode toward lower wavenumbers by a factor of $\sqrt{\frac{M_D}{M_H}} = \sqrt{2}$. Figure 8 shows the BB-SFG spectra recorded for ALD with either H$_2$O or D$_2$O, with all other factors being unchanged. The BB-SFG spectrum for the TMA half-cycle for the TMA/H$_2$O process was identical to that of the TMA/D$_2$O process. This demonstrates that the surface chemistry was not affected when H$_2$O was replaced with D$_2$O. The $-\text{OD}$ groups were successfully detected after the D$_2$O half-cycle at 2725 cm$^{-1}$. Note that the spectral position and shape of the resonance indicate that the $-\text{OD}$ groups on a surface have negligible H-bridges. Such bonding would induce a shift and a significant broadening (spanning $\geq$200 cm$^{-1}$) of the peak otherwise. To recapitulate, both the $-\text{CH}_3$ and the $-\text{OD}$ groups were observed with BB-SFG with a sensitivity better than 10% of a monolayer.

To study the influence of temperature on the surface groups, BB-SFG spectra were also collected for ALD at 150°C using TMA and D$_2$O. Comparing the BB-SFG spectra recorded after the TMA half-cycle in Fig. 9 for ALD at 150 and 250°C reveals a stronger $-\text{CH}_3$ signal at 150°C indicating that more $-\text{CH}_3$ groups are present on the surface. This was attributed to thermally induced dehydroxylation which increases with temperature, resulting in a lower $-\text{OH}$ coverage at high temperatures and therefore a lower TMA uptake. Furthermore, it is known from our earlier work that for ALD of Al$_2$O$_3$ at temperatures below $\sim$200°C there are persistent $-\text{CH}_3$ groups remaining on the surface after the H$_2$O half-cycle. The persistent $-\text{CH}_3$ groups were also observed in this experiment for ALD at 150°C and absent at 250°C. The spectrum recorded after the D$_2$O half-cycle for ALD at 150°C clearly showed both $-\text{CH}_3$ and $-\text{OD}$ groups. The interpretation of the small differences in shape and area of the $-\text{OH}$ signal at 150 and 250°C is not straightforward and beyond the scope of this work. Replacing TMA with a fully deuterated molecule [D-TMA, Al(\text{CD}_3)₃] should lead to a shift of the stretch mode of the $-\text{CH}_3$ groups by a factor of $\sqrt{2}$ toward lower wavenumbers. Figure 10 shows the signal of the C-D stretch mode of the $-\text{CD}_3$ groups which was detected at 2125 cm$^{-1}$ which is indeed shifted by a factor of $\sqrt{2}$ compared to the stretch mode of $-\text{CH}_3$ at 2890 cm$^{-1}$. The signal-to-noise

![Fig. 8. (Color online) BB-SFG spectra recorded after a TMA and a H$_2$O or D$_2$O half-cycle for ALD of Al$_2$O$_3$ at 250°C. (a) The stretch mode of the $-\text{CH}_3$ groups was visible after the TMA half-cycle. Replacing H$_2$O with D$_2$O shows an identical spectrum for the TMA half-cycle. (b) The stretch mode of the $-\text{OD}$ groups after the H$_2$O half-cycle cannot be observed as it falls outside of the spectral range of the measurement. In the D$_2$O half-cycle, a broad feature around 2725 cm$^{-1}$ is visible, which is the stretch mode of $-\text{OD}$ groups on the surface.](image-url)
level is rather poor due to the lower output power of the mid-IR laser at this wavelength used to probe the surface groups. Possibly, the signal-to-noise ratio was reduced even more by a lower SFG cross section due to the deuteration. Nevertheless, not only did the \(-\text{CD}_3\) signal appear at the expected position, it also behaved as described in Eq. (1). The \(-\text{CD}_3\) signal appeared after the D-TMA half-cycle and disappeared after the D$_2$O half-cycle. This additional evidence corroborates the assignment of the signal at 2890 cm$^{-1}$ to the C-H stretch mode of \(-\text{CH}_3\) surface groups.

To summarize, at high temperatures, the chemistry of Al$_2$O$_3$ ALD is described accurately by Eq. (1): After the TMA half-cycle, the surface is covered by \(-\text{CH}_3\) groups. After the H$_2$O half-cycle, there are only \(-\text{OH}\) groups on the surface. For ALD at low temperatures, only \(-\text{CH}_3\) groups were observed after the TMA half-cycle. However, after the H$_2$O half-cycle, both \(-\text{OD}\) and persistent \(-\text{CH}_3\) groups were present on the surface.

