In Situ Reaction Mechanism Studies on Atomic Layer Deposition of ZrO_2 from $(CpMe)_2Zr(OMe)Me$ and Water or Ozone

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Reaction mechanisms in the atomic layer deposition of ZrO_2 from $(CpMe)_2Zr(OMe)Me$ and deuterated water or ozone were studied in situ with a quadrupole mass spectrometer and a quartz crystal microbalance at 350 °C. In the D_2O process the detected reaction byproducts were as expected MeD, MeOD, and DCpMe. About 80% of the MeD, 40% of the MeOD, and 60% of the DCpMe were formed during the $(CpMe)_2Zr(OMe)Me$ pulse in reactions with surface −OD groups and the rest during the D_2O pulse. In the ozone process the most important reaction byproducts were CO_2 and H_2O. Interestingly, about 20% of both of these were released already during the $(CpMe)_2Zr(OMe)Me$ pulse and the rest during the O_3 pulse. In addition, some MeH and HCpMe were formed during the $(CpMe)_2Zr(OMe)Me$ pulse. Furthermore, D_2O was used to probe the state of the surface after the $(CpMe)_2Zr(OMe)Me$ pulse in the O_3 process. Thereby, it could be stated that about 50% of the Me− ligands, 40% of the MeO− ligands, and 60% of the −CpMe ligands were eliminated during the $(CpMe)_2Zr(OMe)Me$ pulse. Similarly, $ZrCl_4$ was used to probe the surface after the O_3 pulse. Thereby, the surface was found to be covered with only about 10% −OH concentration as compared to the water process. To explain the observations, some active oxygen was concluded to be left on the surface after the O_3 pulse.

Introduction

Atomic layer deposition (ALD) is a chemical gas-phase method for depositing thin films.[1−3] In ALD the precursors are pulsed alternately into the reactor. Each precursor saturates the surface on its turn. The precursor pulses are separated from each other by purging unnecessary precursor molecules and reaction byproducts from the reactor with an inert carrier gas. The growth mechanism is self-limiting because the precursors can adsorb on the surface as monomolecular layers at most. Therefore, with ALD one can very easily and accurately control the thickness of the growing films. Furthermore, the films obtained with this method are usually uniform and represent excellent conformality.

Knowledge of the mechanisms of the ALD reactions can help control and optimize growth processes more accurately and develop new processes more quickly. Important issues are surface reactions and onset temperatures of precursor decomposition reactions. Traditionally, the growth processes are studied with growth experiments, i.e., growing films and examining them afterward ex situ.[2] When doing so, one can get only indirect information on the reaction mechanisms. Alternatively, one can study the processes in situ during the growth. This provides information that makes direct conclusions of the reaction mechanisms possible. Another advantage of in situ measurements is that they do not require great amounts of precursors. Furthermore, they would be an effective means to control processes in industry: with in situ measurements process failures could be detected early enough so that great financial losses are avoided.[4]

Reaction mechanisms of ALD processes have been studied in situ with a quadrupole mass spectrometer (QMS) and/or a quartz crystal microbalance (QCM) quite extensively over the past decade by our group.[5−20] The quadrupole mass spectrometer allows us to monitor the gas phase of the reactor and especially the growth reaction byproducts, the amounts of which give direct information concerning the reaction mechanism. The quartz crystal microbalance gives the relative changes of the mass of the film, which give information on the mechanism when one compares the mass change over a complete ALD cycle to the mass changes during each step of the process.

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ZrO_2 is a promising high-permittivity candidate to replace SiO_2 in microelectronics.[21] Quite understandably, ALD is the successful method of choice in meeting the high expectations of the microelectronics industry in depositing premium-quality ZrO_2 thin films.[22] However, the films deposited with the traditional $ZrCl_4-H_2O$ process[23,24] often incorporate some chlorine impurities, and the reaction byproduct, HCl, can also cause serious problems in the fabrication of microelectronic devices. Furthermore, because $ZrCl_4$ is a solid with very fine particle size, there is a risk that these particles are transported onto the substrate, causing defects. These drawbacks have motivated the search for alternative zirconium ALD precursors. Zirconium alkyl amides have been studied extensively, but they generally have problems with their limited thermal stabilities.[25] Recently, cyclopentadienyl-based compounds, especially Cp_2ZrMe_2[26] and $(CpMe)_2Zr(OMe)Me$,[27,28] have proven their value in producing excellent ZrO_2 films with water or ozone as the oxygen source, and these precursors have sufficient thermal stabilities. Our group has already clarified the mechanism of the Cp_2ZrMe_2−water process.[20] It was found that upon adsorption of Cp_2ZrMe_2 on an −OD-terminated surface left after the D_2O pulse 90% of the Me− ligands and 40% of the −Cp ligands were released in deuterated form. The rest of the ligands were released in deuterated form during the D_2O pulse, which also re-formed the −OD-terminated surface.

In the paper at hand, the mechanisms of the $(CpMe)_2Zr(OMe)Me$−water and −ozone processes are discussed and compared. This particular zirconium precursor is mechanistically speaking of special interest since it contains three types of ligands. Quantum chemical calculations and a preliminary investigation of the mechanism of the $(CpMe)_2Zr(OMe)Me$−water process have been reported by Elam et al.[29] The experimental result was that all the Me− ligands and 65% of the −CpMe ligands but none of the MeO− ligands were released during the $(CpMe)_2Zr(OMe)Me$ pulse and the rest during the H_2O pulse, which was also found to agree with the ab initio findings. Here we represent a more detailed experimental study on this mechanism. We also compare the water-based process with the ozone-based chemistry. This is the first time we study mechanisms of ozone-based ALD processes in general. Research on the mechanism of the InCp−O_3 ALD process for depositing In_2O_3 films has been conducted elsewhere.[30]

Experimental Section

The experiments were carried out in a specially modified[7] commercial flow-type ALD reactor manufactured by ASM Microchemistry Ltd. The pressure of the reactor was about 3 mbar and the total area of the soda lime glass substrates about 3500 cm^2. The reaction temperature was otherwise 350 °C, but it was varied in the precursor decomposition experiments. Nitrogen (Oy AGA Ab, 99.999%) was used as a carrier gas, except for a few measurements where argon (Oy AGA Ab, 99.999%) was used.

