

# In Situ Mass Spectrometry Study on Surface Reactions in Atomic Layer Deposition of Al<sub>2</sub>O<sub>3</sub> Thin Films from Trimethylaluminum and Water

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The surface reactions between trimethylaluminum (TMA) and deuterated water (D<sub>2</sub>O) in the deposition of Al<sub>2</sub>O<sub>3</sub> were studied by using a mass spectrometer to determine the amount of the reaction product, methane (CH<sub>3</sub>D), produced in a flow-type atomic layer deposition (ALD) reactor during each deposition step. At low temperatures (<200 °C) more CH<sub>3</sub>D was produced during the TMA pulse whereas at higher temperatures when the dehydroxylation is more extensive more CH<sub>3</sub>D was produced during the D<sub>2</sub>O pulse. In addition to the temperature, the hydroxyl coverage was also noticed to depend on the D<sub>2</sub>O dose, since D<sub>2</sub>O reacts with dehydroxylated alumina sites producing adsorbed –OD groups. According to our results, which agree quite well with previous studies carried out by other methods, the dehydroxylation of the alumina surface seems to play a key role in the surface chemistry of the atomic layer deposition of Al<sub>2</sub>O<sub>3</sub>.

## Introduction

Al<sub>2</sub>O<sub>3</sub> thin films are important insulator and passivating layers in many different applications, for example in dynamic random access memories (DRAM), where Al<sub>2</sub>O<sub>3</sub> films may be used instead of SiO<sub>2</sub> as the gate oxide and capacitor dielectric materials. In the future the gate dimensions will shrink, and very thin oxide films will be needed. In addition, DRAM capacitors will require conformal dielectrics on three-dimensional structures. One of the most promising methods to fulfill the future requirements is atomic layer deposition (ALD), also known as atomic layer epitaxy (ALE). ALD is a gas-phase method for depositing high-quality thin films.<sup>1–4</sup> It is based on sequential saturative surface reactions which are accomplished by introducing the reactant vapors into the reactor in a cyclic manner, one at a time, separated by purging periods. Al<sub>2</sub>O<sub>3</sub> was the first dielectric oxide deposited by ALD, though the precursors in that process were AlCl<sub>3</sub> and water.<sup>1</sup> Since then, Al<sub>2</sub>O<sub>3</sub> films have also been deposited from alkoxides and alkyls.<sup>5–8</sup> Nowadays, trimethylaluminum (TMA) is quite often used as an aluminum source because it is a thermally stable high vapor pressure (8.4 Torr) liquid at room temperature and reacts very facily with water to produce Al<sub>2</sub>O<sub>3</sub>.

Although the deposition of Al<sub>2</sub>O<sub>3</sub> is one of the most studied ALD processes, the chemistry involved is not yet fully understood. Infrared spectroscopy is the most common method in studying the surface reactions of TMA

and water on high surface area powders,<sup>9–14</sup> but it is not suited for thin-film studies because the surface area is too small to obtain adequate signal-to-noise. The ALD reactors used for thin-film deposition on an industrial scale, and thus often also in research, are of the flow type which through fast pulsing and purging and multiple substrate processing offer high productivities, despite the rather low deposition rates of 100–300 nm/h.<sup>15</sup> Unfortunately, the design and operating pressure (around 1 mbar) of these reactors make it rather complicated to characterize the chemical reactions in situ. Somewhat different conditions better suited for characterization have to be used in order to study the chemical reactions. However, the difference in the process conditions, especially exposure time and pressure, leaves an open question of the relevance of the results.

In the flow-type reactors, ALD processes are usually characterized and optimized indirectly by varying the process parameters (temperature, exposure and purge times, reactant pressures, etc.) and observing afterward their effects on the film properties. This is quite laborious and time-consuming and reveals few details of the reaction mechanisms. Therefore, there is a clear need to develop a method for more detailed reaction mechanism studies and faster process optimization in the flow-type reactors. Mass spectrometry is a very promising way to achieve this and has been utilized, for example, in chemical vapor deposition (CVD) studies.<sup>16–18</sup> Mass spectrometry studies could also be valuable in improving process control,

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designing new processes, and screening new precursors. However, mass spectrometry studies on ALD processes in flow-type reactors require rather complicated differentially pumped sampling setups, which is evidently the reason for only sparse utilization of mass spectrometry in the field of ALD until now.<sup>19,20</sup> On the other hand, several ALD oxide processes have been studied by quartz crystal microbalance (QCM), which gives real time results from the weight changes on the crystal surface and helps in the interpretation of the growth mechanisms. However, QCM is difficult to calibrate for the absolute mass measurements at the typical growth temperatures, and the composition of the intermediates on the surface after each ALD deposition step has to be deduced through the relative mass changes during the different steps.<sup>21–24</sup>

In this work, we have used the recently developed quadrupole mass spectrometer–ALD reactor setup<sup>20</sup> for characterizing the TMA–water ALD process. When TMA and water are sequentially dosed onto the surface, methane is formed as a volatile byproduct, and thus the reaction mechanism can be examined by following with in situ mass spectrometry measurements the amount of methane produced during each step at different deposition temperatures and with varying reactant doses.