**B. Reaction kinetics**

Fundamental insight into the surface reactions ruling ALD can be gained by studying the reaction kinetics and their temperature dependence. By definition, the reaction kinetics describes how the reaction rate depends on the reactant exposure. The reaction kinetics of steady-state ALD were measured for both half-cycles by monitoring the \(-\text{CH}_3\) signal as a function of precursor and coreactant exposure. Note that for this experiment the central wavelength of the mid-IR laser was re-tuned to obtain the best possible signal-to-noise ratio for the \(-\text{CH}_3\) signal. Figure 11 shows how the \(-\text{CH}_3\) signal varied as a function of TMA and H$_2$O exposure during ALD at 150 °C. For ALD at 150 °C, the surface is covered with both \(-\text{OH}\) and persistent \(-\text{CH}_3\) groups at the start of the TMA half-cycle. This can be seen in Fig. 11 from the nonzero \(-\text{CH}_3\) signal at the end of the H$_2$O half-cycle and at the start of the TMA half-cycle. This surface, terminated with both \(-\text{OH}\) and \(-\text{CH}_3\) groups, was exposed to TMA by pulsing the ALD valve for 20 ms. The increase in the intensity of the \(-\text{CH}_3\) signal can be seen in Fig. 11(a) reflected an increase in the amount of \(-\text{CH}_3\) groups on the surface. This procedure was repeated until the \(-\text{CH}_3\) signal no longer increased, i.e., saturation was reached. The surface at the end of the TMA half-cycle is the starting surface for the subsequent H$_2$O half-cycle. A BB-SFG spectrum was recorded at the beginning of the H$_2$O half-cycle [see also the top spectrum in Fig. 11(b)]. Then, the surface was exposed to vapor phase H$_2$O by pulsing the ALD valve for 40 ms, resulting in the removal of a part of the \(-\text{CH}_3\) groups. This procedure was repeated until the \(-\text{CH}_3\) coverage no longer changed indicating that saturation was reached. The \(-\text{CH}_3\) groups still present on the surface were no longer reactive toward H$_2$O, i.e., persistent \(-\text{CH}_3\) groups.
Figure 12 shows the relative –CH3 density $\theta_{\text{CH}}$ as a function of the duration of the H2O exposure. The relative –CH3 density was determined from the BB-SFG spectra in Fig. 11 by fitting the spectra with the appropriate peak shape.\textsuperscript{18,23,44} The experiment was performed at temperatures between 100 and 300 °C to determine how temperature affects the reaction kinetics. For high temperatures, the reaction in the H2O half-cycle was fast and removed all the –CH3 groups, whereas for lower temperatures, the reaction slowed down and saturated before all the –CH3 groups were removed, resulting in the aforementioned persistent –CH3 groups. An additional check with a prolonged H2O exposure of 400 and 800 ms exposure (not shown) was performed at 150 °C and did not reveal an additional –CH3 removal.

The reaction kinetics plotted in Fig. 12 describe the relation between the H2O flux, $\Gamma_{\text{H2O}}$, and the change in –CH3 coverage, $d\theta_{\text{CH}}/dt$. The reaction in the H2O half-cycle, given by Eq. (1b), can be described by the following equation:

$$\frac{d\theta_{\text{CH}}}{dt} = -\sigma_{\text{H2O}}\theta_{\text{CH}}\Gamma_{\text{H2O}}. \quad (3)$$

in which $\sigma_{\text{H2O}}$ is the reaction cross section. The reaction cross section (with units cm\(^2\)) is closely related to the initial reaction (or sticking) probability $S_0 = \sigma_{\text{H2O}}N_{\text{full}}$ with $N_{\text{full}}$ the absolute –CH3 coverage after a saturated TMA step. $S_0$ represents the probability that a H2O molecule reacts with a –CH3 group when it impinges on a fully –CH3 covered surface. The solution of Eq. (3) is given by an exponential function $[\exp(-\sigma_{\text{H2O}}\Gamma_{\text{H2O}}t)]$ and describes the reaction kinetics at high temperatures. The decay seen at low temperatures (below 200 °C) cannot be described by this exponential function alone. The reaction saturates before all the –CH3 groups are removed, i.e., the persistent –CH3 groups on the surface. This means that at low temperatures the reaction kinetics cannot be described with a single first-order reaction with a constant cross section.

