In Situ Quadrupole Mass Spectrometry and Quartz Crystal Microbalance Studies on the Atomic Layer Deposition of Titanium Dioxide from Titanium Tetrachloride and Water

Raija Matero,* Antti Rahtu, and Mikko Ritala

Laboratory of Inorganic Chemistry, Department of Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland

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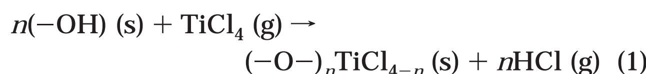
The atomic layer deposition (ALD) of TiO_2 from $TiCl_4$ and D_2O at 150−400 °C was studied in situ with a quadrupole mass spectrometer (QMS) and a quartz crystal microbalance (QCM). The ALD growth proceeds via exchange reactions on the film surface. In the first step, $TiCl_4$ is introduced on a surface covered with −OD groups which then become replaced with −O−$TiCl_x$ species, and DCl is released as a volatile byproduct. In the second step, the incoming D_2O reacts with the surface −Cl atoms replacing them with −OD groups and, again, DCl is released. When the temperature is increased from 150 to 250 °C, the number of −Cl ligands released during the $TiCl_4$ pulse decreases from about two to one. At temperatures higher than 250 °C, less than one −Cl ligand is released, indicating molecular adsorption of $TiCl_4$.

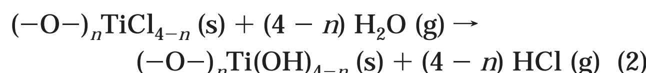
Introduction

Atomic layer deposition (ALD), also called atomic layer epitaxy (ALE),[1] can be regarded as a special modification of the chemical vapor deposition (CVD) method. ALD is a pulsed method in which the reactant vapors are alternately supplied onto the substrate. During each pulse, the precursors chemisorb or react with the surface groups. The reactant pulses are separated with purging periods which prevent the precursor vapors from mixing in the gas phase. When the process conditions are properly chosen, the film growth proceeds via saturative surface reactions and is thus self-limiting. This makes it possible to cover even complex-shaped objects with a uniform film.[2] It is also possible to control the film thickness accurately simply by controlling the number of pulsing cycles repeated.

The ALD growth of TiO_2 from $TiCl_4$ and water has been demonstrated and examined by several groups.[3−6] A mechanism (eqs 1 and 2) for the film growth has been suggested on the basis of literature results on surface processes on stable, crystalline TiO_2 surfaces under equilibrium conditions.[3] In this mechanism, the incoming $TiCl_4$ reacts with the surface hydroxyl groups rather than simply chemisorbs.



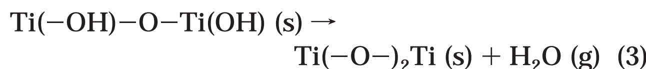
$$n(-OH)\ (s) + TiCl_4\ (g) \rightarrow (-O-)_nTiCl_{4-n}\ (s) + nHCl\ (g) \quad (1)$$



$$(-O-)_nTiCl_{4-n}\ (s) + (4-n)\ H_2O\ (g) \rightarrow (-O-)_nTi(OH)_{4-n}\ (s) + (4-n)\ HCl\ (g) \quad (2)$$

where (s) denotes surface.

As the growth of TiO_2 is supposed to proceed via surface exchange reactions (eqs 1 and 2), the −OH groups play a key role in the film growth. There are two kinds of −OH groups on the TiO_2 surface: terminal and bridging between two cations.[7] The terminal hydroxyls can be either adjacent and hydrogen-bonded with each other or isolated. The −OH groups are not stable at elevated temperatures: they may condense with each other causing dehydroxylation of the surface (eqs 3 and 4).[7]



$$Ti(-OH)-O-Ti(OH)\ (s) \rightarrow Ti(-O-)_2Ti\ (s) + H_2O\ (g) \quad (3)$$

$$2\ (-Ti(OH))\ (s) \rightarrow -Ti-O\ (s) + -Ti\ (s) + H_2O\ (g) \quad (4)$$

Hydrogen-bonded hydroxyls are more favorable for dehydroxylation than the isolated ones; thus, reaction 3 takes place at lower temperatures than reaction 4. As a result, the −OH density is temperature-dependent and decreases with increasing temperature.[8] Dehydroxylation of the surface leaves coordinatively unsatur-

* To whom correspondence should be addressed. E-mail: raija.matero@helsinki.fi. Telephone: +358 9 19150226. Fax: +358 9 19150198.

