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Reaction mechanism studies on the zirconium chloride–water atomic layer deposition process

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Reaction mechanisms in the zirconium chloride–water atomic layer deposition (ALD) process have been studied with a quartz crystal microbalance (QCM) and quadrupole mass spectrometer (QMS) at 250–500 °C The only observed reaction byproduct was HCl. Both the growth rate and the amount of reaction byproduct were the highest at 300 °C as measured with QCM and QMS, respectively. The reaction temperature had no major effect on the reaction mechanism: half of the chloride ligands were released during the $ZrCl_4$ pulse and the other half during the water pulse. However, at higher temperatures the process was slowly moving towards a mechanism where only one chlorine is released during the zirconium pulse and the other three during the D_2O pulse. This was suggested to be due to a lowered amount of OD groups on the surface at high temperatures. The results were compared with the earlier TiO_2, ZrO_2 and HfO_2 ALD processes.

Introduction

The dimensions of the microelectronic devices are shrinking fast according to Moore's law.[1] The key component of the modern microprocessor is a metal oxide semiconductor field effect transistor (MOSFET). The scaling of the MOSFET puts increasing demands especially on the properties of the gate oxide. SiO_2-based materials have been the choice for the gate oxide for the lifetime of the modern transistors but now they are approaching the limits where the gate oxide is about to be scaled so thin that the direct tunneling current through it would become unacceptably high. Therefore, new gate oxide materials with a higher permittivity than SiO_2 ($\varepsilon_r = 3.9$) are needed. When the permittivity is higher, thicker gate oxides can be used for obtaining a given capacitance. With thicker films the tunneling current can be reduced to an acceptable level. The most promising and most studied high permittivity gate oxide materials are Al_2O_3, HfO_2, ZrO_2, Y_2O_3, La_2O_3 and their silicates.[2–4]

Even if high permittivity materials are to be used as gate oxides, the films will still be very thin. In addition, the films must be very uniform, smooth and without any pinholes. An important candidate for depositing gate oxides is atomic layer deposition (ALD), also called atomic layer chemical vapor deposition (ALCVD). It is a gas phase method for depositing high quality thin films.[5–7] ALD is based on alternate saturative surface reactions. Each precursor is pulsed to the reaction chamber alternately, one at a time, and the pulses are separated by inert gas purging periods. With properly chosen growth conditions, the reactions are saturative and the film growth is thereby self-limiting. This offers a lot of practical advantages, such as excellent conformality, accurate and simple thickness control and large area uniformity.[8–10] At the moment, Al_2O_3[11–13] and ZrO_2[13–15] are the most commonly studied gate oxide candidates grown by ALD.

ZrO_2 thin films have been grown by ALD from $ZrCl_4$[13,14,16–18] and ZrI_4.[15,19] The oxygen source is usually water, but hydrogen peroxide (H_2O_2)[15,19,20] has also been used. In the $ZrCl_4$–H_2O process at 500 °C the chlorine content of the films was below 0.5 at.%. The refractive index was 2.2 at the wavelength of 580 nm. Zirconium alkoxides such as $Zr(OC(CH_3)_3)_4$[21] and $Zr(OC(CH_3)_3)_2(dmae)_2$,[22] where dmae = $OCH_2CH_2N(CH_3)_2$, have also been examined as precursors in ALD, but the main problem was their thermal instability.

As an extension to the many film growth experiments, reaction mechanisms in the $ZrCl_4$-based ALD process have also been studied with a quartz crystal microbalance (QCM)[20] which is a very powerful *in situ* method to study ALD reactions.[20,23–25] The oxygen sources used in that study were water and hydrogen peroxide which gave essentially similar results. One to two chlorine atoms were found to be released per $ZrCl_4$ molecule in the reactions with OH groups during the $ZrCl_4$ pulse at 180–380 °C. The remaining chlorine groups on the surface were released during the oxygen source pulse and the surface was converted back to OH group-terminated.