The gas phase was examined with a Hiden HAL/3F 501 RC QMS using a Faraday detector and an ionization energy of 70 eV. The pressure reduction to about 3×10^{-5} mbar in the QMS chamber was accomplished by differential pumping through a 200 μm orifice. The QCM used was a Maxtek TM 400 with a sampling rate of 20 Hz.

$(CpMe)_2Zr(OMe)Me$ (SAFC Hitech) was held inside the reactor in an open source boat at 75 °C and $ZrCl_4$ similarly at 165 °C. Both chemicals are moisture sensitive. $(CpMe)_2Zr(OMe)Me$ was loaded into the source boat in a glovebox and exposed to air only for a couple of seconds when being inserted into the reactor. $ZrCl_4$ was stored in a glovebox, but it was loaded into the boat in the room air. These precursors were pulsed with inert gas valving.[2] D_2O (Euriso-top, 99.9%) was used instead of H_2O to better distinguish the reaction byproducts from species forming in fragmentation and recombination reactions in the QMS ionizator. Still weak background signals were detected at masses corresponding to the deuterated products when the same precursor was pulsed repeatedly, so these were subtracted from the data.[8] Typically, the actual oxygen precursor was first pulsed five times, then ten cycles of the ALD process were run, and finally the zirconium precursor was pulsed five times. D_2O was held in a precursor bottle outside the reactor at room temperature. Ozone (concentration 60 g/Nm^3) was generated from oxygen (Oy AGA Ab, 99.999%) with a Wedeco Ozomatic Modular 4 HC Lab ozone generator. The oxygen precursors were led into the reactor through needle and solenoid valves. The precursor pulses were 5 s long, and the purge time between the precursor pulses was also 5 s except for certain cases when it was much longer, up to 45 s.

Results and Discussion

Fragmentation and Thermal Decomposition of $(CpMe)_2Zr(OMe)Me$. In ALD it is important that the precursor is not decomposing on its own because only then the process is taking place in pure ALD mode with a self-limiting mechanism. Therefore, thermal decomposition reactions of the metal precursor should always be examined prior to any detailed ALD studies and a reaction temperature chosen below the decomposition onset. Furthermore, in reaction mechanism studies with mass spectrometry the fragmentation of the precursors has to be known.

In the present study, the molecular peak of $(CpMe)_2Zr(OMe)Me$ ($m/z = 294$) could not be seen at all. The highest m/z observed was $m/z = 279$, which corresponds to the molecule without the methyl group.

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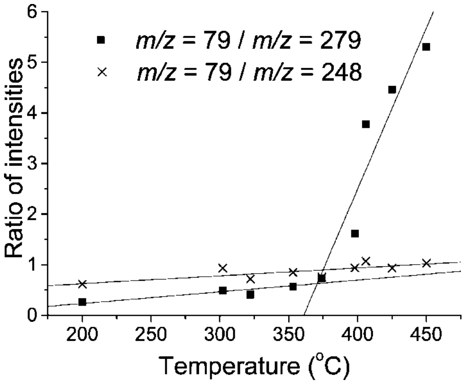

Figure 1. QMS results indicating the onset of the thermal decomposition reaction of $(CpMe)_2Zr(OMe)Me$ at about 380 °C.

An even stronger intensity peak was observed at $m/z = 248$, where the molecule had also lost the methoxy group.

Thermal decomposition of $(CpMe)_2Zr(OMe)Me$ was studied by pulsing the precursor repeatedly into the reactor and monitoring as a function of reaction temperature the ions containing zirconium ($m/z = 279$ and $m/z = 248$) and the peak $m/z = 79$, which corresponds to the −CpMe ligand and may originate both from the intact precursor molecule and from its decomposition products. The ratios of the intensity of $m/z = 79$ to the intensities of the higher m/z peaks are shown in Figure 1 as a function of temperature. At low temperatures where no decomposition occurs, the ratios stay constant and represent only the fragmentation of $(CpMe)_2Zr(OMe)Me$ in the QMS. The onset of a thermal decomposition reaction can be seen at about 375 °C, where the ratio of the intensity of $m/z = 79$ to the intensity of $m/z = 279$ begins to increase. This increase is due to the decrease of $m/z = 279$ relative to $m/z = 79$, which indicates decomposition of the $(CpMe)_2Zr(OMe)$ group ($m/z = 279$). However, the ratio of the intensity of $m/z = 79$ to the intensity of $m/z = 248$ still stays constant. Therefore, the $(CpMe)_2Zr$ group ($m/z = 248$) appears to remain intact in the decomposition reaction in question. In the film growth experiments thermal decomposition of $(CpMe)_2Zr(OMe)Me$ was noted to interfere with the ALD processes starting from about 420 °C.[27,28] Earlier our group observed 25−50 °C lower decomposition onset temperatures with QMS as compared to the film growth experiments for other processes as well.[13,20] The difference is believed to be due to an about 60 times larger substrate area and longer precursor pulses in the QMS reactor, which enable slower decomposition to be noticed.