To explain these reaction kinetics, two models are proposed. Either there are two kinds of –CH3 groups or the reactivity of the –CH3 groups is coverage dependent. In the first model, each of the two kinds of –CH3 groups has its own reaction, and Eq. (1b) consists of two parallel reaction paths. The reaction for the reactive type of –CH3 has a low activation energy and occur at typical ALD temperatures. The reaction for the persistent –CH3 groups has a higher activation energy such that this reaction only occurs at elevated temperatures resulting in persistent –CH3 at low temperatures. In this model, the relative coverage of the reactive groups is described by an exponential function of the H2O exposure (assuming this reaction is a first order reaction). The persistent groups are described by a variable at low temperatures and by exponential function at high temperatures. This model was also discussed in our previous work.\textsuperscript{18} The underlying microscopic cause for the two types of –CH3 groups might be due to different reactivity of various surface sites of the –CH3 groups, analogous to reactions at step edges and terraces on crystalline surfaces. On these ideal surfaces, large differences in reactivity are observed. For example, the reaction rate of H\(_2\) dissociation on a Pt surface depends on the crystal face, e.g., Pt(100) versus Pt(111), and on the step-edge density.\textsuperscript{45}

The second model, a coverage dependent reactivity of the –CH3 groups, is also known from the field of surface science. This occurs, for example, for the oxidation of CO on a rhodium surface where a strong coverage dependence in the reactivity was found.\textsuperscript{46,47} A similar effect was reported for the dimethylamine precursor in CVD, where the adsorption of the precursor showed a coverage dependent reaction cross section.\textsuperscript{48} Moreover, the support for the existence of this mechanism in ALD can be found in recent \textit{ab initio} work by Shirazi and Elliott.\textsuperscript{20} In their DFT simulations, isolated –CH3 groups are not reactive toward H2O (i.e., a high activation energy). On the other hand, clusters of three –CH3 groups are reactive toward H2O. If the microscopic reaction cross section depends on number of neighboring –CH3 groups, it is likely that the macroscopic cross section depends on the surface coverage. This model, assuming a nonconstant reaction cross section $\sigma(\theta)$, leads to an change in Eq. (3) for the H2O half-cycle, substituting $\sigma_{\text{H2O}}$ by $\sigma_{\text{H2O}}(\theta_{\text{CH}}) = \sigma(\theta_{\text{CH}})$. The coverage dependent cross section can be calculated from the data in Fig. 11 by rearranging Eq. (3). Note that the unknowns in the resulting expression for $\sigma_{\text{H2O}}(\theta_{\text{CH}})$ —namely, $\Gamma$, $\theta_{\text{CH}}$, and $d\theta_{\text{CH}}/dt$—were all measured in the experiment which means that $\sigma$ can be calculated from this data set. Figure 13 shows the reaction cross section of the H2O half-cycle as a function of surface coverage calculated from the data in Fig. 12. For ALD at higher temperatures, the cross section is independent of the surface coverage. For lower temperatures, the value of the cross section decreases, and below 200 °C, the cross section shows a coverage dependence. For comparison, the reaction cross section of the TMA half-cycle reported in our previous work was $\sigma = 6.5 \times 10^{-18}$ cm\(^2\). For TMA, the cross section was found to be independent on surface coverage, did not vary with temperature in the investigated range between 100 and 300 °C, and is 2 orders of magnitude larger than that of H2O.\textsuperscript{18}
In the context of the coverage dependent reactivity model, the temperature dependence of the reactivity of the –CH\textsubscript{3} groups toward H\textsubscript{2}O can be described in terms of an activation energy. This temperature dependence, for a reaction dominated by a single rate limiting step, is described by the Arrhenius equation. Figure 14 shows a so-called Arrhenius plot of the reaction cross section (taken from Fig. 13) versus the reciprocal temperature. For $\theta_{\text{CH}} = 1$, the reaction cross sections do indeed fall on a straight line in the Arrhenius plot yielding an activation energy of $E_a = 0.27$ eV. Note that also the sticking probability $S$ is often used in the Arrhenius plot to determine the activation energy. Strictly speaking, the use of $\sigma$ yields results that are the closest to the microscopic description of the reaction, but the results with $S$ are comparable (varying by $\sim 0.01$ eV). The activation energy was also determined for surface coverages $\theta_{\text{CH}} < 1$ with the same procedure using the reaction cross sections at other coverages.