The purpose of this study is to improve the understanding of the reaction mechanism of the important zirconium chloride–water ALD process. The reaction mechanism was examined with QMS and QCM over a wide temperature range. Because QCM is very sensitive to already minor temperature variations, especially at high temperatures, we used a novel reference crystal method[26,27] for also obtaining results above 400 °C.

Experimental

Experiments were carried out with a specially modified[23,28] commercial flow type F-120 ALD reactor manufactured by ASM Microchemistry Ltd. The reaction chamber was loaded with glass substrates so that these formed narrow flow channels between each other. The total area of glass substrates was about 3500 cm^2. The gas composition was measured with a Hiden HAL/3F 501 RC QMS using an electron multiplier detector, a mass range of 1–510 amu and an ionization energy of 70 eV. The sampling and the pressure reduction were accomplished through a 50 μm orifice. The pressure in the ALD reactor is about 1 mbar and in the QMS chamber below 10^{-6} mbar. The surface mass studies were persormed using a Maxtek TM-400 QCM. Commercial crystals (Maxtek SC-101) with gold electrodes were used. Before each experiment series a thin ZrO_2 buffer layer was grown on the crystal to prevent any potential effects of the gold electrode. The crystal operating frequency was 6 MHz, the sampling rate 20 times per second, and the sensitivity was estimated to correspond to a nominal

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thickness of about 0.01 Å for ZrO_2. At high temperature the QCM is very sensitive to temperature variations. Therefore, a reference crystal method was used.[26,27] In that method two closely spaced quartz crystals are used, one being protected against film growth and thus serving as a reference crystal for compensating the temperature effects on the measurement crystal.

$ZrCl_4$ (Strem, 99.95+%) was held inside the reactor in an open boat at 165 °C and the pulsing was accomplished with inert gas valving.[29] $ZrCl_4$ is moisture sensitive and therefore the precursor boat was loaded in a glove box and exposed to air only for a couple of seconds before inserting it into the reactor. D_2O (Euriso-top, 99.9% D) was held outside the reactor in a glass bottle at room temperature (20–22 °C), the flow rate was controlled by a needle valve and the pulsing was accomplished using a solenoid valve. It has been our common practice to use D_2O in the *in situ* studies on processes involving organometallic precursors[23,24,28,30,31] to better distinguish the reaction byproducts from the species forming in the QMS ionization chamber. Although fragmentation did not cause a problem in this study, D_2O was still used for consistency. Weak background signals were also found to arise in the ions from DCl, even when no exchange reactions should have taken place, *i.e.* when subsequent pulses of only one precursor were given. Therefore, the background was subtracted from the data, as described earlier.[30] Nitrogen (99.999%) was used as a purging and carrier gas. Reaction temperatures were 250–500 °C. The precursor pulse times were 3 s and 5 s for $ZrCl_4$ and D_2O respectively. The purge time was 6 s after each precursor pulse.

Results and discussion

Table 1 summarizes the *m*/*z* values studied. All $ZrCl_x^+$ ions (x = 0–4) were observed although the intensities were relatively weak. Owing to the low intensity the thermal decomposition of $ZrCl_4$ was impossible to study. However, according to literature $ZrCl_4$ should be stable against thermal decomposition up to 800 °C.[32]

The only reaction byproduct observed was DCl which was detected at *m*/*z* values 35, 37 and 39. The intensity ratios of these *m*/*z* values correspond to the intensity ratios of HCl[33] and thus it was concluded that all these *m*/*z* values belong to the same molecule. Therefore, in this study only the ion $D^{37}Cl^+$ (m/z = 39) was studied in more detail. The *m*/*z* value of 39 is the only one which can be attributed solely to DCl.