$(CpMe)_2Zr(OMe)Me-D_2O$ Process. The growth reaction byproducts in the $(CpMe)_2Zr(OMe)Me-D_2O$ process were as expected MeD ($m/z = 17$), MeOD ($m/z = 33$), and DCpMe ($m/z = 81$). Therefore, the net growth reaction is

$$(CpMe)_2Zr(OMe)Me(g) + 2D_2O(g) \rightarrow ZrO_2(s) + MeD(g) + MeOD(g) + 2DCpMe(g) \quad (1)$$

The QMS results of one measurement of each gaseous reaction byproduct are shown in Figure 2. From these data one can calculate the ratio of the intensity of a given reaction byproduct observed during the $(CpMe)_2Zr(OMe)Me$ pulse to its total intensity during one ALD cycle, i.e., the sum of the intensities observed during the $(CpMe)_2Zr(OMe)Me$ and D_2O pulses. This ratio indicates which fraction of this reaction byproduct is released during the $(CpMe)_2Zr(OMe)Me$ pulse, the rest being released during the D_2O pulse. During the $(CpMe)_2Zr(OMe)Me$ pulse (80 ± 3)% ($N = 16$) of MeD, (38 ± 1)% ($N = 12$) of MeOD, and (57 ± 3)% ($N = 13$) of DCpMe are released. The numbers (N) of measurements judged successful and thus accommodated in the averages are indicated in parentheses, and these measurements have usually been done on different days after the reactor has been reloaded. Therefore, they are to be considered genuine parallel measurements. The error limits indicated are the average errors of the averages. Since this method gives a quite narrow estimation of the error (if normal distribution is assumed, the reliability of these error limits is 68%), the results can really be considered reliable with only one significant digit.

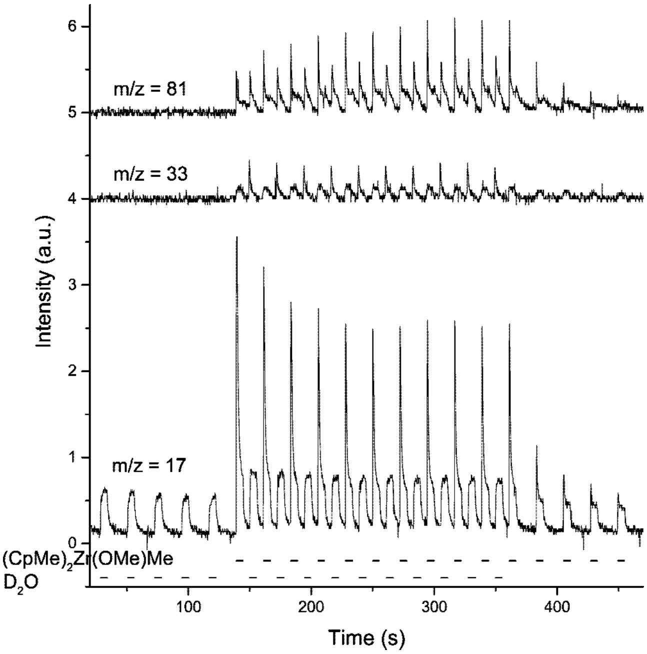

Figure 2. QMS data of the $(CpMe)_2Zr(OMe)Me-D_2O$ ALD process. The ALD byproducts are MeD ($m/z = 17$), MeOD ($m/z = 33$), and DCpMe ($m/z = 81$).

In light of the QMS results, the average growth reaction mechanism appears to be the one given in reactions 2a and 2b. In reaction 2a deuterium atoms of the surface −OD groups bind to ligands of the approaching $(CpMe)_2Zr(OMe)Me$ molecule, whereby those ligands are released in deuterated form. The zirconium atom and the remaining ligands are left on the surface, zirconium being bonded to all the oxygen atoms that lost their deuterium atoms. In reaction 2b 1.7 D_2O molecules release the remaining ligands in deuterated form, leaving behind a corresponding amount of −OD groups bonded to the zirconium atom. The further amount of 0.3 D_2O molecule is dissociatively chemisorbed on the surface. Thereby, the bonds of 0.3 oxygen atom to the zirconium atom are broken. Together reactions 2a and 2b lead to a deposition of stoichiometric ZrO_2 and maintain a constant concentration of −OD groups from cycle to cycle. The latter is necessary as all the cycles were found to be similar.

$$2.3[-OD(s)] + (CpMe)_2Zr(OMe)Me(g) \rightarrow (-O)_{2.3}ZR(CpMe)_{0.9}(OMe)_{0.6}Me_{0.2}(s) + 0.8MeD(g) + 0.4MeOD(g) + 1.1DCpMe(g) \quad (2a)$$

$$(-O)_{2.3}ZR(CpMe)_{0.9}(OMe)_{0.6}Me_{0.2}(s) + 2D_2O(g) \rightarrow (-O)_2Zr(OD)_{2.3}(s) + 0.2MeD(g) + 0.6MeOD(g) + 0.9DCpMe(g) \quad (2b)$$

In the above mechanism m_0/m_1 is 0.69, where m_0 denotes the net mass change of the surface during one complete ALD cycle (i.e., ZrO_2 being deposited by reactions 2a and 2b) and m_1 the mass change of the surface during the $(CpMe)_2Zr(OMe)Me$ pulse in the ALD process (i.e., the adsorbate forming in reaction 2a). The m_0/m_1 ratio is important because it allows cross-checking of the reaction mechanism with the QCM technique.