### Chemistry of Surfaces Related to ALD of Al<sub>2</sub>O<sub>3</sub>

Before going into experimental details and results, it is instructive to survey the literature on the surface chemistry relevant to the process under study. It must be noted, however, that these surface studies have been performed on well-equilibrated samples, while in the ALD film growth process the surface is only allowed to relax for a maximum of a few seconds. So, although the ALD growth experiments have shown that the surfaces are stable enough to ensure that the growth rate is independent of the purge times in a typical range of 0.2–3 s, the prevailing surface species may differ from those on the surfaces that have been stabilized for much longer times. In addition, the way surfaces are created is often fundamentally different, since in the surface studies the surface is usually saturated with the chemical under study for a rather long time at a low temperature and then progressively heated, while in the ALD process the surface is formed rapidly by reacting with the chemical at the chosen constant temperature. Because of these reasons, the surface chemistry studies found in the literature may be considered only as guidelines for understanding the ALD processes, and MS–ALD studies are needed to either verify the dominance of the same surface species or point out differences.

Alumina exists in several crystal structures that have surface hydroxyl groups of varying thermal stability.<sup>25</sup> The structure of a hydroxylated alumina surface is quite complex, and although alumina is a very important and widely used material, the nature and distribution of

hydroxyl groups are still under discussion.<sup>26</sup> However, the dehydroxylation of the alumina surfaces has been well documented.<sup>25,27,28</sup> The hydroxyl group coverages have been shown to decrease as a function of temperature. On amorphous alumina surfaces, which are similar to the surfaces of amorphous Al<sub>2</sub>O<sub>3</sub> thin films, the decrease is quite linear (see Figure 7), and some of the hydroxyl groups persist on the surfaces at temperatures higher than those studied in this work. So although the hydroxyl coverage decreases as a function of temperature, there still are some hydroxyl groups left with which TMA can react. The dehydroxylation of the alumina surface leads to exposed, coordinatively unsaturated surface aluminum and oxygen sites (so-called cus sites). This is different from silica dehydroxylation, which leads to the formation of surface siloxane bridges.<sup>29–31</sup>

The species formed by adsorption of TMA on alumina have been examined by several groups.<sup>10,12,32</sup> It has been claimed that TMA mainly adsorbs onto hydroxyl sites whereas the dehydroxylated sites play a minor role.<sup>10</sup> Soto et al.<sup>12</sup> found that, on the alumina surface dehydroxylated at 127 °C, TMA adsorption at room temperature resulted in either –Al(CH<sub>3</sub>)<sub>2</sub> or >Al(CH<sub>3</sub>) species (denoted together as Al(CH<sub>3</sub>)\*), and their relative coverage was strongly dependent on temperature. The –Al(CH<sub>3</sub>)<sub>2</sub> coverage was found to decrease quite rapidly with temperature. This was claimed to result from –Al(CH<sub>3</sub>)<sub>2</sub> converting to >Al(CH<sub>3</sub>) by reactions with surface hydroxyl groups evolving CH<sub>4</sub>. The remaining methyl group in the >Al(CH<sub>3</sub>) surface species reacts in a similar manner but is significantly less labile than the –Al(CH<sub>3</sub>)<sub>2</sub> species. According to Soto et al., it is unlikely that, on the alumina surface, adsorbed –Al(CH<sub>3</sub>)<sub>2</sub> species would react in a manner analogous to that on silica, where a methyl group is rapidly transferred to a surface silicon yielding both >Al(CH<sub>3</sub>) and –Si(CH<sub>3</sub>).<sup>13,33–36</sup> So, on alumina the dimethyl species are proposed to always react with surface hydroxyl groups to form the monomethyl species. However, at higher adsorption temperatures where the density of hydroxyl groups is lower, the –Al(CH<sub>3</sub>)<sub>2</sub> groups and/or methyl transfer to the cus Al sites may also be possible.

