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In Situ Mass Spectrometry Study on Atomic Layer Deposition from Metal (Ti, Ta, and Nb) Ethoxides and Water

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Reaction mechanisms between titanium, tantalum, and niobium ethoxides and deuterated water in the atomic layer deposition (ALD) of TiO_2, Ta_2O_5, and Nb_2O_5 were studied with a mass spectrometer. The amounts of the reaction product $CH_3CH_2OD^+$ ($m/z = 47$) and its main fragment CH_2OD^+ ($m/z = 32$) increased up to about 300 °C where all the metal precursors started to thermally decompose. Despite the decomposition, significant amounts of the ligands still remained on the surface and were released in the exchange reactions with D_2O. It was also observed that in the titanium dioxide process titanium ethoxide adsorbs on the water-treated TiO_2 surface mostly without obvious exchange reactions, and over 90% of the ligands were released during the water pulse. The adsorption of C_2H_5OH on the TiO_2 surface was also examined, and it can partially explain the low amount of ligands released during the metal precursor pulses. At 325 °C the ALD growth of Ta_2O_5 and Nb_2O_5 can mainly be described as an alternate release of $(C_2H_5)_2O$ during the $Ta(OC_2H_5)_5$ or $Nb(OC_2H_5)_5$ pulses and C_2H_5OD during the D_2O pulse.

Introduction

Atomic layer deposition (ALD), also known as atomic layer epitaxy (ALE),[1−5] is a gas phase method for depositing high-quality thin films. ALD is based on sequential surface reactions which are accomplished by leading the reactant vapors into the reactor in a cyclic manner, one at a time, separated by purging periods. When the process conditions are properly chosen, all the surface reactions are saturative making the film growth self-limiting. This offers specific practical advantages, such as excellent conformality, accurate and simple thickness control, and large area uniformity.[6−8]

Reaction temperature, exposure and purge times, and reactant pressures in ALD processes have usually been optimized in accord with ex situ measurements of the resulting film properties. However, real time reaction mechanism studies, like mass spectrometry, under the same conditions as used in the normal growth experiments can provide much quicker process optimization. Mass spectrometry has been used, for example, in chemical vapor deposition (CVD) studies.[9−11] We have recently developed and integrated an in situ quadrupole mass spectrometry (QMS) system to a flow type ALD reactor.[12,13]

Titanium dioxide (TiO_2) thin films are possible candidates for microelectronic and optic applications. TiO_2 thin films grown by ALD have high refractive index (n(580 nm) ∼ 2.6),[14−17] but they suffer from low resistivity which is apparently due to oxygen deficiency and is characteristic of TiO_2 films prepared also by other methods. TiO_2 thin films have been grown by ALD from alkoxides such as $Ti(O^iC_3H_7)_4$[16] and $Ti(OC_2H_5)_4$[17,18] and from halides $TiCl_4$[14,15] and TiI_4.[19,20] The oxygen source has usually been water. The $Ti(OC_2H_5)_4−H_2O$ process

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has been studied in a growth temperature range of 200−400 °C.[17] From 250 to 300 °C the growth rate was constant at about 0.35 Å/cycle. Above 300 °C the film growth was not totally self-limiting due to thermal decomposition of the titanium precursor. The contribution of the decomposition to the growth rate was estimated to be about 5% at 300 °C.[17] Using higher water fluxes, the deposition rate could be increased up to 0.6 Å/cycle.[21] The same process has been investigated also in another kind of a flow type ALD reactor.[18] Growth rates as high as 0.8 Å/cycle at 100−200 °C and 0.9 Å/cycle at 350 °C were achieved with optimized precursor dosing. In situ quartz crystal microbalance (QCM) measurements in this reactor indicated that at 200−275 °C less than one ligand is released during the $Ti(OC_2H_5)_4$ pulse. At higher temperatures the thermal decomposition of $Ti(OC_2H_5)_4$ is affecting the growth mechanism; therefore, about half of the ligands are released during the $Ti(OC_2H_5)_4$ pulse at 350 °C.[18] Within the accuracy limits of Rutherford backscattering spectrometry (RBS) the films were stoichiometric TiO_2. The carbon impurity content was below the detection limit of X-ray photoelectron spectroscopy (XPS) and the hydrogen content was below 0.3 at. % as measured with nuclear reaction analysis (NRA). According to X-ray diffraction (XRD) measurements the film structure was anatase.[17]