With QCM and $(CpMe)_2Zr(OMe)Me$ some unexpected features were encountered. A measurement of the ALD process is shown in Figure 3. The signal starts to ascend always when the $(CpMe)_2Zr(OMe)Me$ supply is closed, although it has settled during the $(CpMe)_2Zr(OMe)Me$ pulse. Separate experiments verified this increase to be an artifact, but it could never be eliminated nor its origin understood. Anyway, when this behavior is omitted, i.e., m_1 taken from the beginning to the end of the $(CpMe)_2Zr(OMe)Me$ pulse, QCM measurements give results such as $m_0/m_1 = 0.78 \pm 0.03$ and $m_0/m_1 = 0.74 \pm 0.02$. These are in fairly good agreement with the QMS results. Therefore, the above mechanism can be considered quite well grounded with a tolerance of about 10% for all the quantities. Also, the relative stabilities of the metal ligand bonds toward hydrogen attacks agree with theory. That is to say, the MeO− ligand bonds the strongest (is eliminated in the smallest relative amount during the $(CpMe)_2Zr(OMe)Me$ pulse), the Me− ligand the weakest, and the −CpMe ligand intermediately strong as is expected both on the basis of formal charges and on the basis of ab initio calculations.[29] This is also consistent with studies on precursors resembling the current precursor, i.e., Cp_2ZrMe_2[20] and Me_2AlCl,[19] and with the earlier results concerning the current precursor,[29] although no release of MeO− ligands was detected in the earlier study during the $(CpMe)_2Zr(OMe)Me$ pulse as compared to our 38%. Also we found only 80% of the Me− ligands to be released during the $(CpMe)_2Zr(OMe)Me$ pulse as compared to 100% in the earlier study.[29] With the −CpMe ligands the results were most consistent (65%[29] vs 57%).

$(CpMe)_2Zr(OMe)Me-O_3$ Process. The most important growth reaction byproducts in the $(CpMe)_2Zr(OMe)Me-O_3$ process were CO_2 ($m/z = 44$) and H_2O ($m/z = 18$). In addition, some MeH ($m/z = 16$) and HCpMe ($m/z = 80$) could be detected but no MeOH ($m/z = 32$). The QMS results of one measurement of each gaseous reaction byproduct are shown in Figure 4. Most interestingly, CO_2 and H_2O are formed not only during the O_3 pulse but also during the $(CpMe)_2Zr(OMe)Me$ pulse. By contrast at least HCpMe is formed only during the $(CpMe)_2Zr(OMe)Me$ pulse. These results do not give very detailed information about the state of the surface after the two precursor pulses. For example, one cannot tell which ligands combust during the $(CpMe)_2Zr(OMe)Me$ pulse. To get a better picture of the surface species involved, different kinds of surface-probing measurements were performed.

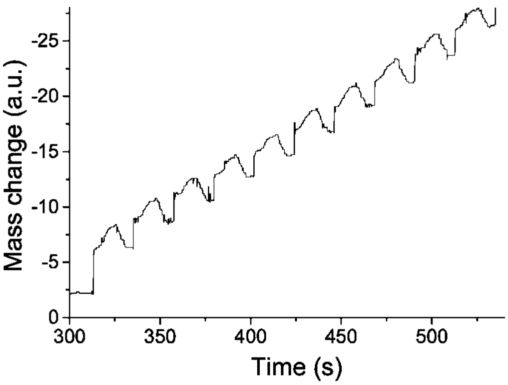

Figure 3. QCM data of 10 cycles of the $(CpMe)_2Zr(OMe)Me-D_2O$ ALD process. The signal increases during the $(CpMe)_2Zr(OMe)Me$ pulse and decreases during the D_2O pulse.

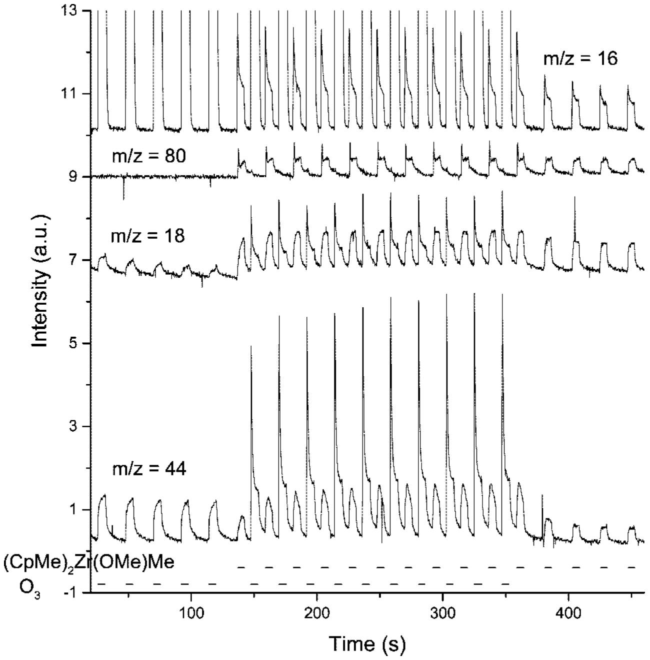

Figure 4. QMS data of the $(CpMe)_2Zr(OMe)Me-O_3$ ALD process. The ALD byproducts are CO_2 ($m/z = 44$), H_2O ($m/z = 18$), HCpMe ($m/z = 80$), and MeH ($m/z = 16$).

The surface species after the $(CpMe)_2Zr(OMe)Me$ pulse were probed using D_2O. In the measurements, after the D_2O background metering, the $(CpMe)_2Zr(OMe)Me-D_2O$ process was run first for comparison purposes, then the $(CpMe)_2Zr(OMe)Me-O_3$ process, and then again the $(CpMe)_2Zr(OMe)Me-D_2O$ process (Figure 5). The amounts of deuterated ligands released during the first D_2O pulse in the latter $(CpMe)_2Zr(OMe)Me-D_2O$ process give the amounts of the corresponding ligands remaining on the surface after the $(CpMe)_2Zr(OMe)Me$ pulse in the $(CpMe)_2Zr(OMe)Me-O_3$ process. The QMS results of one measurement of each deuterated ligand are shown in Figure 5. From these measurements the relative results were calculated, i.e., how much of the different ligands remain on the surface after the $(CpMe)_2Zr(OMe)Me$ pulse, and