Al<sub>2</sub>O<sub>3</sub> has been deposited by the ALD technique from TMA and water over a rather wide temperature range (150–500 °C), and the optimal growth temperature has been reported to be around 250 °C.<sup>10,37</sup> It has been shown that the reactions are thermally activated and do not go to completion at the lowest temperatures.<sup>38</sup> Above the optimal growth temperature the growth rate was found to decrease, and this has been claimed to result from the decrease in the number of AlOH\* and Al(CH<sub>3</sub>)\* functional groups on the surface.<sup>10</sup> The surface hydroxyl groups have

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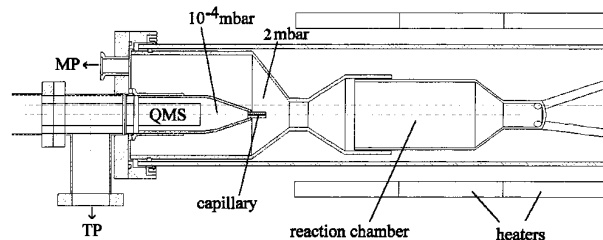
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**Figure 1.** Schematics of the sampling in the MS-ALD equipment. The reactants and carrier gas are coming from the right and are pumped by a mechanical pump (MP). Only a small part of the flow goes through the capillary, and it is pumped by a turbo pump (TP).

been noticed to play an important role as intermediate species remaining on the surface of the growing oxide film after water exposure. In a quite recent study it was shown that the growth rate could be increased by increasing the water dose and the growth rate saturated only with very high water doses.<sup>37</sup> This is believed to result from increased density of surface hydroxyl groups. Since the most important parameters found to have an effect on the  $\text{Al}_2\text{O}_3$  growth are the deposition temperature and the water dose, we will mainly concentrate on these.

### Experimental Section

**Design of the MS-ALD Equipment.** The QMS used in this work was a Leybold TSP 300 with a Faraday cup detector and a mass range of 1–300 amu. The most critical issues and solutions in integrating a quadrupole mass spectrometer (QMS) to a flow type ALD reactor are discussed here only briefly since a more detailed description has been given elsewhere.<sup>20</sup>

(i) A pressure reduction from the operation pressure of 2–10<sup>−4</sup> mbar in the QMS chamber was realized by using a short and small diameter glass capillary inserted at the conical end of a glass envelope which separated the QMS from the main chamber of the ALD reactor (Figure 1).

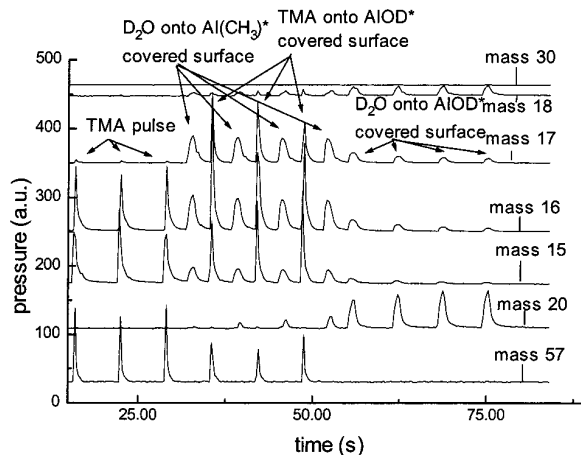
(ii) Many of the precursors used in ALD, though not in this work, are solids with only modest vapor pressure. To avoid their condensation, the QMS sampling should take place at elevated temperatures, preferably close to the substrate temperature. However, the operation temperature of the QMS should not exceed 250 °C. Therefore, the QMS was coaxially inserted partly into the resistively heated ALD reactor tube in a region where a rather steep temperature gradient exists. This ensured that the sampling port was close to the substrate temperature while the rest of the instrument remained closer to room temperature.

(iii) The amount of byproducts released in one cycle is typically on the order of 10<sup>14</sup> molecules/cm<sup>2</sup> of surface. To ensure that detectable amounts of byproducts are formed, the reaction chamber was enlarged and fully loaded with glass substrates forming narrow 2 mm flow channels between each other so that the total surface area was about 3500 cm<sup>2</sup>.

**Experimental Parameters Used in the Deposition of  $\text{Al}_2\text{O}_3$ .** When TMA reacts with  $\text{H}_2\text{O}$ , the expected reaction product is  $\text{CH}_4$  ( $m/e = 16$ ) which, however, is also formed directly from the decomposition of TMA in the QMS. To distinguish the amount of methane formed as a reaction product from that formed directly from TMA, deuterated water,  $\text{D}_2\text{O}$ , was used instead of  $\text{H}_2\text{O}$ .

TMA (Witco GmbH) and  $\text{D}_2\text{O}$  (Euriso-top, 99.9% D) were vaporized at room temperature. Both precursors were used without further purification. The reactant doses were controlled by needle valves. While for TMA a fixed dose was used, the  $\text{D}_2\text{O}$  dose was varied with a needle valve. The exact amounts of the reactants used were not measured since the aim of this study was to follow how temperature and reactant doses affect the relative amounts of the reaction products formed during each step. Deposition temperatures were varied between 150 and 400 °C.