Both Ta_2O_5 and Nb_2O_5 have been studied as possible candidates for dielectrics in integrated circuits, and Ta_2O_5 is considered as one of the most promising capacitor dielectrics.[22,23] Ta_2O_5 films have been grown by ALD mainly from $TaCl_5$ or $Ta(OC_2H_5)_5$ while water has usually been applied as an oxygen source.[24−26] The films grown from $Ta(OC_2H_5)_5$ were amorphous with smooth surface, possessing a relative dielectric constant of 25. The films were stoichiometric $Ta_{2\pm0.1}O_{5\pm0.1}$ and at 325 °C the impurity contents were 0.6 at. % and 2−3 at. % for hydrogen and carbon, respectively.[26] Nb_2O_5 films have also been successfully deposited by ALD from $Nb(OC_2H_5)_5$ and water[27] while the attempts to grow films from $NbCl_5$ failed, apparently due to the volatility of niobium oxychlorides formed as intermediate reaction products.[28] The films grown on glass substrates were amorphous, while the films on polycrystalline indium tin oxide (ITO) were identified as monoclinic Nb_2O_5. According to RBS measurements the films grown at 325 °C were stoichiometric Nb_2O_5 and had impurity contents below 0.1 at. %.[27]

Besides binary oxides, metal ethoxides have been used as precursors also for growing complex oxide structures such as solid solutions and nanolaminates.[29,30] Exploitation of the ethoxide precursors has resulted in appreciable reproducibility and uniform film properties. Thus, metal ethoxides are an important class of ALD precursors.

In this study, mechanisms of the ALD surface reactions between metal ethoxides and water have been studied, and similarities and differencies between the growth processes of different oxides have been outlined. The knowledge of the growth mechanisms gives us an opportunity to control these processes more precisely. The surface reactions will be described in detail for the $Ti(OC_2H_5)_4-H_2O$ process, while the $Ta(OC_2H_5)_5-H_2O$ and $Nb(OC_2H_5)_5-H_2O$ processes were examined mainly for comparison in order to specify possible differences between the growth mechanisms of the different metal oxides.

Experimental Section

Experiments were made in a specially modified[12,13] version of the commercial flow type reactor F-120 manufactured by ASM-Microchemistry Ltd. Gas composition was measured with a Leybold TSP 300 quadrupole mass spectrometer with a Faraday cup detector, a mass range of 1−300 amu and a fixed 102 eV ionization energy. Typically used dwell time was 32 ms, and the total time/scan was 350 ms. For ensuring detectable amounts of volatile byproducts, the reaction chamber was enlarged from the normal configuration of the F-120 research ALD reactor wherein the surface area of the substrates is only 50 cm^2. In the enlarged reactor the number and size of the substrates can be modified. In this study the total area of glass substrates was about 3500 cm^2. The pressure in the reactor during the experiments was about 2 mbar. Differentially pumped sampling for the QMS was accomplished through a short (3 mm) and small diameter (0.2 mm) glass capillary which was inserted at the conical end of a glass envelope separating the QMS from the reaction chamber. The pressure in the QMS chamber was below 10^{-4} mbar. A more detailed description of the experimental setup has been given elsewhere.[12,13] Argon (99.99%) was used as a carrier and purging gas.