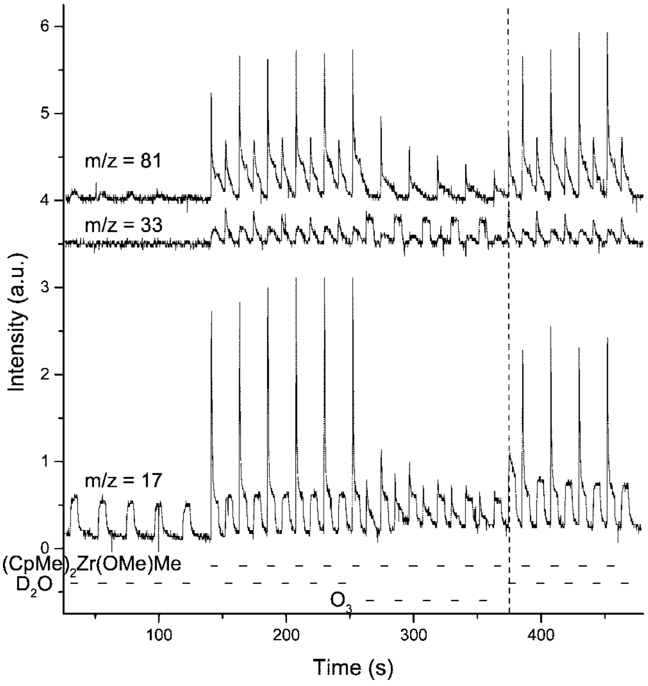

Figure 5. QMS measurements where the amounts of the different kinds of ligands remaining on the surface after the $(CpMe)_2Zr(OMe)Me$ pulse in the $(CpMe)_2Zr(OMe)Me-O_3$ ALD process are determined using D_2O. The interesting peak here is the peak during the first D_2O pulse after the $(CpMe)_2Zr(OMe)-O_3$ ALD process has been run.

are thus eliminated during the O_3 pulse in the $(CpMe)_2Zr(OMe)Me-O_3$ process, as compared to the D_2O pulse in the $(CpMe)_2Zr(OMe)Me$-D_2O process. The results were that Me− remained in a 3.44 ± 0.52 ($N = 6$) fold amount, MeO− in a 1.19 ± 0.04 ($N = 4$) fold amount, and −CpMe in a 1.14 ± 0.02 ($N = 4$) fold amount. The results of Me− show greater variation as the amounts detected are small compared to the D_2O background.

The above results together with the results on the $(CpMe)_2Zr(OMe)Me-D_2O$ process will give the state of the surface after the $(CpMe)_2Zr(OMe)Me$ pulse in the $(CpMe)_2Zr(OMe)Me-O_3$ process when the differences in the $(CpMe)_2Zr(OMe)Me$ surface saturation are taken into account. Here the growth rate may be taken as a measure of the $(CpMe)_2Zr(OMe)Me$ surface saturation. The most accurate results for growth rates are obtained from growth experiments, where the growth rate in the $(CpMe)_2Zr(OMe)Me-O_3$ process was (28 ± 10)% greater than in the $(CpMe)_2Zr(OMe)Me-H_2O$ process.[27,28] Accordingly (53 ± 11)% of the Me− ligands, (58 ± 5)% of the MeO− ligands, and (39 ± 4)% of the −CpMe ligands are eliminated during the O_3 pulse compared to a complete ALD cycle in the $(CpMe)_2Zr(OMe)Me-O_3$ process. For example, the result of 53% of the Me− ligands is obtained as follows. Let us say that x mol of $(CpMe)_2Zr(OMe)Me$ reacts in one cycle of the $(CpMe)_2Zr(OMe)Me-D_2O$ process, i.e., reactions 2a and 2b. Thereby, $0.2x$ mol (20%; see above) of Me− ligands is eliminated during the D_2O pulse. Now during the O_3 pulse in the $(CpMe)_2Zr(OMe)Me-O_3$ process are eliminated $3.44 \times 0.2x$ mol of Me− ligands. On the other hand, the amount of reacting $(CpMe)_2Zr(OMe)Me$ in one cycle of the $(CpMe)_2Zr(OMe)Me-O_3$ process is 1.28-fold compared to the $(CpMe)_2Zr(OMe)Me-H_2O$ process, and thereby, a total $1.28x$ mol of Me− ligands is eliminated during one cycle. Therefore, the fraction of Me− ligands eliminated during the O_3 pulse is $(3.44 \times 0.2)/1.28$. The error limits above have been calculated using the average error accumulation law.

Possible surface species after the O_3 pulse include (1) a plain ZrO_2 surface ("pure", coordinatively unsaturated), (2) hydroxyl groups, (3) carbonate groups, and (4) in one or another fashion chemisorbed active oxygen, i.e., oxygen that is not fully reduced to −II and is thus capable of oxidizing hydrocarbons. Here carbonate groups do not seem likely since Zr hardly forms solid carbonates. This is supported by the fact that ZrO_2 films deposited with the $(CpMe)_2Zr(OMe)Me-O_3$ process do not contain carbon impurities.[28] On the other hand, the $Ca(thd)_2-O_3$ and $Sr(thd)_2-O_3$ ALD processes resulted in $CaCO_3$ and $SrCO_3$ film growth, respectively,[31,32] as calcium and strontium easily form solid carbonates. Also the $La(thd)_3-O_3$ ALD process grew $La_2O_2CO_3$ at lower temperatures and La_2O_3 with carbonate impurities at higher temperatures[33] as lanthanum(III) is known to form even $La_2(CO_3)_3$ in the solid state. With zirconium(IV) only basic carbonates appear to be known, so no carbonate groups result on the ZrO_2 thin film surface.