To summarize, at high temperatures, the reactions in the H\textsubscript{2}O half-cycle obey first-order reaction kinetics. Below 200°C, the reaction kinetics can no longer be described as a first-order reaction and persistent –CH\textsubscript{3} groups remain on the surface. Two possible models were proposed to account for these observations: (1) There are two types of –CH\textsubscript{3} groups each with its own reactivity. (2) The reactivity of the –CH\textsubscript{3} groups depends on the surface coverage at low temperatures. Both models are established in the field of surface science, they can equally well describe the data, and both models are not necessarily mutually exclusive. However, we prefer the coverage dependent model because this effect has been observed in the related deposition process of CVD and was actually predicted for the Al\textsubscript{2}O\textsubscript{3} ALD process by \textit{ab initio} DFT simulations.

C. Quantification of the –CH\textsubscript{3} density

The relative –CH\textsubscript{3} coverage after the TMA and the H\textsubscript{2}O half-cycle was measured with BB-SFG spectroscopy for
ALD between 100 and 450 °C. At each temperature, five ALD cycles were performed to ensure steady-state growth at that temperature. During the subsequent ALD cycle, BB-SFG spectra were collected after each half-cycle. Then, the temperature was raised by 50 °C, and the measurement procedure repeated after the temperature had settled. It was not practical to simultaneously investigate the reaction kinetics and determine the –CH3 coverage in a single experiment. BB-SFG spectra can only be compared if the optical alignment of the setup remained unaltered. The daily adjustments to the setup limited the number of spectra which could be measured in a single run. To cover a wider temperature range in a single run, spectra were only collected after a saturated half-cycle. With this approach, it was possible to measure the –CH3 coverage from 100 up to 300 °C in one run and from 300 up to 450 °C in a second run. By measuring the –CH3 coverage at 300 °C twice, the influence of possible changes to the optical alignment could be determined. The spectra recorded in this fashion are shown in Fig. 15. For the TMA half-cycle, a gradual decrease of the –CH3 signal with temperature was observed. Comparing the spectra for the TMA half-cycle, the depletion of undercoordinated oxygen sites is the cause of saturation. Both the trend in the –CH3 signal with temperature and the absolute values of the –CH3 coverage point toward the depletion of reactive sites. The absolute –CH3 densities reached after the TMA half-cycle, taken to select an appropriate temperature for the calibration procedure as the accuracy of the data is only as good as the calibration. At 300 °C, the calibration data are not affected by low temperature effects such as precursor condensation and persistent surface groups or by high-temperature effects such as precursor decomposition. The right axis of Fig. 16 shows the absolute –CH3 density as a function of temperature for both half-cycles resulting from this procedure. Note that the trend in the relative –CH3 data is independent of the temperature trend in the absolute –CH3 data is independent of the calibration. The –CH3 density after the TMA half-cycle decreases with temperature up to 400 °C, dropping off more rapidly above 400 °C. The trend up to 400 °C can be attributed to temperature induced dehydroxylation leading to a reduction of the density of the –OH groups. The sharp drop can be a combination of decomposition of the chemisorbed TMA, e.g., demethylation, and precursor desorption. For the H2O half-cycle, the persistent –CH3 groups are observed at low temperatures and absent above ~200 °C.