The reaction product from TMA and  $\text{D}_2\text{O}$  is expected to be  $\text{CH}_3\text{D}^+$  ( $m/e = 17$ ). Figure 2 shows how the most important  $m/e$  ratios behave during the ALD growth of  $\text{Al}_2\text{O}_3$  from TMA and



**Figure 2.** Time behavior of different masses. The data have been normalized against background and then multiplied and vertically shifted for clarity. The carrier gas used in this experiment was  $\text{N}_2$ .

$\text{D}_2\text{O}$ . The carrier gas used when measuring this spectra was  $\text{N}_2$ , although in the actual mechanism studies the carrier gas used was Ar. When only TMA is pulsed, the  $m/e$  ratios 15 ( $\text{CH}_3^+$ ), 16 ( $\text{CH}_4^+$ ), and 57 ( $(\text{CH}_3)_2\text{Al}^+$ ) increase as expected, but unfortunately a slight increase can be seen also at  $m/e = 17$ . An increase at  $m/e = 17$  can also be seen when only  $\text{D}_2\text{O}$  is pulsed. The exact explanation to this kind of behavior is not clear, but it may be caused by the limited mass resolution, since the effect of the neighboring peak can be as high as 10%. In the case of TMA,  $\text{CH}_4^+$  ( $m/e = 16$ ) may contribute to the peak 17. On the other hand, during the  $\text{D}_2\text{O}$  pulse  $\text{OD}^+$  ( $m/e = 18$ ) and  $\text{O}^+$  ( $m/e = 16$ ) are produced and may cause the same effect. Because the reaction mechanisms were studied by following the amount of  $\text{CH}_3\text{D}$  produced during each deposition step, the reactant contributions to mass 17 had to be taken into account (see below). No detectable amounts of ethane ( $m/e = 30$ ) were formed, which is an indication that no recombination of methyl groups occurred.

To examine the reactions in detail the following pulsing sequence was used:

8 times 1.0 s TMA pulse/5.0 s purge  
3 times 1.0 s TMA pulse/2.0 s purge + 1.0 s  $\text{D}_2\text{O}$  pulse/  
2.0 s purge  
2 times 1.0 s TMA pulse/5.0 s purge  
3 times 1.0 s TMA pulse/2.0 s purge + 1.0 s  $\text{D}_2\text{O}$  pulse/  
2.0 s purge  
4 times 1.0 s  $\text{D}_2\text{O}$  pulse/5.0 s purge

First, eight 1.0 s TMA pulses are supplied to saturate the surface fully with TMA and to stabilize the TMA dose coming through the needle valve, thereby also stabilizing the contribution of TMA to the mass 17 signal. Then the ALD reaction sequence to deposit  $\text{Al}_2\text{O}_3$  begins, and the reaction product ( $\text{CH}_3\text{D}$ ) is found to form during both TMA and  $\text{D}_2\text{O}$  pulses. The same reaction sequence is repeated after two 1.0 s TMA pulses in between. The two intermediate TMA pulses are used in order to check that the TMA dose is large enough to saturate the surface fully. Similarly, the purpose of the last four  $\text{D}_2\text{O}$  pulses is to examine whether the surface is saturated with respect to  $\text{D}_2\text{O}$ . In both cases, the mass 17 signal obtained when TMA ( $\text{D}_2\text{O}$ ) is dosed onto a surface that already previously had been exposed to TMA ( $\text{D}_2\text{O}$ ) should immediately return to its background level, i.e., the level obtained directly from TMA ( $\text{D}_2\text{O}$ ). If the return is gradual, stabilizing to the background level only with increasing number of subsequent TMA ( $\text{D}_2\text{O}$ ) pulses, the dose is not high enough to saturate the surface during one pulse.

We observed that the amount of reactants pulsed into the reactor is dependent not only on the pulse time but also on the



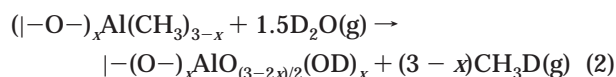
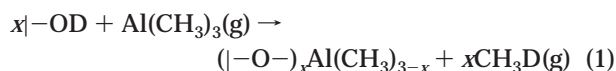
time between the pulses, which seems to be somehow related to the flow dynamics in the source line. So in order to maintain stable TMA and D<sub>2</sub>O doses throughout the process, it was important to keep the time interval between subsequent TMA (D<sub>2</sub>O) pulses constant. This was realized by varying the purge times.