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ated oxygen (−Ti−O) and titanium (−Ti) ions which can form Ti−O−Ti bridge bonds with neighboring surface ions. It is important that the surface can also be rehydroxylated if reaction 3 is reversed and dissociative chemisorption of water molecules occurs.[7−9] The titanium ions produced in reaction 4 can at low temperatures adsorb coordination-bonded water molecules.[7,9−10] The growth rates in many ALD processes can be increased by increasing the water dose; this was attributed to increased hydroxyl group density.[11] However, in the $TiCl_4$−H_2O process at 300 °C, the effect was small which could be explained by absence of rehydroxylation or by rapid dehydroxylation back to the stable −OH coverage.

The reactions of $TiCl_4$ with the −OH groups on high-surface-area silica powder have been studied with NMR and FTIR spectroscopies by Haukka et al.[4] They found that at 175 °C, $TiCl_4$ reacted with the surface hydroxyls in a way corresponding to $n = 1$ or 2 in eq 1. Real-time investigation of the ALD reactions on planar surfaces has been done with a quartz crystal microbalance (QCM) by Aarik et al.[5] They discussed possible growth mechanisms leading to formation of different TiO_2 crystal structures. Cameron et al.[6] have studied the TiO_2 growth in alumina tubular membranes. They observed changes in the gas flow through the membrane and, on the basis of these results, drew conclusions on the growth mechanism using eqs 1 and 2. Additional information about the growth reactions could be obtained by following the release of the volatile byproducts, but until now that has not been done. One possible way to investigate these is a mass spectrometer integrated to an ALD reactor, as recently has been introduced.[12,13]

In this work, a setup comprising a quadrupole mass spectrometer (QMS) and a QCM[13] was used to study the ALD growth mechanism of TiO_2 from $TiCl_4$ and water. As the in situ measurements with the QCM and QMS were made at the same time, they give simultaneous information about both the film and the species leaving the surface in each ALD process step.

Experimental Section

The QMS−QCM−ALD Setup. The experiments were made in a specially modified commercial flow-type ALD reactor manufactured by ASM Microchemistry Ltd. A schematic view of the equipment is depicted in Figure 1. The equipment has been described in detail elsewhere.[13] The gas composition was measured with a Hiden HAL/3F 501 RC QMS which has a mass range of 1−510 amu. A Faraday cup detector was used. The pressure in the ALD reaction chamber was about 2 mbar, and it was reduced to about 10^{-7} mbar in the QMS chamber by differential pumping through an orifice of 20 μm in diameter. The mass balance studies were made using a Maxtek TM 400 QCM. The operating frequency of the crystal was 6 MHz; the sampling rate was 20 times per second.

Deposition Parameters. The precursors were $TiCl_4$ (Riedel-de-Haën, 99.5%) and D_2O (Euriso-top, 99.9% D). It has been a common practice to use D_2O in the in situ studies of processes involving organometallic precursors[13] to better distinguish the reaction byproducts from the species forming in the QMS ionizator. Although fragmentation did not cause a problem in this study, D_2O was still used for consistency. The precursors were led into the reactor through solenoid valves. The $TiCl_4$ reservoir was held in a tempered bath at 18 °C and D_2O at room temperature. The water dose was controlled using a needle valve. The deposition temperature was varied between 150 and 400 °C. The QCM was used only up to 350 °C, however, because above that temperature even a small temperature instability caused large frequency variation and made the signal unreliable. Argon (99.99%, flow rate 50 sccm) was used as the carrier and purging gas. The reaction chamber ($V = 550$ cm^3) was loaded with soda-lime glass substrates so that the total surface area was about 3500 cm^2.