The metal precursors were $Ti(OC_2H_5)_4$ (Strem Chemicals), $Ta(OC_2H_5)_5$ (Aldrich, 99.98%), and $Nb(OC_2H_5)_5$ (ABCR) while D_2O (Euriso-top, 99.9% D) served as an oxygen source. Evaporation temperatures were 55−90 °C for $Ti(OC_2H_5)_4$, 95−140 °C for $Ta(OC_2H_5)_5$, 85−120 °C for $Nb(OC_2H_5)_5$, and room temperature (20−22 °C) for D_2O. Reaction temperatures were 150−400 °C for TiO_2 and 325 °C for Ta_2O_5 and Nb_2O_5. Deuterated water was used instead of normal water to distinguish the deuterated (C_2H_5OD) and protonated (C_2H_5-OH) ligands. Deuterated ligands should be produced only in the surface reactions with D_2O while protonated ligands may also be produced in the fragmentation of the metal precursor. However, there were weak background signals also in the ions arising from the deuterated ligands ($m/z = 32, 47$) even when no exchange reactions should have taken place, i.e., when a precursor was pulsed over a surface covered with the same precursor. There are many possibilities that could cause this background: rearrangement reactions during the ionization; condensation of the titanium precursor to the cooler end of the reactor tube behind the QMS sampling capillary; incomplete relaxation of the electronics of the QMS during the fast experiments; insufficient mass resolution of the QMS. In this study it remained unclear what was the main reason causing the background. Anyhow, to compensate for the background, the intensities measured during the ALD process with alternate pulsing were corrected by subtracting the intensities measured during the separate precursor pulses (see Table 1).

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Table 1. Pulsing Sequencings and Their Purposes[a]

reaction and sequencing	purpose
$-M(OC_2H_5)_{n-x}$ + $M(OC_2H_5)_n(g)$ 5 times (2.0 s $M(OC_2H_5)_n$ pulse/12 s purge)	background caused by the pulsing of the metal precursor.
$-OD$ + $M(OC_2H_5)_n(g)$ and $-M(OC_2H_5)_{n-x}(s)$ + $D_2O(g)$ 4 times (2.0 s $M(OC_2H_5)_n$ pulse/ 5.0 s purge + 2.0 s D_2O pulse / 5.0 s purge)	ALD process
$-M(OC_2H_5)_{n-x}$ + $M(OC_2H_5)_n(g)$ 2 times (2.0 s $M(OC_2H_5)_n$ pulse / 12 s purge)	check for the sufficiency of the $M(OC_2H_5)_n$ dose
$-OD$ +$M(OC_2H_5)_n(g)$ and $-M(OC_2H_5)_{n-x}(s)$ + $D_2O(g)$ 4 times (2.0 s $M(OC_2H_5)_x$ pulse / 5.0 s purge + 2.0 s D_2O pulse / 5.0 s purge)	ALD process monitoring
$-OD$ + $D_2O(g)$ 5 times (2.0 s D_2O pulse / 12 s purge)	check for the sufficiency of the D_2O dose; The background caused by the pulsing of D_2O

[a] M refers to Ti ($n = 4$) or Ta or Nb ($n = 5$); x is the number of ethoxide ligands released during the metal precursor pulse.

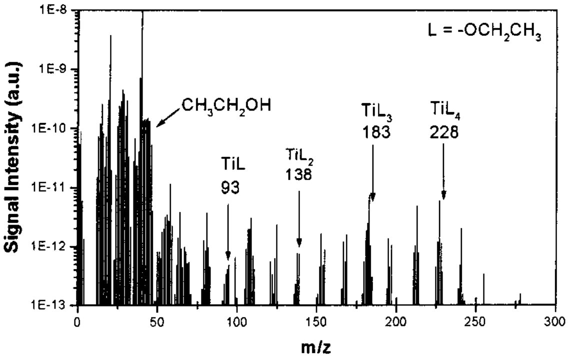

Figure 1. Mass spectrum of $Ti(OC_2H_5)_4$. The source temperature for $Ti(OC_2H_5)_4$ was 90 °C.

In the ethanol adsorption experiments the gas composition was measured with a Hiden HAL/3F 501 RC mass spectrometer and the mass balance studies were done with a Maxtek TM- 400 QCM. A more detailed description of this new system is given elsewhere.[31] Before each ethanol adsorption experiment, a TiO_2 film was grown on the QCM sensor from $TiCl_4$ and D_2O at 250 °C. The pulse lengths were 0.5 s, and the purge time was 6 s. TiO_2 surface was first exposed to a 2 s ethanol pulse and then, after a 60 s purge period, to five 0.5 s D_2O pulses.