Fig. 1 shows the simultaneously measured QCM and QMS data. The reaction byproducts were released during both the $ZrCl_4$ and D_2O pulses (Fig. 1b). In the QCM data (Fig. 1a), the weight increase during the $ZrCl_4$ adsorption is labeled as m_1. During the D_2O pulse the mass decreases because the heavier Cl surface groups are replaced by OD groups or oxide ions. The mass increment during a complete ALD cycle is m_0 which is linearly related to the growth rate. Because these masses are related to the adsorbate $ZrCl_{4-n}$ (m_1) and ZrO_2 (m_0), from their ratio one can estimate how many ligands are released during the metal precursor and water pulses (eqn. 1).

Table 1 The studied *m*/*z* values and the corresponding ions. The *m*/*z* values are based on ^{90}Zr (51% of natural zirconium) and ^{35}Cl (75.4% of natural chlorine) if not otherwise stated

m/*z*	Ion	Observed	*m*/*z*	Ion	Observed
35	Cl^+	Yes	179	$Zr(OD)_3Cl^+$	No
37	$^{37}Cl^+$ or $D^{35}Cl^+$	Yes	178	$ZrCl_2OD^+$	No
39	$D^{37}Cl^+$	Yes	192	$ZrO_2Cl_2^+$	No
70	Cl_2^+	No	195	$ZrCl_3^+$	Yes
90	Zr^+	Yes	196	$Zr(OD)_2Cl_2^+$	No
125	$ZrCl^+$	Yes	211	$ZrOCl_3^+$	No
160	$ZrCl_2^+$	Yes	213	$ZrCl_3OD^+$	No
176	$ZrCl_2O^+$	No	230	$ZrCl_4^+$	Yes

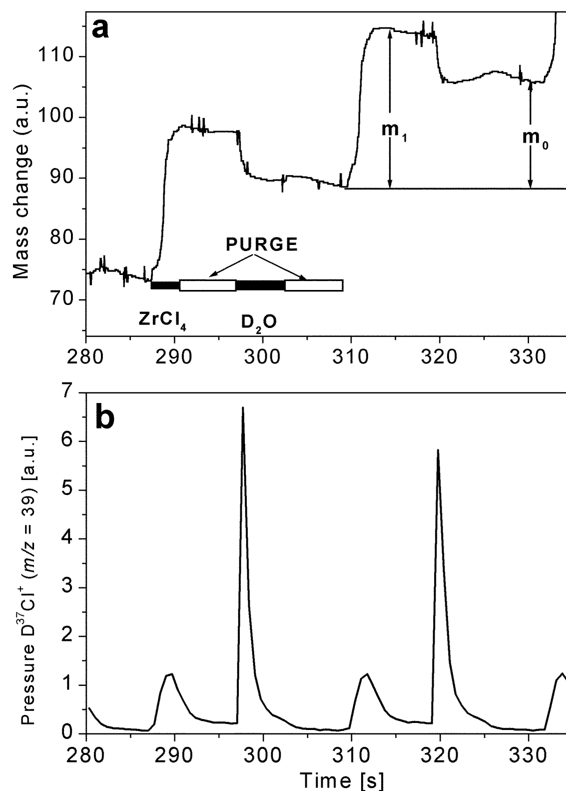
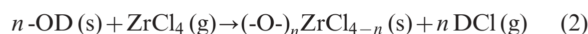


Fig. 1 (a) QCM mass change and (b) QMS data in two complete ALD cycles at 300 °C. In (a) m_0 is the mass change during one complete ALD cycle and m_1 is the mass increment during the $ZrCl_4$ pulse. $ZrCl_4$ and D_2O pulse times were 3 and 5 s and purge times 6 s, respectively.

$$\frac{m_0}{m_1} = \frac{M(ZrO_2)}{M(ZrCl_4) - nM(DCl)} \quad (1)$$

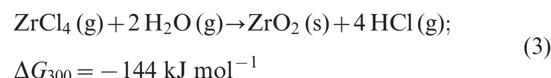
where n is the amount of ligands released during the $ZrCl_4$ pulse:



$$n\text{-OD (s)} + ZrCl_4\text{ (g)} \rightarrow (\text{-O-})_nZrCl_{4-n}\text{ (s)} + n\,DCl\text{ (g)} \quad (2)$$