In these experiments the mass spectra were collected by monitoring masses 15 (CH<sub>3</sub><sup>+</sup>), 17 (CH<sub>3</sub>D<sup>+</sup>), and 57 (Al(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>), with 16 ms dwell times resulting in 104 ms/scan. This measuring time is short enough to keep track of the reaction products formed during each step.

To examine the relative amounts of CH<sub>3</sub>D formed during both TMA and D<sub>2</sub>O pulses, the mass 17 signal was followed as a function of time, and the measured peaks corresponding to the TMA and D<sub>2</sub>O pulses were integrated. To eliminate the effects of the reactants (TMA or D<sub>2</sub>O), the integrated intensities of mass 17 during the TMA or D<sub>2</sub>O reference pulses were subtracted. However, since part of TMA or D<sub>2</sub>O is consumed in the reactions, this approach may somewhat overestimate the contribution of the reactants. After subtraction the integrated intensities of mass 17 represent the amount of reaction product formed and are thus used in examining the ALD deposition mechanism of Al<sub>2</sub>O<sub>3</sub> thin film from TMA and D<sub>2</sub>O.

### Results and Discussion

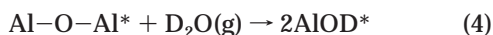
As Figures 2 and 3 indicate, CH<sub>3</sub>D is formed during both TMA and D<sub>2</sub>O pulses, and the film growth may be concluded to proceed according to the following alternate reactions:



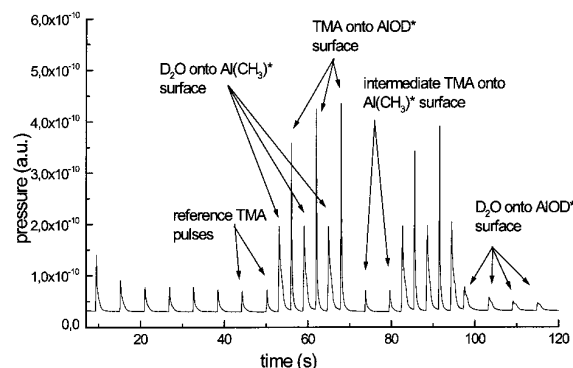
where  $|-$  denotes the surface, and reaction 2 is formulated to reproduce the same hydroxyl group density  $x$  as in the beginning of the ALD cycle. To simplify the discussion, the intermediate surface species  $|-\text{OD}$  and  $(|-\text{O}-)_x\text{Al}(\text{CH}_3)_{3-x}$  are from now on referred to as AlOD\* and Al(CH<sub>3</sub>)<sub>3-x</sub>\*, respectively.

A reaction mechanism similar to ours has been suggested earlier by George et al.<sup>39</sup> on porous substrates, though in their experiments considerably longer exposure times were used in comparison to the 1 s used in the present study. Apparently, the exposure time scale does not seem to affect the basic mechanism of the intermediate Al(CH<sub>3</sub>)<sub>3-x</sub>\* and AlOD\* surface species. The sharpness of the CH<sub>3</sub>D peaks (Figures 2 and 3) in turn implies that the reactions between the surface species and the incoming TMA or D<sub>2</sub>O are very fast.

Since after the TMA pulse the surface contains Al(CH<sub>3</sub>)<sub>3-x</sub>\* and coordinatively unsaturated Al sites, denoted as Al-O-Al\*, the incoming D<sub>2</sub>O may react by two possible mechanisms:

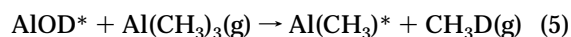


On the basis of the known high reactivity of aluminum alkyls toward water, it may be expected that reaction 4 becomes significant only after completion of reaction 3, i.e., only when all the Al(CH<sub>3</sub>)<sub>3-x</sub>\* species have reacted. The completion of reaction 3 can be seen as a saturation of the CH<sub>3</sub>D evolution; i.e., when two subsequent D<sub>2</sub>O doses are



**Figure 3.** An example of the behavior of mass 17 during the pulsing sequence. AlOD\* and Al(CH<sub>3</sub>)<sub>3-x</sub>\* represent all the possible adsorbed species after TMA pulse.

given, the latter one does not cause any extra rise in the mass 17 signal in comparison to that coming directly from D<sub>2</sub>O. On the other hand, the occurrence of reaction 4 is difficult to detect by the MS measurements during the D<sub>2</sub>O pulse itself. Rather, reaction 4 will affect the overall amount of CH<sub>3</sub>D evolved during the next TMA pulse



since both reactions 3 and 4 contribute to the overall density of the AlOD\* groups. In addition, because the AlOD\* density obviously affects the uptake of Al(CH<sub>3</sub>)<sub>3</sub>, reaction 4 will also have an effect on the deposition rate, as was recently speculated in a study where the oxide ALD rates were increased by increasing the water doses.<sup>37</sup> On the other hand, since an increase in temperature decreases the AlOD\* group density through dehydroxylation,