Results and Discussion

$Ti(OC_2H_5)_4-D_2O$ Process. First, the behavior of $Ti(OC_2H_5)_4$ as a function of the source and reaction temperatures is discussed. $Ti(OC_2H_5)_{4-x}{}^+$ ($x = 0-3$) ions could not be detected when the source temperature was below 70 °C. When the temperature was above 85 °C, the titanium precursor was consumed quite fast. The reaction mechanism studies were thus made with the source temperature of 80 °C. That is quite close to the temperature 83 °C used in the earlier film growth experiments.[17]

The thermal decomposition of the titanium precursor at 250 °C is low according to the film growth experiments.[17] However, $Ti(OC_2H_5)_4$ was rather heavily fragmented because of the high ionization energy (102 eV) of the QMS (Figure 1). All fragments $Ti(OC_2H_5)_{4-x}{}^+$ ($x = 0-3$) were detected. Between these main fragments there were also fragments from which methyl ($m/z = 15$) and ethene ($m/z = 28$) or ethyl ($m/z = 29$) groups were lost. The protonated ethoxide ligand, $C_2H_5OH^+$ ($m/z = 46$), and its main fragment CH_2OH^+ ($m/z = 31$) were also among the dominant peaks. They were probably formed in rearrangement reactions in the ionizator of the QMS. The peaks with larger m/z values than the molecular peak of $Ti(OC_2H_5)_4$ ($m/z = 228$) were possibly caused by a fragmentation of a dimer.[32] The unreacted titanium precursor was best resolved at $m/z = 227$ [$Ti(OC_2H_5)_3(OC_2H_4)^+$] and $m/z = 183$ [$Ti(OC_2H_5)_3{}^+$].

The amounts of $Ti(OC_2H_5)_3(OC_2H_4)^+$ ($m/z = 227$) and $Ti(OC_2H_4)_3{}^+$ ($m/z = 183$) detected when pulsing $Ti(OC_2H_5)_4$ over a surface covered with $-Ti(OC_2H_5)_{4-x}$ species (two first pulses in Figure 2) were quite constant in the reaction temperature range from 150 to 300 °C (Figure 3). At higher temperatures the amounts of the titanium containing species decreased indicating the decomposition of the precursor. At temperatures below 300 °C, the ratio between the amounts of $Ti(OC_2H_5)_3(OC_2H_4)^+$ and $Ti(OC_2H_4)_3{}^+$ was quite constant. Above 300 °C, $Ti(OC_2H_5)_3(OC_2H_4)^+$ disappeared more quickly than $Ti(OC_2H_4)_3{}^+$. This was evidently due to a partial decomposition of $Ti(OC_2H_4)_4$. The amounts of CH_2OH^+ ($m/z = 31$) and $CH_2CH_2{}^+$ ($m/z = 28$) were in quite constant ratios to the amount of $Ti(OC_2H_5)_3(OC_2H_4)^+$ below 300 °C (Figure 4). At higher temperatures, the amounts of CH_2OH^+ and $CH_2CH_2{}^+$ related to that of $Ti(OC_2H_5)_3(OC_2H_4)^+$ increased, which also indicates that above 300 °C the decomposition of $Ti(OC_2H_5)_4$ begins. This threshold temperature of 300 °C is in a good agreement with the earlier film growth experiments.[17] Diethyl ether ($m/z = 74$) was detected only at temperatures above 350 °C, and its amount was the same when the titanium precursor was pulsed on $-OD$ or $-Ti(OC_2H_5)_{4-x}$ terminated surfaces (Figure 5). Therefore it was not formed in the exchage reactions but only via the decomposition of the titanium precursor.