The temperature trend in the –CH3 coverage yields insights into the mechanism causing the self-limiting nature of the TMA half-cycle. For Al2O3 ALD, two key mechanisms have been proposed: (1) Steric hindrance. (2) Depletion of “reactive sites.” There are proponents for both mechanisms. For example, Puurunen attributed the self-limiting nature of the surface reactions in the TMA half-cycle to steric hindrance. On the other hand, Shirazi and Elliott concluded from their DFT simulations that for the TMA half-cycle the depletion of undercoordinated oxygen sites is the cause of saturation. Both the trend in the –CH3 coverage with temperature and the absolute values of the coverage point toward the depletion of reactive sites. The absolute –CH3 densities reached after the TMA half-cycle,
≤6 nm\(^{-2}\) as shown in Fig. 16, are not high enough for steric hindrance. For example, on Si(111) densities as high as eight –CH\(_3\) groups per nm\(^2\) have been observed.\(^{50,51}\) A stronger argument, not depending on the difficult to measure absolute densities, can be found in the temperature trend of the –CH\(_3\) density in Fig. 16. For small and immobile surface groups such as the –CH\(_3\) groups, the surface area that these groups occupy is temperature independent.\(^{14}\) This implies that if steric hindrance is the limiting factor, the same –CH\(_3\) coverage should be observed at all temperatures. If, for the sake of argument, it is assumed that steric hindrance is the limiting factor at 100°C it and follows that at higher temperatures a different mechanism must be responsible for the self-limiting behavior. Apart from steric hindrance, the self-limiting nature of the TMA half-cycle can be caused by depletion of reactive sites. This can be subdivided into two categories: (1) Depletion of protons/H-atoms. (2) Depletion of under-coordinated O atoms. The first factor, depletion of protons, can be ruled out from the fact that these Al\(_2\)O\(_3\) films are known to contain a significant amount of hydrogen, partly in the form of –OH in the bulk of the film.\(^{21,52,53}\) This leaves the depletion of under-coordinated O sites as the likely reason for the self-limiting nature of the TMA half-cycle which is in agreement with mechanism proposed by Shirazi and Elliott.\(^{20}\)

Another topic that can be addressed with this data is the chemisorption of TMA on the -OH groups. TMA can chemisorb on a –OH covered surface in several configurations: TMA can chemisorb monofunctionally, i.e., react with a single -OH group in Pe –CH\(_3\) groups attached to the Al atom. Alternatively, TMA can chemisorb bifunctionally, i.e., react with two -OH groups leaving a single –CH\(_3\) group attached to the Al atom.\(^{20,49}\) It is not likely that TMA reacts with three -OH groups upon chemisorption.\(^{20,49}\) The number of remaining –CH\(_3\) groups per Al after chemisorption was calculated from the change in –CH\(_3\) density in Fig. 16. For the thermal ALD process at low temperature, ∆θCH equals the coverage reached after TMA minus the persistent –CH\(_3\) coverage. At higher temperatures, no persistent –CH\(_3\) are present, and ∆θCH is equal to the coverage reached in the TMA half-cycle. Figure 17 shows the ∆θCH to Al ratio for the Al\(_2\)O\(_3\) ALD process. At low temperatures, TMA chemisorbs bifunctionally, i.e., with one –CH\(_3\) group remaining after chemisorption. The number of –CH\(_3\) groups remaining after TMA chemisorption gradually increases toward 1.5 for higher temperatures. The related process of PE-ALD of Al\(_2\)O\(_3\) can be treated in a similar fashion. For the PE-ALD process, it is expected that even at low temperatures the plasma is reactive enough to completely remove all the –CH\(_3\) groups. This was demonstrated in our previous work, where the GPC(at) of the PE-ALD process could be predicted accurately from the –CH\(_3\) coverage with this assumption.\(^{18}\) Figure 17 also shows the –CH\(_3\) to Al ratio for PE-ALD of Al\(_2\)O\(_3\). For the PE-ALD process, 1.5 –CH\(_3\) groups remain attached to the Al atom after chemisorption. The number of –CH\(_3\) groups remaining on the surface after the chemisorption of TMA is independent of temperature up to 400°C for PE-ALD. Above this temperature, precursor decomposition and desorption might affect the data.

The trend observed for thermal ALD could be explained by a cooperative effect in TMA chemisorption proposed by Shirazi and Elliott.\(^{20}\) Their DFT results show that when a single TMA molecule chemisorbs on a fully –OH covered surface, it is likely to adsorb monofunctionally. On the other hand, if there is already TMA chemisorbed on the surface, new TMA can adsorb bifunctionally. A similar mechanism could be responsible for the transition from monofunctional to bifunctional chemisorption seen for the thermal ALD process at lower temperatures. At low temperatures, the presence of persistent –CH\(_3\) ensures that TMA can chemisorb bifunctionally. At higher temperatures the surface starts out –OH covered and no –CH\(_3\) groups are present. Therefore, TMA chemisorbs monofunctionally initially. The chance of bifunctional chemisorption increases with TMA uptake because the already chemisorbed TMA allows new TMA to chemisorb bifunctionally. The average of the monofunctional and bifunctional adsorption could result in the average of 1.5 –CH\(_3\) groups per Al atom as observed at high temperatures.