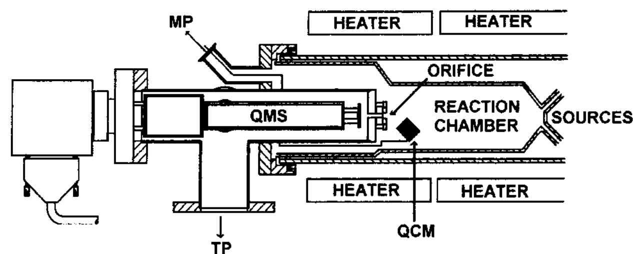

Figure 1. A schematic view of the reactor. The precursors are transported with the carrier gas to the reactor chamber from the right and are pumped by the mechanical pump (MP). A small part of the total flow is pumped by the turbomolecular pump (TP) through the sampling orifice and the QMS chamber.

The following pulsing sequence was used:

Step 1. 5 times (0.5 s $TiCl_4$/15.0-s purge).

Step 2. 4 times (0.5 s $TiCl_4$/6.0-s purge + 3.0 s D_2O/6.0-s purge).

Step 3. 2 times (0.5 s $TiCl_4$/15.0-s purge).

Step 4. 6 times (0.5 s $TiCl_4$/6.0-s purge + 3.0 s D_2O/6.0-s purge).

Step 5. 5 times (3.0 s D_2O/15.0-s purge).

Experiments were also made using a shorter (0.5 s) water pulse. To keep the cycle time constant in each step, the 15.0-s purges were shortened accordingly to 12.5 s.

The purpose of step 1 is to stabilize the $TiCl_4$ dose and its contribution to the reaction product signal followed with the QMS. This step thus gives the background signal caused by $TiCl_4$. Steps 2 and 4 are the ALD process itself. The amount of the reaction byproduct formed in the ALD process is subtracted from the signal during these steps. Step 3 is used to check the sufficiency of the $TiCl_4$ dose to saturate the surface: no mass increase or byproduct release in excess to the background (step 1) should be observed. Similarly, step 5 is for checking the sufficiency of the D_2O dose to saturate the surface and for observing the background signal caused by D_2O. An example of the QMS and QCM signals produced by such a pulsing sequence is shown in Figure 2. As HCl (here DCl as D_2O was used) is produced in the growth of TiO_2 according to eqs 1 and 2, the mass data was collected by monitoring masses $m/z = 39$ (DCl^+) and $m/z = 153$ ($TiCl_3^+$). The latter originates from $TiCl_4$ and was used only to follow the pulsing sequence. The existence of the following masses was also checked: $m/z = 70$ and 74 (Cl_2); $m/z = 119$, 136, 154, and 171 ($Ti(OD)_xCl_y$); $m/z = 134$, 150, and 169 (TiO_xCl_y). None of these were observed (see Comparison of QMS and QCM results below).

Results and Discussion

Properties of ALD Grown TiO_2 Films. Before proceeding to the results of the mechanistic study, it is instructive to review earlier studies on the properties

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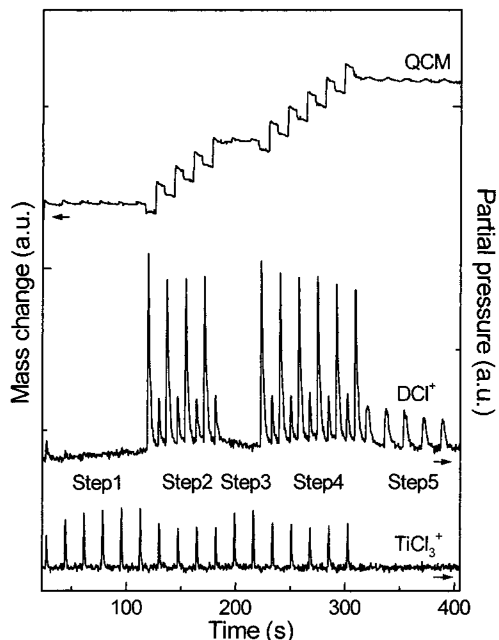

Figure 2. Data recorded at 200 °C with the QMS and the QCM during the whole pulsing sequence. Two masses were followed with the QMS: the main reaction byproduct DCl^+ ($m/z = 39$) and $TiCl_3^+$ ($m/z = 153$).