In this study, first n is calculated from eqn. (1) and then it is divided by the total number of ligands in the zirconium precursor (4) to give n/4. Similar n/4 values can be calculated also from the QMS data by dividing the amount of reaction byproducts released during the $ZrCl_4$ pulse by the total amount of reaction byproducts released during one cycle. In fact, more generally it can be stated that the reaction mechanisms obtained from the QMS results are more reliable because these are contributed by only the exchange reactions. Therefore, for example, decomposition of the precursor does not affect the results. In addition, in some cases when desorption occurs during the purge period, m_1 is somewhat difficult to determine. On the other hand, QCM is a more reliable method for obtaining the growth rate because the size of the sampling orifice of QMS varies during the measurements as film grows on it.

Fig. 2 shows two complete ALD cycles measured at three different temperatures. At 250 and 300 °C the overall shape of the mass signal during the ALD growth is the same. The mass increases rapidly during the $ZrCl_4$ pulse indicating violent reactions between $ZrCl_4$ and OD groups. This is in line with the thermodynamic calculations[34] for the overall reaction



$$ZrCl_4\text{ (g)} + 2\,H_2O\text{ (g)} \rightarrow ZrO_2\text{ (s)} + 4\,HCl\text{ (g)}; \quad \Delta G_{300} = -144\text{ kJ mol}^{-1} \quad (3)$$

which suggests relatively exothermic reaction. The mass decreases rapidly during the D_2O pulse. When all of the

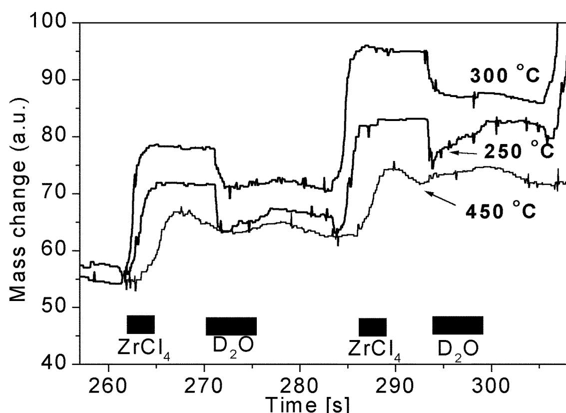


Fig. 2 QCM mass change in two complete ALD cycles at different temperatures. The $ZrCl_4$ and D_2O pulse lengths were 3 and 5 s, respectively. The purge time was 6 s.

Cl groups are consumed the mass increases somewhat, but decreases during the purge period. The same hump has been observed in quite a few oxide ALD studies above 250 °C.[20,23,24,26,31] There are basically two explanations for this hump. The first is the dissociative adsorption and desorption of water. The second is that the temperature of the QCM crystal first cools and then warms up again. Especially at high temperatures QCM is very sensitive to even minor temperature changes. D_2O was pulsed from outside the reactor with a quite high flow rate and therefore it is possible that the D_2O vapor did not heat up to the same temperature as the QCM. Above 400 °C the effect of this hump was already so significant that it overlapped with the mass increment caused by the $ZrCl_4$ chemisorption and therefore the overall shape of the signal was different from those at lower temperatures. Therefore, above 400 °C the QCM measurements were carried out with a lower water dose. The obtained results were in line with the QMS results. Therefore, even if it was lowered, it seems that the water dose was high enough to saturate all the ALD reactions also at high temperatures.