The amount of hydroxyl groups on the surface after the O_3 pulse was studied using $ZrCl_4$. The $(CpMe)_2Zr(OMe)Me-O_3$ process was stopped after an O_3 pulse, and then five $ZrCl_4$ pulses were given. The amount of HCl ($m/z = 36$) released during the first $ZrCl_4$ pulse minus the amount released during the last $ZrCl_4$ pulse (i.e., the background) is considered to be proportional to the amount of hydroxyl groups on the surface. For calibration purposes similar measurements were performed subsequently with the $(CpMe)_2Zr(OMe)Me-D_2O$ process; i.e., this process was stopped after a D_2O pulse, $ZrCl_4$ pulses were given, and the amount of DCl ($m/z = 37$) released was followed. The QMS results of one such pair are shown in Figure 6. The signals during the ALD processes are mainly fragments of −MeCp ligands. The result was that the amount of −OH groups on the surface after the O_3 pulse was (14 ± 3)% ($N = 5$) of the amount of −OD groups on the surface after the D_2O pulse. This means that in the ozone process there is $[(0.14 \times 2.31)/1.28] = 0.25$ −OH group for 1 reacting $(CpMe)_2Zr(OMe)Me$ molecule. This result is obtained with a similar kind of deduction already given for the fractions of ligands remaining after the $(CpMe)_2Zr(OMe)Me$ pulse. There is no way this low surface −OH concentration would explain the total amounts of ligands eliminated during the $(CpMe)_2Zr(OMe)Me$ pulse. Furthermore, only −OH groups would not explain the formation of CO_2 and H_2O during the $(CpMe)_2Zr(OMe)Me$ pulse. Therefore, some form of chemisorbed active oxygen is concluded to be present on the surface after the O_3 pulse.

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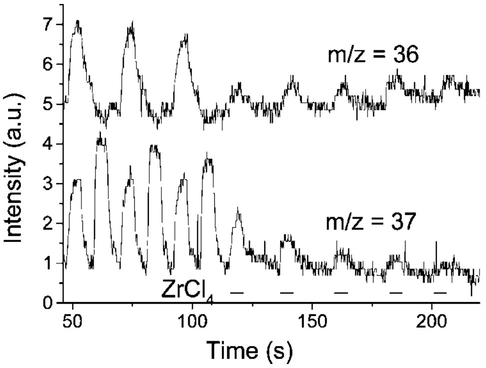

Figure 6. QMS measurements where the amount of −OH groups remaining on the surface after the O_3 pulse in the $(CpMe)_2Zr(OMe)Me-O_3$ ALD process (top) is determined relative to the amount of −OD groups remaining on the surface after the D_2O pulse in the $(CpMe)_2Zr(OMe)Me-D_2O$ process (bottom). The quantification is done using $ZrCl_4$, which gives either DCl ($m/z = 37$) or HCl ($m/z = 36$).

Of the growth reaction byproducts in the $(CpMe)_2Zr(OMe)Me-O_3$ process (23 ± 2)% ($N = 11$) of the CO_2 and (22 ± 5)% ($N = 10$) of the H_2O are released during the $(CpMe)_2Zr(OMe)Me$ pulse. As already mentioned also some MeH and HCpMe could be detected during the $(CpMe)_2Zr(OMe)Me$ pulse. At least HCpMe does not appear to be formed during the O_3 pulse. During the $(CpMe)_2Zr(OMe)Me$ pulse no release of MeOH ($m/z = 32$) was seen. MeH and MeOH have m/z values (16 and 32, respectively) that are also formed in great amounts as fragments of O_3. Therefore, these reaction products would be difficult to prove during the O_3 pulse. Since all −CpMe eliminated during the O_3 pulse appears to combust, it is likely that all Me− and MeO− ligands combust as well during the O_3 pulse. Then there also is the question of complete or incomplete combustion of the ligands. Actually both $m/z = 28$ (CO and corresponding fragments formed in the ionizer) and $m/z = 30$ (CH_2O and corresponding fragments formed in the ionizer) were seen during the O_3 pulse. This however does not mean that the molecules CO and CH_2O would necessarily be actual reaction byproducts, since these groups can easily be formed in the ionizer from CO_2 and H_2O. Furthermore, these m/z species are formed as fragments of $(CpMe)_2Zr(OMe)Me$, but they do not show appreciably greater signals during the ALD process as compared to the background. Therefore, it would appear that the possible reaction byproducts CO and CH_2O at least are not formed during the $(CpMe)_2Zr(OMe)Me$ pulse. Since everything that combusts during the $(CpMe)_2Zr(OMe)Me$ pulse, when there in any case is less oxygen available, appears to combust completely, it is reasonable to conclude that everything that combusts during the O_3 pulse also combusts completely.

The amounts of MeH and HCpMe released during the $(CpMe)_2Zr(OMe)Me$ pulse are still to be clarified. We chose to quantify these relative to the amounts of corresponding deuterated molecules released during the specific D_2O pulse that in the measurements already described substituted an O_3 pulse and therefore released in deuterated form the ligands that were usually combusted by O_3 in the $(CpMe)_2Zr(OMe)Me-O_3$ process. Hereby, it was found that the amount of MeH released was (173 ± 34)% ($N = 5$) and the amount of HCpMe released was (85 ± 28)% ($N = 4$) of the amounts of MeD and DCpMe, respectively.

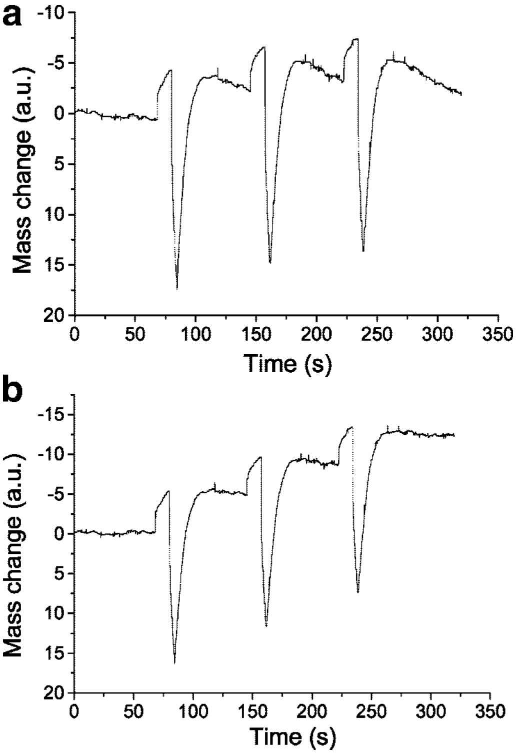

Figure 7. QCM data of three cycles of the $(CpMe)_2Zr(OMe)Me-O_3$ ALD process (a) in raw form and (b) temperature corrected. The signal increases during the $(CpMe)_2Zr(OMe)Me$ pulse and shows an enormous negative artifact during the O_3 pulse.