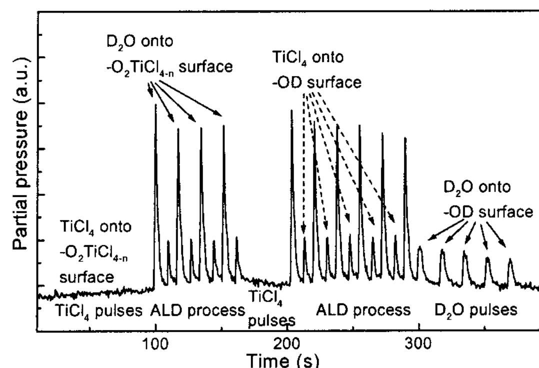

Figure 3. The time dependence of DCl released in the ALD process at 200 °C when using the 3.0-s D_2O pulse.

Table 1. Possible Reactions Occurring on the Surface during the $TiCl_4$ and the D_2O Pulses[a]

n	reactions	m_0/m_1
0	$TiCl_4$ (g) → $TiCl_4$ (s) $TiCl_4$ (s) + 2D_2O (g) → −TiO_2 (s) + 4DCl (g)	0.42
1	−OD (s) + $TiCl_4$ (g) → −O−$TiCl_3$ (s) + DCl (g) −O−$TiCl_3$ (s) + 2D_2O (g) → (−O−)$_2$Ti(OD) (s) + 3DCl (g)	0.53
2	2 (−OD) (s) + $TiCl_4$ (g) → (−O−)$_2TiCl_2$ (s) + 2DCl (g) (−O−)$_2TiCl_2$ (s) + 2 D_2O (g) → (−O−)$_2$Ti(OD)$_2$ (s) + 2DCl (g)	0.70

[a] The m_0/m_1 values for different values of n have been calculated using eq 6 m_0/m_1 = M(TiO_2)/[M($TiCl_4$)−nM(DCl)].

of ALD grown TiO_2 films from $TiCl_4$ and water.[3,14] X-ray diffraction[3,14] studies revealed that the film grown at 150 °C was amorphous; the films grown at 200−400 °C were polycrystalline having either anatase (below 300 °C) or rutile (above 300 °C) structure depending on the deposition temperature. The films have been analyzed for chlorine and hydrogen residues by TOF-ERDA[15] (time-of-flight elastic recoil detection analysis) and NRB[15] (nuclear resonance broadening), respectively.[14] In the film grown at 150 °C, there was a uniformly distributed chlorine content of about 2 atom %. The chlorine content decreased with increasing temperature. Hydrogen contents were found to have maxima both at the outer surface and at the film−substrate interface. The maxima were related to water and hydrocarbons adsorbed on the substrate surface before film deposition and on the film surface after deposition. In the bulk of the film, the hydrogen contents were low (below 0.1 atom %), the films grown at the lowest temperatures (150−200 °C) making an exception: therein hydrogen content of about 0.4 atom % was determined. The refractive index of the films increased with increasing growth temperature from 2.4 to 2.6.[3] According to Ottermann et al.,[16] a high refractive index indicates dense film structure and is correlated with low hydrogen content. Thus, the film quality improves when the ALD growth temperature is increased.

QMS Results. The time dependence of DCl^+ detected during the pulsing sequence from step 1 to step 5 is depicted in Figure 3. It can be seen that DCl is produced also during the D_2O reference pulses (step 5). To eliminate the effect of this background, the amount of the reaction product DCl formed in the ALD process during the D_2O pulse was evaluated by integrating the peaks corresponding to this pulse and subtracting the background caused by the reference D_2O pulses (step 5). As no DCl was liberated during the $TiCl_4$ reference pulses (step 1), no such correction was required for $TiCl_4$.

On the basis of our results presented in detail below, it may be suggested that depending on the surface −OD group density, the growth of TiO_2 takes place via one of the reactions listed in Table 1. These are modified from the generalized eqs 1 and 2 (n = 0−2) in a way that the −OD density on the surface remains the same after each ALD cycle. This is supported by the experimental results which show that each ALD cycle is similar.