To summarize, from the quantification of the –CH\(_3\) coverage, it was possible to deduce that the self-limiting nature of the TMA half-cycle is caused by depletion of under-coordinated O sites. Moreover, for thermal ALD at low temperatures, it was shown that TMA retains one of its –CH\(_3\) ligands after chemisorption. This increases to 1.5 –CH\(_3\) ligands at higher temperatures.
D. Carbon incorporation

The Al2O3 films have been reported to be carbon-free even when deposited at low temperatures. This suggests that the persistent –CH3 groups are not incorporated into the film. Therefore, a dedicated experiment was designed to test the hypothesis that –CH3 groups are not incorporated into the film. This was done by intentionally leaving –CH3 groups on the surface by not saturating the H2O half-cycle for ALD. Two samples were prepared by performing 300 cycles of ALD of Al2O3 at a deposition temperature of 200 °C. The first sample, labeled “saturated,” consisted of a Si(100) substrate on which an Al2O3 film was deposited using the normal process parameters with each process step in saturation. The preparation of the second sample differed only in the duration of the H2O exposure. The H2O exposure was chosen to be roughly half of the exposure needed for saturation. This sample was labeled “unsaturated.” The film thickness and optical properties of the Al2O3 films after deposition were determined with SE and are listed in Table I. The Al2O3 film thickness of the unsaturated sample is roughly 60% of the Al2O3 thickness found for the saturated sample. For both samples, a similar refractive index was found for the Al2O3 film, which is an indication of a similar atomic density. This shows that indeed the H2O exposure was not saturated for the unsaturated sample but that nevertheless high quality Al2O3 was grown in both cases.

The elemental composition of both the samples was analyzed by XPS. The Al2p, C1s, and O1s contribution were measured, and the atomic O to Al ratio and the C content of the material were calculated from the area of the peaks using the appropriate sensitivity factors. A depth profile was made by stepwise sputtering the Al2O3 film with Ar ions, measuring an XPS spectra after each sputter step. The [O] to [Al] atomic ratio and the atomic C percentage are shown in Fig. 18 as a function of etch time. At the surface (before the first etch step), adventitious carbon was observed, which is not related to the ALD process. From the first etch step on, the carbon signal for both samples was below the detection limit of the XPS experiment that was ruled out by the aforementioned XPS experiment that showed negligible incorporation of surface –CH3 groups in the film. The second cause is not expected to occur in the unsaturated sample.

For comparison, the expected C content of the unsaturated sample was calculated assuming the worst-case scenario, i.e., full incorporation of unreacted –CH3 groups. Judging from the precursor usage and the throughput of the ALD system. This approach might affect uniformity and conformality, but it does not necessarily lead to carbon incorporation.

One of the reasons for the absence of carbon incorporation might be related to the specific chemistry of this ALD process. Two plausible mechanisms of carbon incorporation for processes such as thermal ALD of Al2O3 are (1) incorporation of unreacted precursor ligands and (2) incorporation of carbon containing reaction intermediates formed from the precursor ligands in the coreactant half-cycle. The first cause was ruled out by the aforementioned XPS experiment that showed negligible incorporation of surface –CH3 groups in the film. The second cause is not expected to occur in

![Fig. 18](Color online) XPS depth profile of two samples with an ALD Al2O3 film on Si(100) prepared at 200 °C. The sample labeled saturated was prepared using an ALD recipe where both half-cycles were fully saturated. The sample labeled unsaturated was prepared with the same recipe with a shortened H2O exposure which resulted in ~60% of the normal GPC. (a) Both films were stoichiometric throughout. (b) In both cases, the carbon content was below the XPS detection limit. The carbon seen at t=0 is adventitious carbon unrelated to the ALD process. The samples were prepared in an Oxford Instruments FlexAL and examined with a Thermo Scientific K-Alpha XPS.