Next, the effects of the reaction temperature on the amount of volatile byproducts formed in the ALD growth are discussed. Figure 2 shows how the intensities of various m/z values behave in the course of the growth experiment at 250 °C. The main reaction product in the $Ti(OC_2H_5)_4-D_2O$ process was C_2H_5OD, which was detected as $C_2H_5OD^+$ ($m/z = 47$) and CH_2OD^+ ($m/z = 32$).

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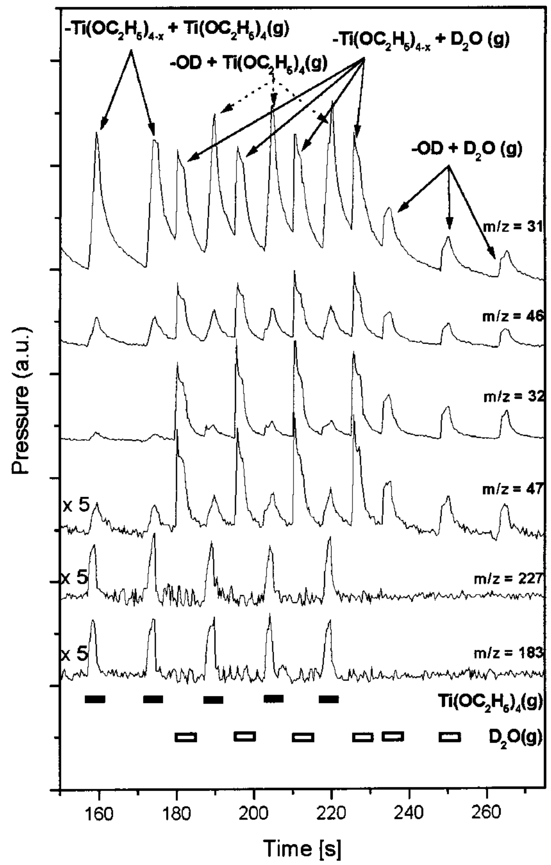

Figure 2. Selected masses in the $Ti(OC_2H_5)_4$–D_2O process at a reaction temperature of 250 °C as a function of time. The data have been shifted vertically for clarity.

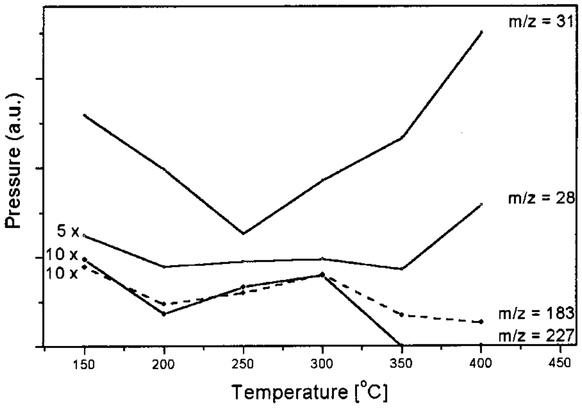

Figure 3. Amount of $Ti(OC_2H_5)_4$ detected (m/z = 183, 227) and the main fragments and/or thermal decomposition products (m/z = 28, 31) as a function of the reaction temperature.

However, these signals rose also during the $Ti(OC_2H_5)_4$ and D_2O reference pulses. Therefore, when the total amounts of the ligands liberated during the D_2O and $Ti(OC_2H_5)_4$ pulses are calculated, the background was subtracted from the intensities of the peaks (see Experimental Section).

In the ALD growth, the CH_2OD^+ (m/z = 32) and $CH_3CH_2OD^+$ (m/z = 47) species were mostly detected during the water pulse (Figure 2). These species were also detected during the $Ti(OC_2H_5)_4$ pulse, although in a smaller extent, comparable to that detected when the titanium precursor was pulsed over a surface covered with $-Ti(OC_2H_4)_{4-x}$. It appears that during the $Ti(OC_2H_5)_4$ pulse almost all signals at m/z =32 and m/z = 47 were caused by the background rather than exchange reactions. When this is accounted for, it can be estimated that over 90% of the ligands were released during the water pulse. The reason for that only a small amount of CH_3CH_2OD was detected during the titanium precursor pulse could be its dehydration resulting in either ethene (CH_2CH_2, m/z = 28) or diethyl ether ($(C_2H_5)_2O$, m/z = 74). The fragmentation of the titanium precursor caused a very intensive signal at m/z = 28; therefore, the possible small amounts of ethene coming from the surface reactions would be hard to detect. On the other hand, as noted above, diethyl ether was formed only in the decomposition of the $Ti(OC_2H_5)_4$.