In the QCM measurements there was one additional drawback with the $(CpMe)_2Zr(OMe)Me-O_3$ process as compared to the $(CpMe)_2Zr(OMe)Me-D_2O$ process. Because O_3 is greatly diluted with O_2, this mixture has to be fed into the reactor at a quite high pressure. During the O_3 pulse the pressure can be noted to increase significantly both in the ALD reactor and in the QMS chamber. Since QCM is sensitive to the surrounding pressure, a large artifact appears in the QCM signal during the O_3 pulse. The settling of this pressure effect requires much longer purging times than usual. Then the pressure effect is succeeded by a temperature effect that is somewhat cumulative. Therefore, the purge times must be so long that the temperature change rate settles, after which the temperature changes can be compensated in the fashion our group has previously demonstrated.[14] Raw and temperature effect compensated QCM data are shown in parts a and b, respectively, of Figure 7. The QCM results are like $m_0/m_1 = 1.09 \pm 0.05$.

On the basis of the experimental results, it would appear that four kinds of reactions take place in the $(CpMe)_2Zr(OMe)Me-O_3$ process. First, the small amount of −OH groups remaining on the surface after the O_3 pulse release a few ligands in the protonated form during the $(CpMe)_2Zr(OMe)Me$ pulse. Second, the active oxygen remaining on the surface after the O_3 pulse eliminates some ligands as CO_2 and H_2O during the $(CpMe)_2Zr(OMe)Me$ pulse. Third, the H_2O thereby formed releases some more ligands in protonated form still during the $(CpMe)_2Zr(OMe)Me$ pulse. Finally, the ligands remaining

Table 1. Results of the Mechanism of the $(CpMe)_2Zr(OMe)Me-O_3$ ALD Process and the Appropriate Leveling of the Experimental Errors[a]

	experimental result	calculation starting value	calculation result
fraction (%) of ligand eliminated (italic) or substance released (italic) during the given precursor (bold) pulse as compared to a complete ALD cycle			
Me−, **O_3**	53 ± 11	42	
MeO−, **O_3**	58 ± 5	53	
−*CpMe*, **O_3**	39 ± 4	42	
CO_2, **$(CpMe)_2Zr(OMe)Me$**	23 ± 2		24
H_2O, **$(CpMe)_2Zr(OMe)Me$**	22 ± 5		18
relative amount of −OH groups (%)	14 ± 3	17	
relative amount of HCpMe released (%)	85 ± 28	113	
relative amount of MeH released (%)	173 ± 34	140	
m_0/m_1	1.09 ± 0.05		1.10

[a] Leveling is needed since there are nine experimental results but only six degrees of freedom. Therefore, six results have been chosen as calculation starting values, and the others have been calculated. The division into these two groups has been made so that the calculation is as simple as possible. Subsequently, the starting values have been varied within the error limits of their experimental results so that also the calculation results fall within the error limits of their experimental results. The variation has been done simply by means of trial and error. The amount of −OH groups is given relative to that in the $(CpMe)_2Zr(OMe)Me-D_2O$ process, and the amounts of HCpMe and MeH released during the $(CpMe)_2Zr(OMe)Me$ pulse in the $(CpMe)_2Zr(OMe)Me-O_3$ process are given relative to the amounts of corresponding deuterated molecules released during a D_2O pulse that substituted an O_3 pulse (Figure 5). m_0 denotes the net mass change of the surface during one complete ALD cycle and m_1 the mass change of the surface during the $(CpMe)_2Zr(OMe)Me$ pulse in the ALD process.

on the surface after the $(CpMe)_2Zr(OMe)Me$ pulse are eliminated as CO_2 and H_2O during the O_3 pulse. Some H_2O stays on the surface as −OH groups.

It has to be noted that all the results are not independent. As a matter of fact, the fractions of ligands eliminated during the different precursor pulses together with the amounts of −OH groups remaining on the surface after the O_3 pulse and of ligands released in protonated form during the $(CpMe)_2Zr(OMe)Me$ pulse uniquely determine the fractions of CO_2 and H_2O being released during different precursor pulses. Now the first mentioned experimental results give by calculation that 37% of CO_2 and 23% of H_2O would be released during the $(CpMe)_2Zr(OMe)Me$ pulse and that m_0/m_1 would be 2.25. These results as such do not very well match with the direct experimental ones. However, such a calculation is sensitive to the input values: if the experimental results used as starting values in the calculation are varied within their error limits, also the calculated results can be made to fall within the error limits of their corresponding experimental values. Such a fit more closely demonstrated in Table 1 describes the following mechanism (O* is active oxygen):

$$0.3[-OH(s)] + 5.1[-O^*(s)] + (CpMe)_2Zr(OMe)Me(g) \rightarrow -ZR(CpMe)_{0.8}(OMe)_{0.5}Me_{0.4}O_{1.3}(s) + 0.6MeH(g) + 0.9HCpMe(g) + 1.9CO_2(g) + 0.9H_2O(g) \quad (3a)$$

$$-ZR(CpMe)_{0.8}(OMe)_{0.5}Me_{0.4}O_{1.3}(s) + 21.7O_3(g) \rightarrow -ZrO_2O^*_{5.1}(OH)_{0.3}(s) + 5.9CO_2(g) + 4.2H_2O(g) + 21.7O_2(g) \quad (3b)$$

The mechanism is based on the final best fit in Table 1. The fit was done so that both the chosen starting values and the resulting calculation values remain within the error limits of the experimental results, so they all agree. Since nine results are used in the leveling where six would be adequate, the procedure involves possibilities for cross-checking and thereby partly compensates for bigger uncertainties in some of the results. Therefore, the mechanism can be considered practically as reliable as the D_2O process mechanism, i.e., with a 10% tolerance for all the quantities.