40% reduction of the GPC(nm), roughly 40% of –CH3 groups were left on the surface after the H2O half-cycle during ALD on the unsaturated sample. For each Al atom which is deposited, ~1.5 –CH3 groups will be on the surface after TMA chemisorption. For the unsaturated sample, this means that 0.6 –CH3 groups per Al atom will be left on the surface after the unsaturated H2O exposure. If all of these C atoms would be incorporated, the stoichiometry of the film would be significantly affected. The composition would be: 32 at. % Al, 19 at. % C, and 48 at. % O. The carbon content was evidently much lower for the unsaturated sample. Moreover, there were no significant differences between the saturated and unsaturated samples with respect to film composition. In short, from this experiment, it can be concluded that –CH3 groups remaining on the surface after the H2O exposure have a relatively low probability to be incorporated into the film. Most likely, the unreacted –CH3 groups have a chance to react in subsequent coreactant half-cycles.

This is of interest for, e.g., industrial applications where ALD is occasionally operated with reduced (subsaturation) precursor and coreactant exposures to optimize the efficiency of precursor usage and the throughput of the ALD system. This approach might affect uniformity and conformality, but it does not necessarily lead to carbon incorporation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>GPC (Å)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated</td>
<td>30.0</td>
<td>1.00</td>
<td>1.67</td>
</tr>
<tr>
<td>Unsaturated</td>
<td>16.5</td>
<td>0.55</td>
<td>1.67</td>
</tr>
</tbody>
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Table I. Film thickness, refractive index, and GPC determined with spectroscopic ellipsometry for two samples deposited by 300 cycles of ALD. The sample labeled saturated was prepared using an optimized ALD process, while the sample labeled unsaturated was prepared with the same process with a smaller H2O dose such that the H2O dose was insufficient to reach saturation.

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**Fig. 18.** (Color online) XPS depth profile of two samples with an ALD Al2O3 film on Si(100) prepared at 200 °C. The sample labeled saturated was prepared using an ALD recipe where both half-cycles were fully saturated. The sample labeled unsaturated was prepared with the same recipe with a shortened H2O exposure which resulted in ~60% of the normal GPC. (a) Both films were stoichiometric throughout. (b) In both cases, the carbon content was below the XPS detection limit. The carbon seen at t=0 is adventitious carbon unrelated to the ALD process. The samples were prepared in an Oxford Instruments FlexAL and examined with a Thermo Scientific K-Alpha XPS.
thermal ALD of Al$_2$O$_3$ because there are no stable carbon containing reaction intermediates expected or known for the reaction in the H$_2$O half-cycle described by Eq. (1b). The impact of the presence of a carbon containing reaction intermediates is best illustrated by the related PE-ALD process of Al$_2$O$_3$ using TMA and an O$_2$ plasma as the co-reactant. For this ALD process, it has been shown that stable carbon containing reaction intermediates exist in the form of a carbonate.\textsuperscript{24,25} These carbonates are quickly formed at the beginning of the O$_2$ plasma half-cycle and gradually combusted by a prolonged O$_2$ plasma exposure.\textsuperscript{24,25} For Al$_2$O$_3$ films prepared using an O$_2$ plasma duration just sufficient for GPC(nm) saturation, a significant amount of C incorporation is reported.\textsuperscript{53,54} On the other hand, virtually C free films are deposited with a similar GPC(nm) for the same process using a prolonged O$_2$ plasma exposure.\textsuperscript{53,54} This trend clearly points toward the carbonates as the main source of the carbon incorporated into the Al$_2$O$_3$ film grown by PE-ALD. The carbon incorporation during PE-ALD is probably exacerbated by TMA readily chemisorbing on the carbonates.\textsuperscript{24,25} To conclude, this example highlights the impact that stable carbon containing reaction intermediates can have on carbon incorporation by comparing the related PE-ALD and thermal ALD processes for Al$_2$O$_3$.

V. CONCLUSION

The growth mechanism of the prototypical ALD process of Al$_2$O$_3$ was studied with BB-SFG spectroscopy. Several dedicated experiments were performed to elucidate several key aspects of the ALD process: the reaction kinetics, the origin of the self-limiting nature of the surface reactions, the number of -OH groups consumed by the chemisorption of TMA, and the apparent paradox between persistent -CH$_3$ groups at low temperatures and negligible carbon incorporation into the Al$_2$O$_3$ films.