The growth rate

The growth rate measured with QMS increased when the temperature was increased from 250 to 300 °C (Fig. 2 and 3). At the same time the growth rate measured with QCM stayed at a quite constant level. The increase can be explained by different surface sites. ZrO_2 grown by ALD is polycrystalline[20] and therefore it is likely to have surface sites with slightly different activation energies. Surface kinks and steps usually have a smaller activation energy due to the possibility of the formation of more chemical bonds with the surface atoms.[35] At low temperatures there is not enough thermal energy for all of

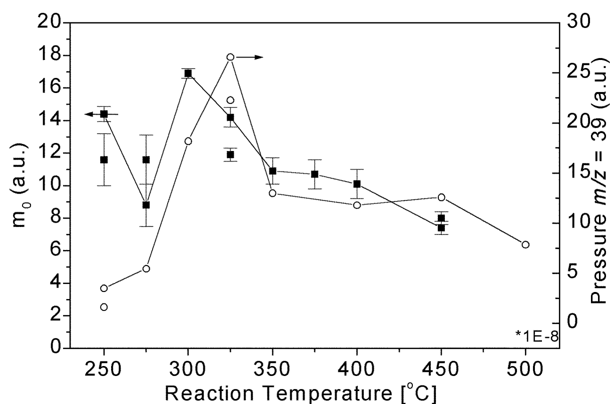


Fig. 3 Total amount of reaction byproduct $D^{37}Cl$ (m/z = 39) and m_0 during one complete ALD cycle at different reaction temperatures.

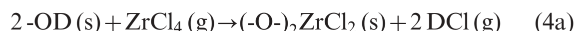
the reactions to go to completion. Because the mass increment measured by QCM is quite high, but the amount of gaseous reaction byproducts is low, it could be suggested that a proportion of the precursor molecules would form a $ZrO_{2-(x+y)/2}Cl_x(OD)_y$ surface complex. The formation of this complex could explain the differences in the QCM and QMS data at 250–300 °C. In growth experiments[20] the observed chlorine contents of the films decreased from 2 at.% at 230 °C to 0.6 at.% at 300 °C. This is in line with the explanation suggested above. However, it should be stressed that there is a larger difference between the QMS and QCM results than the difference in the chlorine contents would suggest. However, at low temperatures this process is not well established and therefore the different reactor design can have an impact on the results.

Above 300–325 °C the growth rate measured with QCM and QMS slowly decreased and from 350 to 500 °C the growth rate stayed at an almost constant level. Hydroxy groups have usually been identified as reactive sites in ALD oxide growth.[6,8,24,36–39] The amount of hydroxy groups has been observed to have an impact on the growth rate and reaction mechanism.[24,36] Agron *et al.*[40] have shown that the Zr–OH surface should be relatively stable against dehydroxylation. This is in accordance with the observed relatively slow decrease in the growth rate. However, this is quite different from what has been observed with other oxide surfaces. For example, the dehydroxylation of the Al_2O_3 surface is an almost linear function of temperature.[41–43]

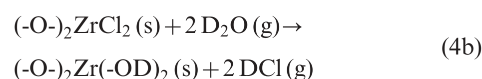
The overall behavior of the m_0 is quite different from what has been observed earlier[20] in the same process. In that study both the optically measured film thickness and m_0 decreased as the temperature was increased.

The reaction mechanism

The $n/4$ values calculated from the QMS and QCM data were used to study the reaction mechanism. Half of the chlorines were released during the $ZrCl_4$ pulse and the rest during the D_2O pulse (Fig. 4a). This reaction mechanism can be written as:

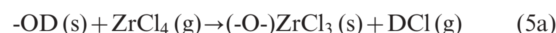


$$2\,\text{-OD}\,(s) + ZrCl_4\,(g) \rightarrow (\text{-O-})_2ZrCl_2\,(s) + 2\,DCl\,(g) \quad (4a)$$

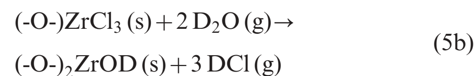


$$(\text{-O-})_2ZrCl_2\,(s) + 2\,D_2O\,(g) \rightarrow (\text{-O-})_2Zr(\text{-OD})_2\,(s) + 2\,DCl\,(g) \quad (4b)$$