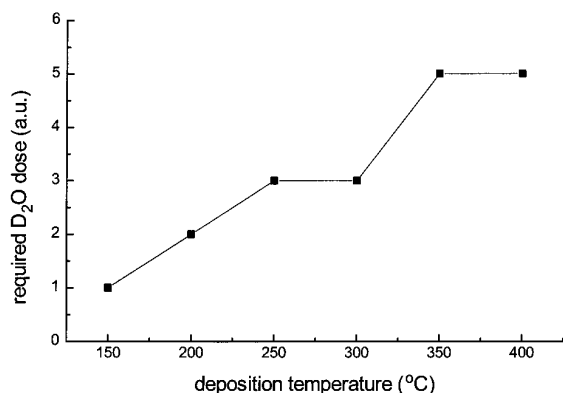


it is important to study the combined effect of water dose and temperature on the evolution of CH<sub>3</sub>D during both D<sub>2</sub>O (reaction 3) and TMA pulses (reaction 5). To examine the effect of the water dose, a complete pulsing sequence described in the Experimental Section was performed with each dose. Here it must be emphasized that, provided that the doses are large enough to saturate reactions 3 and 5, the amounts of CH<sub>3</sub>D liberated during the D<sub>2</sub>O and TMA pulses are actually measures of Al(CH<sub>3</sub>)<sub>3-x</sub>\* and AlOD\* groups, respectively, remaining on the surface after the preceding reactant pulse and purging steps. In other words, the D<sub>2</sub>O and TMA pulses probe (titrate) the Al(CH<sub>3</sub>)<sub>3-x</sub>\* and AlOD\* groups.

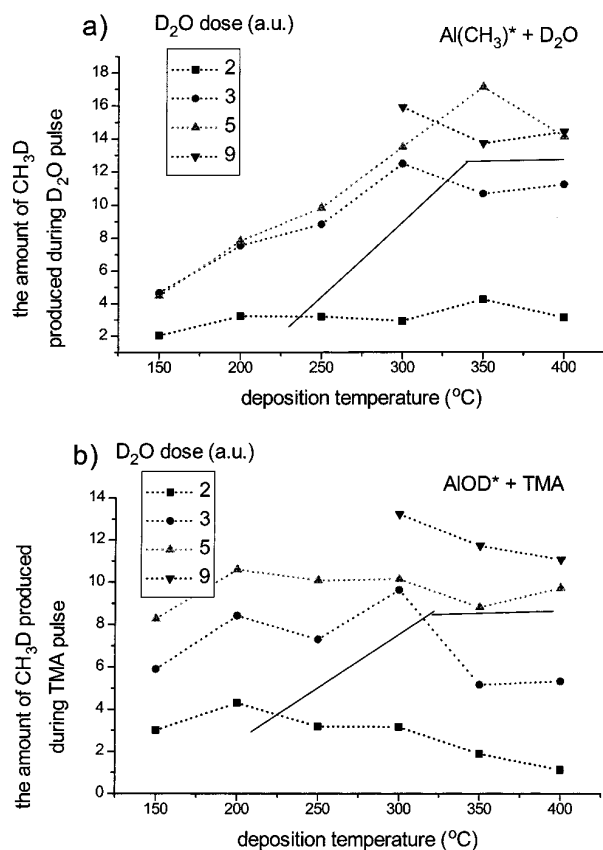
Figure 4 exhibits the D<sub>2</sub>O dose required to saturate the CH<sub>3</sub>D evolution, i.e., to react with all the Al(CH<sub>3</sub>)<sub>3-x</sub>\* species during the D<sub>2</sub>O pulse (reaction 3), at each temperature studied. An increase in the required D<sub>2</sub>O dose is observed as a function of the growth temperature. This can be understood in terms of the decrease of the AlOD\* group coverage with increasing temperature. At low temperatures the AlOD\* groups are numerous, and TMA loses most of its methyl ligands already during the TMA pulse. Therefore, only a small D<sub>2</sub>O dose is required to remove the rest of the methyl groups from the Al(CH<sub>3</sub>)<sub>3-x</sub>\* species. On the other hand, once the temperature is increased, the surface coverage of AlOD\* groups decreases, and more methyl groups remain on the surface after the TMA pulse, thereby requiring higher D<sub>2</sub>O doses.

Figure 5 indicates the total amounts of CH<sub>3</sub>D evolved during the D<sub>2</sub>O (a) and TMA (b) pulses for different D<sub>2</sub>O

(39) George, S. M.; Sneh, O.; Dillon, A. C.; Wise, M. L.; Ott, A. W.; Okada, L. A.; Way, J. D. *Appl. Surf. Sci.* **1994**, 82/83, 460.