The overall surface chemistry was monitored for ALD using either TMA or Al(CD$_3$)$_3$ (D-TMA) as precursor and H$_2$O or D$_2$O as co-reactant. Comparing BB-SFG spectra of the C-H stretch region using TMA and H$_2$O versus TMA and D$_2$O at 250°C demonstrated that at this temperature the ALD process showed virtually ideal behavior: TMA chemisorbs on the -OH sites and H$_2$O is reactive enough to remove all -CH$_3$ groups. At 150°C, TMA did chemisorb on the -OH groups. However, H$_2$O was not reactive enough at this temperature to remove all -CH$_3$ groups. Both -OD groups and persistent -CH$_3$ groups were present on the surface after the D$_2$O half-cycle. Replacing TMA with D-TMA showed the typical isotope shift in the C-H/C-D stretch mode of the -CH$_3$ groups. These experiments established that both the -CH$_3$ and the -OD groups could be monitored with submonolayer sensitivity with BB-SFG spectroscopy.

The reaction kinetics of the growth mechanism was investigated with BB-SFG spectroscopy by monitoring the -CH$_3$ coverage during the H$_2$O half-cycle. At high temperatures, the reaction during the H$_2$O half-cycle was fast, removed all -CH$_3$ groups, and obeyed first-order reaction kinetics. At lower temperatures, the reaction slowed down and persistent -CH$_3$ groups remained on the surface. The initial sticking probability and the reaction cross section were quantified. An initial sticking probability $S_0 = 1 \times 10^{-4}$ (cross section $\sigma = 1 \times 10^{-18}$ cm$^2$) was found for the reactions in the H$_2$O half-cycle at 300°C. This decreased rapidly with temperature, with an initial sticking probability of $S_0 = 1 \times 10^{-6}$ (cross section $\sigma = 1 \times 10^{-20}$ cm$^2$) at 100°C. For comparison, the initial sticking probability and reaction cross section in the TMA half-cycle reported in our previous work was $S_0 = 2 \times 10^{-3}$ and $\sigma = 6.5 \times 10^{-18}$ cm$^2$ and independent of temperature.

Both the reaction kinetics and the persistent surface groups could be interpreted in two ways: either two “kinds” of -CH$_3$ exist (e.g., different sites) leading to different reaction paths or the reaction cross section is coverage dependent. Both models could describe the data. The coverage dependent reaction cross sections was determined from the data. From the temperature dependence of the reaction cross section, an activation energy of 0.27 eV was found for the reaction in the H$_2$O half-cycle. This is comparable to what has been predicted in recent DFT studies (0.25–0.62 eV). In these DFT studies, a coverage dependent reactivity is also reported. Furthermore, in CVD processes, such a coverage dependence is also observed. These facts provide supports for the coverage dependent model, making this the most appropriate model.

The -CH$_3$ coverage was measured with BB-SFG after the TMA and H$_2$O half-cycles for deposition temperatures between 100 and 450°C. The trend in the -CH$_3$ coverage after the TMA step showed that the self-limiting behavior in the TMA half-cycle cannot be caused by steric hindrance. The most likely mechanism responsible for the self-limiting nature in the TMA half-cycle is the depletion of under-coordinated O atoms. Furthermore, the -CH$_3$ coverage was quantified in absolute terms and the number of -OH groups consumed in the chemisorption of a TMA molecule on the surface could be determined as a function of temperature. It was found that at 100°C TMA chemisorbs bifunctionally on the -OH groups with one -CH$_3$ group remaining on the surface after chemisorption. With increasing temperature, this increases to 1.5 -CH$_3$ groups remaining on the surface after TMA chemisorption at 250°C.

Possible incorporation of the persistent -CH$_3$ groups into the Al$_2$O$_3$ films was investigated using a dedicated study with XPS. Virtually carbon free films were found when intentionally trying to incorporate -CH$_3$ groups. This result demonstrated that the persistent -CH$_3$ groups are not incorporated in the film and do not necessarily lead to carbon impurities.

Overall, these results demonstrate that BB-SFG spectroscopy can be used to obtain fundamental insight into subtle and intricate elements of the surface chemistry of ALD. The combination of submonolayer sensitivity, inherent surface selectivity, and relatively short acquisition times make BB-SFG spectroscopy ideally suited for mechanistic studies of ALD processes with metal-organic reactants.

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34See supplementary material at http://dx.doi.org/10.1116/1.4993597 for description of the procedure used for calculation of the GPC(at) from the GPC(nm) and original data set.