In this mechanism $ZrCl_4$ reacts with two OD groups and gaseous DCl is formed. During the D_2O pulse D_2O reacts with the surface chlorides, DCl is released and the surface again becomes OD group-terminated and thus ready for the next ALD cycle. There is more scatter in the QCM data because the m_1 value is more difficult to determine accurately as discussed earlier. However, the QCM data points scatter around the values obtained from the QMS data so both methods seem to agree. At higher temperatures the $n/4$ values start to decrease somewhat and the mechanism is shifting to a direction where $ZrCl_4$ reacts with only one OD group:



$$\text{-OD}\,(s) + ZrCl_4\,(g) \rightarrow (\text{-O-})ZrCl_3\,(s) + DCl\,(g) \quad (5a)$$



$$(\text{-O-})ZrCl_3\,(s) + 2\,D_2O\,(g) \rightarrow (\text{-O-})_2ZrOD\,(s) + 3\,DCl\,(g) \quad (5b)$$

This is in line with the known fact that the ZrO_2 surface dehydroxylates somewhat at higher temperatures. However, it should be stated that the dehydroxylation seems to be relatively slow even at 500 °C.[40] In an earlier study the temperature was not observed to have any major effect on the reaction

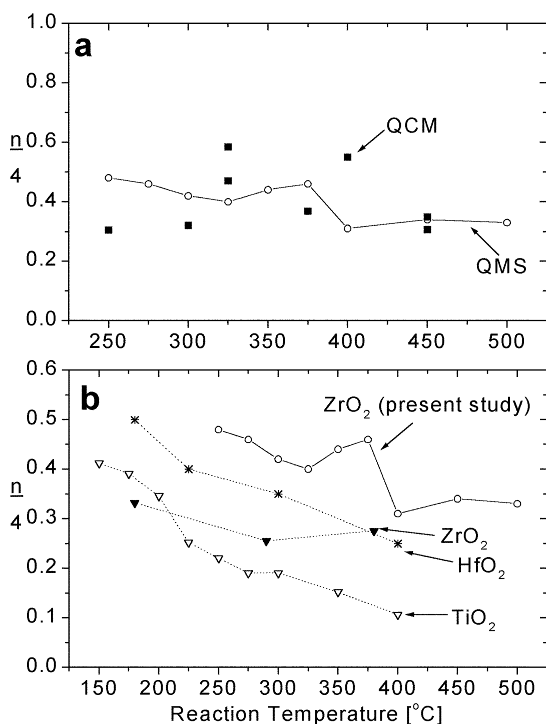


Fig. 4 (a) The fraction of ligands released during the $ZrCl_4$ pulse as calculated from QMS (○) and QCM (■) data at different reaction temperatures. (b) The corresponding *n*/4 values from the earlier studies on ZrO_2 (...▼...),[20] HfO_2 (...*...)[45] and TiO_2 (...▽...)[44] ALD processes are shown.

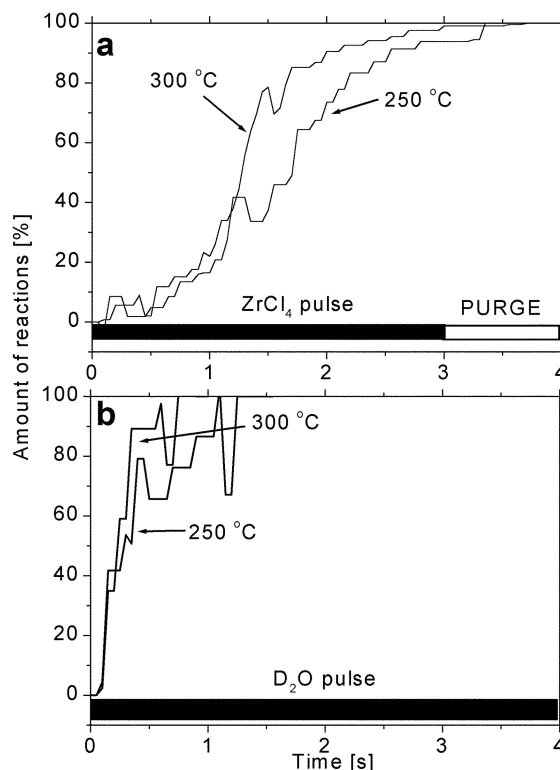


Fig. 5 The amount of reaction during the (a) $ZrCl_4$ and (b) D_2O pulses measured with QCM at different temperatures. In each case the results are normalized to give 100% at the end of the pulse–purge period.

mechanism at 180–380 °C (Fig. 4b).[20] The *n*/4 values were somewhat lower than what was observed in this study. However, the difference is still quite small.