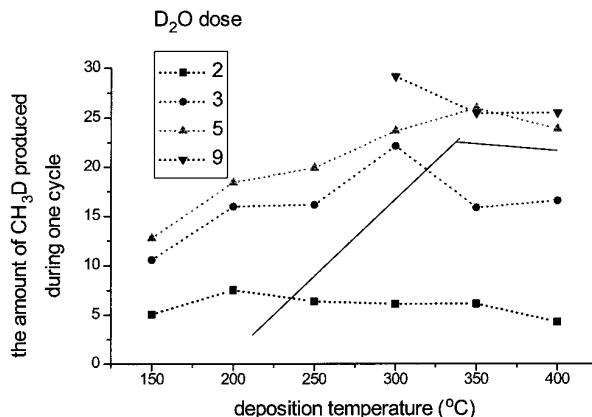
**Figure 4.** D<sub>2</sub>O dose required to saturate the CH<sub>3</sub>D evolution, i.e., to react with all the Al(CH<sub>3</sub>)<sup>\*</sup> species, at different temperatures.



**Figure 5.** Amount of CH<sub>3</sub>D produced during (a) the D<sub>2</sub>O and (b) the TMA pulse as a function of deposition temperature. The solid lines divide the data into two groups depending on whether the D<sub>2</sub>O dose has been high enough to saturate reaction 3 (above the line) or not (below the line).

doses at different temperatures. The solid lines divide the data into two groups depending on whether the D<sub>2</sub>O dose has been high enough to saturate reaction 3 (above the line) or not (below the line). Some care is required while examining the data, since there inevitably are some variations in the precursor doses during the experiments with long times.

The behavior of the CH<sub>3</sub>D evolved during the D<sub>2</sub>O pulse (Figure 5a) may be reasoned in a similar manner as above; i.e., the higher the temperature, the lower the AlOD<sup>\*</sup> coverage on the surface upon which TMA is dosed and thus the higher the methyl group density left on the surface



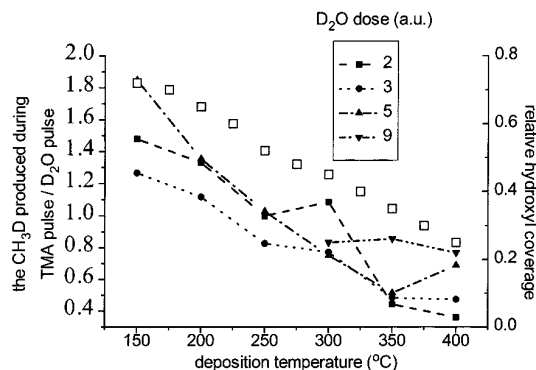
**Figure 6.** Total amount of CH<sub>3</sub>D produced during one deposition cycle. The solid line divides the data into two groups depending on whether the D<sub>2</sub>O dose has been high enough to saturate the reaction 3 (above the line) or not (below the line).

after the TMA pulse to react with D<sub>2</sub>O and evolve CH<sub>3</sub>D. Of course, if the D<sub>2</sub>O dose is too low to saturate reaction 3, i.e., to react with all the Al(CH<sub>3</sub>)<sup>\*</sup> species, the amount of CH<sub>3</sub>D evolved remains lower. The overdosing of D<sub>2</sub>O has essentially no effect on the CH<sub>3</sub>D liberated during the D<sub>2</sub>O pulse.

The behavior of the CH<sub>3</sub>D evolved during the TMA pulse is by contrast much more complicated (Figure 5b). For a constant water dose, the amount of CH<sub>3</sub>D liberated decreases slightly with increasing temperature, but the temperature dependence is much weaker in comparison to the CH<sub>3</sub>D evolved during the D<sub>2</sub>O pulse, when the amount of CH<sub>3</sub>D liberated increases significantly (Figure 5a). There is also no clear change in the amount of CH<sub>3</sub>D liberated during the TMA pulse when moving across the line dividing the D<sub>2</sub>O doses to those that saturated reaction 3 and to those that did not. Rather, for a given temperature, the amount of CH<sub>3</sub>D formed during the TMA pulse (Figure 5b) increases much more clearly with the D<sub>2</sub>O dose as compared with CH<sub>3</sub>D released during the D<sub>2</sub>O pulse (Figure 5a). This behavior verifies the coexistence of reactions 3 and 4; i.e., the AlOD<sup>\*</sup> groups are formed not only by reaction 3 but also by reaction 4. As a consequence of the increased AlOD<sup>\*</sup> density, an increased CH<sub>3</sub>D liberation is observed during the TMA pulse (reaction 5). On the other hand, with increasing temperature the dehydroxylation affects the AlOD<sup>\*</sup> density at all D<sub>2</sub>O dose levels, causing the observed slight decrease in the CH<sub>3</sub>D liberated. The deviations of the data measured at 150 °C from the overall trend are most probably due to kinetic reasons; i.e., the reactions are not thoroughly completed at this temperature within the 1 s pulse times.