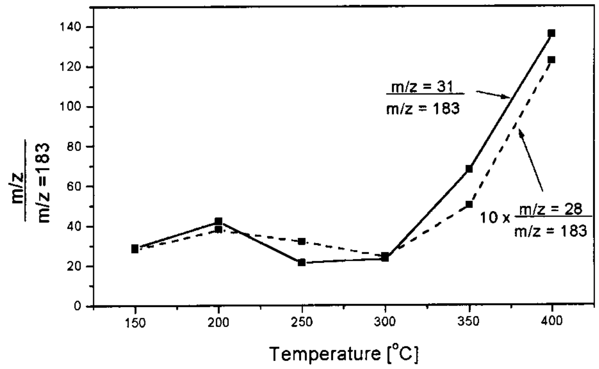

Figure 4. Ratio between intensities of the signals at m/z = 28 and 31 to the signal at m/z = 183 as a function of the reaction temperature. The intensities were measured during the $Ti(OC_2H_5)_4$ pulse over a surface covered with $-Ti(OC_2H_5)_{4-x}$.

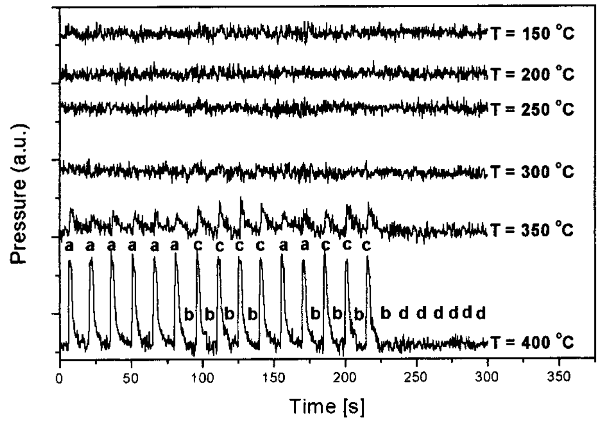

Figure 5. Amount of $(C_2H_5)_2O$ (m/z = 74) during the $Ti(OC_2H_5)_4$–D_2O process as a function of the reaction temperature. The source temperature for $Ti(OC_2H_5)_4$ was 80 °C. Key: a = $-Ti(OC_2H_5)_{4-x}(s) + Ti(OC_2H_5)_4(g)$; b = $-Ti(OC_2H_5)_{4-x}(s) + D_2O(g)$; c = $-OD + Ti(OC_2H_5)_4(g)$; d = $-OD + D_2O(g)$.

Figure 6 shows the amount of $CH_3CH_2OD^+$ released during the water pulse as a function of temperature. The amounts of CH_2OD^+ (m/z = 32) and $CH_3CH_2OD^+$ (m/z = 47) were the largest in the temperature range of 250–300 °C. This temperature range could thus be identified as the best growth temperature, because the surface reactions are fast enough and the decomposition of $Ti(OC_2H_5)_4$ is not yet extensive. This result is in a good agreement with the earlier growth experiments and in situ monitoring with QCM where the growth rate of TiO_2 was only weakly dependent on temperature in the range of 250–300 °C.[17,18] The species CH_2OD^+ (m/z = 32) and $CH_3CH_2OD^+$ (m/z = 47) were detected at