For comparison, the *n*/4 values for the other Group 4 metal chloride-based ALD oxide processes are shown in Fig. 4b. These *n*/4 values were obtained from the QCM data. For the present study the QMS results were used because there was less scatter in the data (Fig. 4a). In the following discussion the chemisorption of the metal chloride is referred to as the first step and the following water pulse the second step. The chlorine residues in the films have usually been in the order of only a couple of atomic percentages and especially at high temperatures the amounts of residues were almost negligible. Therefore, one can assume that all the chlorides left on the surface during the first step are removed during the second step.

In the $TiCl_4$–D_2O ALD process[44] at low temperatures (150 °C) half of the chlorides were released during the first step. However, already at 250 °C the *n*/4 value was approaching zero which suggests molecular adsorption. However, this simple model, where all the reactions are supposed to occur though hydroxy groups, can be oversimplified in this case. It is possible that the $TiCl_4$ molecules actually react with the hydroxy groups but the released HCl readsorbs on the TiO_2 surface and therefore HCl was observed mostly during the second step. In the $Ti(OC_2H_5)_4$-based process it has been proved experimentally that the reaction byproduct, *i.e.* in that case ethanol, adsorbs on the TiO_2 surface and is released when water is dosed on the surface.[30]

As expected from the similar ionic size and chemistry, the reaction mechanism in the HfO_2 ALD process[45] seems to resemble the ZrO_2 process. At 180 °C two chlorine ligands were released during the first step. The *n*/4 value decreased smoothly to 0.25 at 400 °C suggesting that during the first ALD step three chlorines were left on the surface per hafnium atom. It is interesting to notice that ZrO_2 and HfO_2 show the same kind of behavior whereas titanium from the same group acts differently.

Precursor transportation and reaction kinetics

Fig. 5 shows the cumulative percentage of reactions occurring as a function of time as measured with QCM. At each temperature the mass change was normalized to obtain 100% at the end of the pulse–purge period. In this way it is easier to compare the two half reactions despite the difference in the absolute mass change. As stated earlier, half of the reaction byproducts were released during each precursor pulse (Fig. 4a). The overall shape of the curves is similar at 250 and 300 °C. At both temperatures the mass increases slowly at first ($0 < t < 1$ s) which is most probably due to the concentration profile in the precursor pulse. QCM is in the rear of the reaction chamber and at the beginning of the precursor pulse most of the precursor is consumed in the reactions on the glass substrates in front of the QCM crystal. Only when most of the glass substrate surface is saturated will unreacted precursor also reach the QCM. After the initial slow mass increase the mass increment becomes fast and linear. This suggests that the surface reactions are fast and the limiting factor is precursor transportation. This is in accordance with the quantum chemical calculations where the reaction time was estimated to be in the order of milliseconds.[46] When the reaction level increases above 80%, the mass increment starts to slow down. This suggests that there are also slower reactions involved in the growth mechanism. For example, rearrangement of the chemisorbed species may be needed to reopen the temporarily blocked nearby surface sites for another precursor molecule to chemisorb, and, therefore, reaching full saturation can take time despite the fast initial chemisorption reactions. In other words, in addition to the fast parallel reactions there can be some slow serial reactions. The full saturation of the reactions during the $ZrCl_4$ pulse is attained somewhat faster at 300 than at 250 °C (Fig. 5a) which is natural because at higher temperatures the reactions are usually faster.