The coefficient for −OH(s) in eq 3a was deduced earlier. The amounts of the ligands remaining on the surface after the $(CpMe)_2Zr(OMe)Me$ pulse are given directly by the three first results in Table 1 (noting that 0.42 for the −CpMe ligands has to be multiplied by 2). Then the coefficients for MeH(g) and HCpMe(g) are obtained as 1.40 × 0.42 and 1.13 × 2 × 0.42, respectively, from Table 1. Subsequently, the amount of oxide ions left on the surface after the $(CpMe)_2Zr(OMe)Me$ pulse is obtained by charge balance. Then in eq 3a carbon is balanced with the coefficient of $CO_2(g)$, hydrogen with the coefficient of $H_2O(g)$, and finally oxygen with the coefficient of $-O^*(s)$. In eq 3b the surface product is the starting point of eq 3a plus ZrO_2. Then again carbon is balanced with the coefficient of $CO_2(g)$ and hydrogen with the coefficient of $H_2O(g)$. Finally, oxygen is balanced with the coefficients of $O_3(g)$ and $O_2(g)$.

The first apparent saving grace with the above mechanism is that the relative stabilities of the metal ligand bonds toward hydrogen attacks agree qualitatively with the findings in the $(CpMe)_2Zr(OMe)Me-D_2O$ process. Also in the $(CpMe)_2Zr(OMe)Me-O_3$ process during the $(CpMe)_2Zr(OMe)Me$ pulse the MeO− ligand is eliminated in protonated form the least (not at all actually), the Me− ligand the most, and the −CpMe ligand in intermediate amounts.

The suggested mechanism is somewhat surprising in that some chemisorbed active oxygen remains on the surface after the O_3 pulse. This however appears experimentally quite well grounded by the formation of CO_2 and H_2O during the $(CpMe)_2Zr(OMe)Me$ pulse (Figure 4). The question of the chemisorbed active oxygen species in the mechanism under discussion still remains. First, ozone molecules are usually understood to perform oxidation in such a manner that only one oxygen atom from each ozone molecule is reduced and the two remaining atoms leave as a dioxygen molecule (cf. reaction 3b). There is no reason to think that this would not be the case here as well, although it is also possible that all atoms of the O_3 molecules reacting are reduced during the O_3 pulse or left on the surface as active oxygen atoms.

However, the QCM data suggest that all active oxygen atoms remaining on the surface after the O_3 pulse are reduced during the $(CpMe)_2Zr(OMe)Me$ pulse. Otherwise, m_1 would have to be significantly larger. Some chemisorbed active oxygen species have been identified on oxide surfaces in catalysis studies.[34] Here we do not want to speculate on these species, since we cannot identify them with our equipment. We only want to notice that the growth rate in the $(CpMe)_2Zr(OMe)Me{-}O_3$ process is about 1/5 of a monolayer per cycle.[28] Therefore, the most simple explanation would be that one active oxygen atom (oxygen radical) bonded to each surface zirconium atom would remain on the surface after the O_3 pulse. Because of the low growth rate, the surface can accommodate enough active oxygen to follow the suggested reaction mechanism.

One reaction that could also be taking place during the $(CpMe)_2Zr(OMe)Me$ pulse, but which unfortunately cannot be confirmed in this case, is the following:

$$5{-}O^*(s) + {-}CpMe(s) \rightarrow Cp{=}O(g) + CO_2(g) + H_2O(g) + {-}OH(s) \quad (4)$$

Here part of the −CpMe ligands of the adsorbed $(CpMe)_2Zr(OMe)Me$ molecule reacting with the surface would be partially combusted so that the methyl group is combusted completely, but the cyclopentadienyl ring reacts with only one oxygen atom and forms cyclopentadienone. The molecular peak of this substance is $m/z = 80$, the same as for HCpMe, which certainly is formed in the ALD process during the $(CpMe)_2Zr(OMe)Me$ pulse, since its fragments can also be seen. Therefore, it is impossible to tell on the basis of the data at hand whether cyclopentadienone is also formed. One result supporting this is the observation of $m/z = 80$ in small amounts during the $(Cp^iPr)_3La$ pulse in the $(Cp^iPr)_3La{-}O_3$ process.[35] Cyclopentadienone is however a very unstable molecule, so from this point of view its formation is not very likely.

In the $InCp{-}O_3$ ALD process for growing In_2O_3 films, only HCp was released during the InCp pulse and only CO_2 during the O_3 pulse.[30] The QMS and QCM data gave such a mechanism that five −Cp ligands were released as HCp during the InCp pulse and one −Cp ligand was released as five CO_2 molecules during the O_3 pulse, thus leaving five −OH groups on the surface, the amount that was needed to release the five HCp molecules during the following InCp pulse. Even in this mechanism one surface oxygen species per six reacting InCp molecules was needed on the surface after the O_3 pulse to adsorb the one intact InCp molecule. Whether this was an oxide ion or active oxygen was not discussed, but the absence of CO_2 formation during the InCp pulse suggests that it was not active oxygen, similar to our case. Otherwise, the suggested mechanism for the $(CpMe)_2Zr(OMe)Me{-}O_3$ process includes all the elements found in the previous study, although the relative amounts are substantially different.

In any case the above mechanism for the $(CpMe)_2Zr(OMe)Me{-}O_3$ process is able to explain all our experimental data. Also it is quite consistent with previous studies. Therefore, it can be considered reasonably substantiated though complicated.

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