As can be seen in Figures 2 and 3, the reaction byproduct DCl is formed during both the $TiCl_4$ and the D_2O pulses. When the growth temperature was raised from 150 to 400 °C, the amount of DCl produced during the $TiCl_4$ pulse decreased which can be seen in Figure 4 showing the amount of DCl formed at different temperatures during the D_2O and $TiCl_4$ pulses. There seems to be only little difference between the 0.5- and 3.0-s water pulses. In general, the amount of DCl produced during the $TiCl_4$ pulse is small; however, below 200 °C a larger amount of DCl is liberated especially when the longer water pulse is used. There is not much variation in the DCl amount produced during the D_2O pulse at different temperatures. When the shorter water pulse is used, the DCl amount settles to a lower level than with the longer pulse, which suggests that a higher −OD coverage of the surface is obtained with the longer water pulse. The decrease in the DCl amounts at higher temperatures can be ex-

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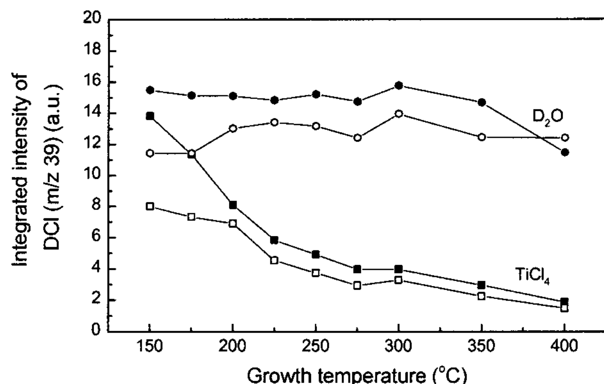


Figure 4. The amounts of DCl released during the D_2O (circles) and $TiCl_4$ (squares) pulses at different temperatures. The open circles and squares refer to the experiments with the 0.5-s water pulse and the solid circles and squares with the 3.0-s water pulse. The line connecting the data points is only to guide the eye.

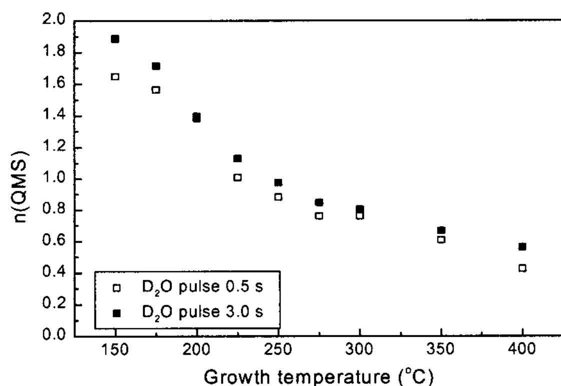
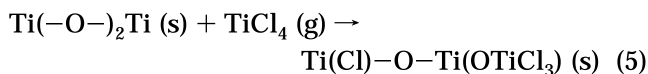


Figure 5. The n values calculated from the QMS results. These refer to the number of ligands released during the $TiCl_4$ pulse (see reactions in Table 1).

plained by dehydroxylation of the surface. In fact, the DCl amounts actually measure the chlorine and hydroxyl densities on the surfaces upon which D_2O and $TiCl_4$, respectively, are dosed.

An n value referring to the number of $-Cl$ ligands released during the $TiCl_4$ pulse (Table 1) can be calculated from the QMS results. This value is obtained as follows: the amount of DCl released during the $TiCl_4$ pulse is divided by the total amount of DCl (the amount released during the $TiCl_4$ pulse plus the amount released during the D_2O pulse) and then multiplied by 4, the number of $-Cl$ ligands in $TiCl_4$. These n values are displayed in Figure 5. With the 0.5-s water pulse, the n value decreases from 1.7 to 0.4 as the temperature is increased. Elongating the water pulse to 3.0 s gives slightly higher values (from 1.9 to 0.6). This decrease in the n value suggests that dehydroxylation of the surface has happened at higher temperatures[8] and, thus, there are fewer $-OD$ groups on the surface for the incoming $TiCl_4$ to interact with. At these temperatures, the growth then probably proceeds at least partially via molecular adsorption of $TiCl_4$ ($n = 0$ in Table 1) or perhaps also via dissociative chemisorption leading to bond formation with $-Ti-O-Ti-$ bridges (eq 5).



$$Ti(-O-)_2Ti\ (s) + TiCl_4\ (g) \rightarrow Ti(Cl)-O-Ti(OTiCl_3)\ (s) \quad (5)$$