Figure 6 shows the total amount of CH<sub>3</sub>D liberated during one cycle; i.e., it summarizes the data given in Figure 5a,b.

Figure 7 depicts the ratio of CH<sub>3</sub>D liberated during the TMA pulse to that liberated during the D<sub>2</sub>O pulse. Here a ratio of 2 would mean that after the TMA pulse the surface would be covered exclusively by monomethyl Al(CH<sub>3</sub>) species, while a ratio of 0.5 would correspond to an exclusive dimethyl Al(CH<sub>3</sub>)<sub>2</sub> termination of the surface. Despite some scatter in the data, it may be concluded that with all water doses, whether or not they are high enough to saturate the CH<sub>3</sub>D liberation (reaction 3), the ratios are rather independent of the D<sub>2</sub>O doses and exhibit a general trend of an increase in methyl groups remaining on the surface after the TMA pulse with increasing temperature. However, except a few high-



**Figure 7.** Amount of CH<sub>3</sub>D produced during the TMA pulse divided by that produced during the D<sub>2</sub>O pulse plotted as a function of deposition temperature (left axis). For comparison is shown the relative hydroxyl coverage of amorphous alumina surface as a function of temperature (open squares, right axis).<sup>25</sup>

temperature data points with nonsaturated D<sub>2</sub>O doses, the exact values are always somewhere between the two limiting values of 0.5 and 2.0. This implies a coexistence of  $\text{Al}(\text{CH}_3)$  and  $\text{Al}(\text{CH}_3)_2$  or methyl transfer from  $\text{Al}(\text{CH}_3)_2$  to a nearby surface aluminum ion. For example, at 250 °C where the ratio is about 1, equal amounts of  $\text{Al}(\text{CH}_3)$  and  $\text{Al}(\text{CH}_3)_2$  seem to have resulted from the reactions between TMA and AlOD\*. Finally, the correlation between the temperature dependencies of the relative amount of CH<sub>3</sub>D liberated during the TMA pulse and the reported relative hydroxyl group density on amorphous alumina surface<sup>25</sup> is remarkable (Figure 7). These results verify the significance of reactions 3 and 5 with respect to the overall deposition mechanism. On the other hand, while the methyl-to-aluminum ratio on the intermediate  $\text{Al}(\text{CH}_3)^*$  terminated surface appears to be clearly related to the thermal stability of the hydroxyl groups, the hydroxyl coverage is not necessarily strictly constant but may be increased to a certain extent through reaction 4, especially at the low temperatures where dehydroxylation is less extensive (Figure 5b), and thus the extra AlOD\* groups may be kinetically stable enough to survive the purging step.

## Conclusions

In situ mass spectrometry has been proven to be a useful tool in analyzing the chemistry involved in depositing Al<sub>2</sub>O<sub>3</sub> thin films by ALD from TMA and water. The deposition temperature and water dose were the main parameters studied because they have been seen to have the largest effect on the film growth. The reaction mechanisms were studied by examining the integrated intensity of the main gaseous reaction product (CH<sub>3</sub>D) during different reaction steps by varying D<sub>2</sub>O doses in the temperature range 150–400 °C. It was found that at higher deposition temperatures more D<sub>2</sub>O was needed to complete the reactions than at lower temperatures. This was interpreted to be caused by surface dehydroxylation, which is known to increase with temperature. It was also found that at low temperatures (<200 °C) more CH<sub>3</sub>D was produced during the TMA pulse than during the D<sub>2</sub>O pulse. At temperatures higher than 350 °C the trend reversed, and in between about the same amount of CH<sub>3</sub>D was produced during both reactant pulses. This indicates that, at low temperatures where the surface contains more –OD groups, the methyl removal from TMA takes place largely during the TMA pulse. When the temperature is increased and thus the density of hydroxyl groups is lower, the same amount or even more methyl groups are removed during the D<sub>2</sub>O pulse. These results are in good agreement with the previously suggested growth mechanism. This is remarkable in the sense that the previous studies were performed using long, tens of seconds pulse times, while in the present study the reactant pulses were short, 1 s, corresponding to real ALD film growth processes. Being the first detailed study with the new MS–ALD equipment, these results give confidence for the future use of this approach in studying ALD thin-film deposition mechanisms.

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