Saturation is clearly reached faster during the D_2O pulse than during the $ZrCl_4$ pulse, even if the same amounts of ligand are released during both precursor pulses (Fig. 4a). This is

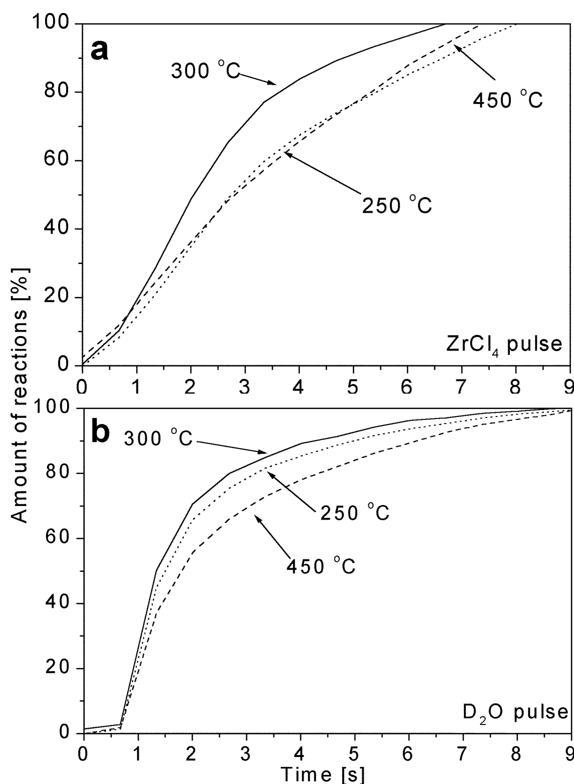


Fig. 6 The amount of reaction during the (a) $ZrCl_4$ and (b) D_2O pulses measured with QMS at different temperatures. In each case the results are normalized to give 100% at the end of the pulse–purge period. The $ZrCl_4$ and D_2O pulse lengths were 3 and 5 s, respectively. The purge time was 6 s.

understandable because the D_2O partial pressure is higher than that of $ZrCl_4$ and therefore the precursor transportation is also faster.

When analyzing the reaction saturation curves obtained with QMS (Fig. 6) it should be kept in mind that the reaction byproducts analyzed are forming all around the relatively large reaction chamber and therefore it takes some time for the precursor to reach all the substrates. From the QCM data it can be estimated that it takes about 1–2 s for the precursors to reach the end of the reaction chamber. Therefore, precursor transportation has a more important effect on the QMS data than on the QCM data. During the $ZrCl_4$ pulse at 300 °C the shape of the curve resembles the curves obtained with QCM (Fig. 5a). However, at 250 and 450 °C the curves are almost linear. Despite the transportation time, during the D_2O pulse the 80% reaction level was reached relatively quickly (Fig. 6b). Above the 80% reaction level the growth rate slows down as was seen also in the QCM data (Fig. 5b).

Summary

The only observed reaction byproduct in the $ZrCl_4$–D_2O ALD process was DCl. The growth rate measured with QMS increased when the temperature was increased from 250 to 300 °C. At the same time the growth rate measured with the QCM stayed at a relatively constant level. The difference between these two results can be partly explained by the non-volatile $ZrO_{2-(x+y)/2}Cl_x(OD)_y$ complex. At higher temperatures the growth rate measured by both methods decreased slowly. This was most probably due to the slow dehydroxylation of the Zr–OD surface.

At 300 °C half of the chlorides were released during the $ZrCl_4$ pulse in the exchange reactions with the surface OD groups. The remaining chlorides were released during the D_2O pulse which converted the surface back to being OD group-terminated. At higher temperatures where the surface OD coverage decreased, the growth mechanism was shifting to the direction were during the $ZrCl_4$ pulse only one chlorine was released per molecule, the other three being liberated during the D_2O pulse.

The reactions were observed to be relatively fast and therefore the saturation of the reactions was concluded to be limited mainly by the precursor transportation. However, when the 80% reaction level was attained some slower reactions also seemed to affect the reaction mechanism.

Acknowledgement

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