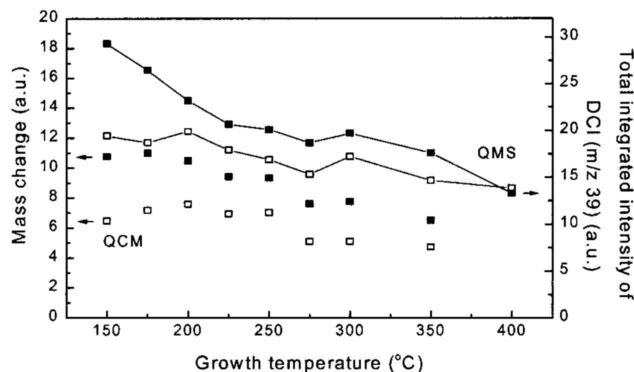


Figure 6. The QCM mass change after one complete ALD cycle (squares) and the total amount of DCl released in the ALD process as detected with the QMS (circles). The open circles and squares refer to the experiments with the 0.5-s water pulse and the solid circles and squares with the 3.0-s water pulse. The line connecting the QMS data points is only to guide the eye.

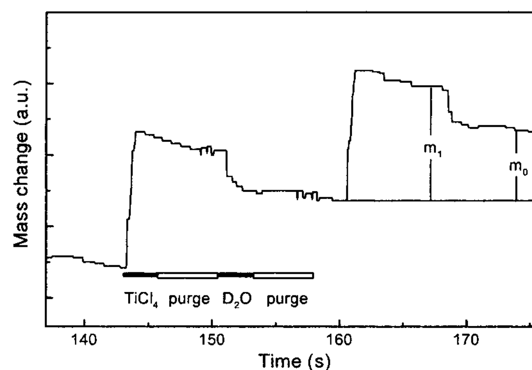


Figure 7. QCM mass change during two complete ALD cycles at 200 °C. The mass increment during the $TiCl_4$ pulse is m_1 and the mass change after one complete ALD cycle is m_0. The $TiCl_4$ and D_2O pulse lengths were 0.5 and 3.0 s, respectively.

Figure 6 presents the total amount of DCl produced during one complete ALD cycle at different temperatures; hence, it indirectly depicts the TiO_2 growth rate per cycle. The growth rate settles to a higher level when the longer water pulse is used. This observation is in parallel with the earlier study where a larger water dose was found to produce higher growth rates in many ALD processes, and it can be attributed to increased density of hydroxyl groups on the film surface.[11] High total DCl amounts are detected at temperatures below 200 °C when the 3.0-s D_2O pulse is used (cf. Figure 4); otherwise the two curves follow the same trend. The drop in the DCl amount while going from 150 to 250 °C in the case of the longer water pulse is most probably caused by the decrease of surface $-OD$ coverage. Up to 350 °C, the film growth appears to be controlled by surface kinetics because elongation of the D_2O pulse increases the growth rate. At the highest temperature (400 °C), the longer water pulse does not give any benefit and the growth rate settles to the same level regardless of the D_2O pulse length. At high temperatures, dehydroxylation decreases the amount of DCl produced (the growth rate).

QCM Results. Part of the QCM signal recorded during the pulsing sequence is shown in Figure 7. One ALD cycle ($TiCl_4$ pulse/purge/D_2O pulse/purge) is marked to give an idea of what kind of changes it causes in the signal. During the $TiCl_4$ pulse, the mass increases

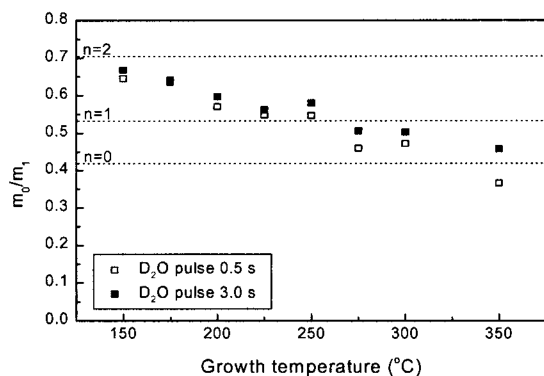


Figure 8. The m_0/m_1 ratio calculated from the QCM results at different temperatures using eq 6.

because of the chemisorption of $-TiCl_x$ species. The D_2O pulse causes a decrease in the mass as the $-Cl$ ligands are replaced by lighter $-OD$ groups or oxide ions. The mass increment during the $TiCl_4$ pulse is marked with m_1 and the mass increment after a complete ALD cycle with m_0. As TiO_2 is deposited, m_0 corresponds to TiO_2. Therefore, analysis of the m_0/m_1 ratio reveals details of the species formed during the $TiCl_4$ pulse. The m_0/m_1 values presented in Table 1 for $n = 0$, 1, and 2 were calculated using eq 6.[5] In this equation, n, again, refers to the number of $-Cl$ ligands (DCl molecules) released during the $TiCl_4$ pulse.

$$\frac{m_0}{m_1} = \frac{M(\mathrm{TiO_2})}{M(\mathrm{TiCl_4}) - nM(\mathrm{DCl})} \qquad (6)$$

The mass increment (m_0 = the growth rate) detected at 150−350 °C is depicted in Figure 6. The trend is similar with both D_2O pulse lengths: the growth rate decreases with increasing temperature. When the water pulse is longer, the growth rate is higher than with the shorter pulse. Again, this suggests a higher surface $-OD$ density with the longer water pulse.[11] Figure 8 shows the m_0/m_1 values deduced from the QCM results. There is not much difference between the values obtained with the two water pulse lengths, as also the m_1 is higher when the longer water pulse is used. The m_0/m_1 ratio decreases as the temperature is increased: the highest value is 0.67 at 150 °C when the 3.0-s D_2O pulse is used; the lowest value with the same pulse length is 0.46 at 350 °C. These values refer to $n = 1.9$ and 0.4, respectively (Figure 9, eq 6). With the shorter water pulse, the m_0/m_1 ratio changes from 0.65 ($n = 1.8$) at 150 °C to 0.37 at 350 °C. The smallest value is less than the value referring to $n = 0$ in Table 1 and, therefore, strongly suggests growth on dehydroxylated surface. Aarik et al.[5] have reported m_0/m_1 values of 0.39, 0.43, and 0.57 for increasing water dose at 400 °C. Our results at 350 °C show a similar trend and are in agreement with their values.

Comparison of the QMS and QCM Results. The results obtained with the QMS and QCM seem to be in good agreement with each other as can be seen by comparing Figures 5 and 9 and examining Figure 6. The largest difference is found at the lowest temperatures in the curves depicting the growth rate (Figure 6). The higher increase in the growth rate with decreasing temperature obtained with the QMS comes from the high DCl amounts released during the $TiCl_4$ pulse

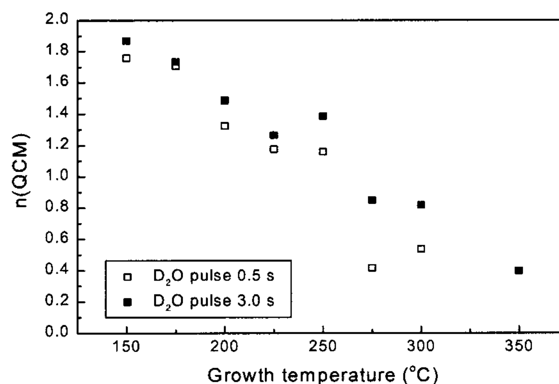
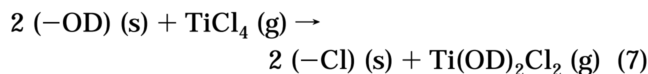


Figure 9. The n values calculated from the QCM results at different temperatures using eq 6. These refer to the number of ligands released during the $TiCl_4$ pulse (see reactions in Table 1).

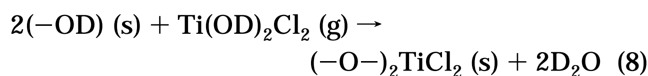
(Figure 4). This could be explained by adsorption of molecular water[8] onto the substrates during the D_2O pulse and its subsequent reaction with the $TiCl_4$ pulse. It is possible that this adsorption is so extensive that the QCM located behind the substrates does not receive as large a water dose as the substrates. Here, it must be emphasized that while the QCM examines the reactions locally at its surface, the QMS averages all the reactions occurring in the reaction chamber that produce volatile byproducts.

It has been proposed earlier that $TiCl_4$ could react with the hydroxyl groups on TiO_2 surface by producing volatile hydroxychlorides, for example, $Ti(OH)_2Cl_2$ (eq 7).[4,17−19]

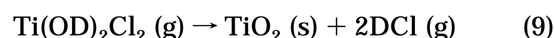


$$2\,(-\mathrm{OD})\ (s) + \mathrm{TiCl_4}\ (g) \rightarrow 2\,(-\mathrm{Cl})\ (s) + \mathrm{Ti(OD)_2Cl_2}\ (g) \qquad (7)$$

These $Ti(OD)_xCl_y$ species (see Experimental) were not observed with the QMS, however. Thus, they were either not formed, their lifetime was very short, or the amounts were too small to be detected. If this reaction occurred on the QCM, it would decrease the mass increment m_0 and also the ratio m_0/m_1, hence, the n value would actually be increased. It has also been proposed[4,17−19] that these volatile species may react further with surface hydroxyls (eq 8) or decompose to TiO_2 or $TiOCl_2$ (eqs 9 and 10). None of the TiO_xCl_y species (see Experimental Section) that were checked with the QMS were observed.



$$2(-\mathrm{OD})\ (s) + \mathrm{Ti(OD)_2Cl_2}\ (g) \rightarrow (-\mathrm{O}-)_2\mathrm{TiCl_2}\ (s) + 2\mathrm{D_2O} \qquad (8)$$



$$\mathrm{Ti(OD)_2Cl_2}\ (g) \rightarrow \mathrm{TiO_2}\ (s) + 2\mathrm{DCl}\ (g) \qquad (9)$$

$$\mathrm{Ti(OD)_2Cl_2}\ (g) \rightarrow \mathrm{TiOCl_2}\ (g) + \mathrm{D_2O}\ (g) \qquad (10)$$

It has also been proposed that the reaction byproduct HCl/DCl may readsorb onto the TiO_2 surface during the $TiCl_4$ pulse.[3,20,21] In front of the $TiCl_4$ pulse, the DCl

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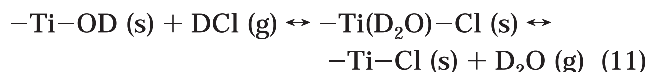
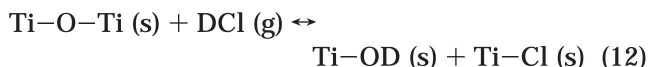
concentration is high, and it may interact with hydroxyl groups (eq 11) or with Ti−O−Ti bridges (eq 12), and it can also produce volatile hydroxychlorides (reverse of eq 9).



$$-\mathrm{Ti-OD\ (s)} + \mathrm{DCl\ (g)} \leftrightarrow -\mathrm{Ti(D_2O)-Cl\ (s)} \leftrightarrow -\mathrm{Ti-Cl\ (s)} + \mathrm{D_2O\ (g)} \quad (11)$$



$$\mathrm{Ti-O-Ti\ (s)} + \mathrm{DCl\ (g)} \leftrightarrow \mathrm{Ti-OD\ (s)} + \mathrm{Ti-Cl\ (s)} \quad (12)$$

As the QCM is situated behind the substrates (Figure 2), it is exposed to a large amount of DCl traveling in front of the precursor pulses. Therefore, it is possible that DCl adsorbs onto the crystal decreasing the −OD density and consuming sites for the incoming $TiCl_4$ pulse to react with and, hence, decreasing m_0 (the growth rate). This could be an alternative explanation for the difference in the trend the growth rate follows (Figure 6), that is, the smaller increase in the growth rate at the low temperatures observed with the QCM than with the QMS.

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Conclusions

The ALD growth of TiO_2 from $TiCl_4$ and D_2O takes place via −OD to $-O-TiCl_x$ and −Cl to −OD surface exchange reactions. As the temperature is increased from 150 °C to 400 °C, the number of −OD groups with which the incoming $TiCl_4$ reacts decreases. The number of ligands that are released during the $TiCl_4$ pulse is about two at the lowest temperature and close to zero at the highest temperature indicating molecular adsorption of $TiCl_4$. The results obtained with the QMS and the QCM are in agreement with each other indicating that these two methods can be used together to get reliable information on the growth mechanism. One should take into account, though, that also reactions other than the −OD/−Cl exchange can take place and complicate the growth. For example, short-lived volatile $Ti(OD)_xCl_y$ intermediates may form, although these species were not observed. The readsorption of the reaction byproduct DCl on the surface is also possible, and it should be examined separately.

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