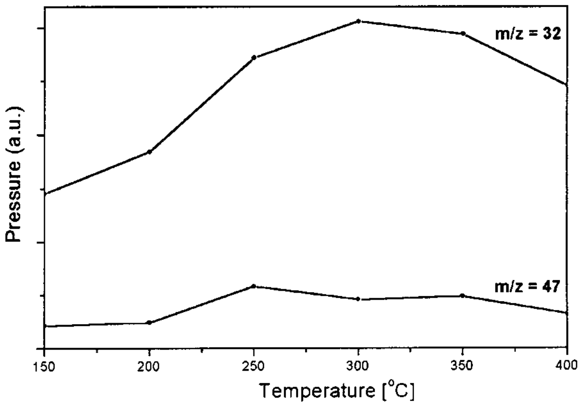

Figure 6. Amount of deuterated reaction products ($m/z = 32$ and 47) as a function of the reaction temperature. The intensities were measured during the D_2O pulse over a surface covered with $-Ti(OC_2H_5)_{4-x}$.

temperatures up to 400 °C in nearly as large amounts as at 250 and 300 °C (Figure 6). Therefore it seems that despite the thermal decomposition of $Ti(OC_2H_5)_4$, the surface remains quite fully $-Ti(OC_2H_5)_{4-x}$ terminated. This suggests that the decomposition is surface controlled. Indeed, in the earlier studies[17,18] it was found that even though the growth was not fully controlled by the exchange reactions, the film thickness was uniform up to temperatures as high as 350 °C.

On the basis of the general understanding of the ALD oxide processes, the amount of $-OH$ groups left on the surface after the water pulse is considered to be a very important factor affecting the exchange reactions.[5,6,13,33−41] Our earlier QMS study on the $Al(CH_3)_3$−D_2O process indeed indicated that the amount of $-OD$ groups had an important effect to the ALD growth mechanism.[13] It is also known that in the temperature range under investigation in this study the water treated TiO_2 surface should be partially covered with $-OH$ groups.[42] Thus it could be suggested that TiO_2 grows via reactions 1 and 2.

$$x\,-\mathrm{OD} + \mathrm{Ti(OC_2H_5)_4(g)} \rightarrow (-\mathrm{O}-)_x\mathrm{Ti(OC_2H_5)}_{4-x}\mathrm{(s)} + x\mathrm{CH_3CH_2OD(g)} \tag{1}$$

$$(-\mathrm{O}-)_x\mathrm{Ti(OC_2H_5)}_{4-x}\mathrm{(s)} + 2\mathrm{D_2O(g)} \rightarrow (-\mathrm{O}-)_2\mathrm{Ti(OD)}_{4-x}\mathrm{(s)} + (4-x)\mathrm{CH_3CH_2OD(g)} \tag{2}$$

According to the reactions 1 and 2, the chemisorbing $Ti(OC_2H_5)_4$ reacts with the surface $-OD$ groups and CH_3CH_2OD is released, and during the D_2O pulse the rest of the ethoxide groups are released and the surface becomes again $-OD$ terminated. If x were 2, the amount of the released CH_3CH_2OD would be the same during both the $Ti(OC_2H_5)_4$ and D_2O pulses.

In this study we found, however, that almost all the ligands are released during the D_2O pulse. This suggests that the film would grow mainly via the reactions 3 and 4. Here $Ti(OC_2H_5)_4$ adsorbs molecularly and no ligands

$$\mathrm{Ti(OC_2H_5)_4(g)} \rightarrow \mathrm{Ti(OC_2H_5)_4(s)} \tag{3}$$

$$\mathrm{Ti(OC_2H_5)_4(s)} + 2\mathrm{D_2O(g)} \rightarrow \mathrm{TiO_2(s)} + 4\mathrm{CH_3CH_2OD(g)} \tag{4}$$

are released in this step. During the D_2O pulse the ligands are released and the surface is ready to receive the next $Ti(OC_2H_5)_4$ pulse.

Another possibility could be that deuterated ethanol released according to the reaction 1 would adsorb to the surface and form with a coordinatively unsaturated Ti atom a surface species $-Ti(CH_3CH_2OD)$ where the bonding would be through an oxygen free electron pair:

$$-\mathrm{Ti} + \mathrm{CH_3CH_2OD(g)} \rightarrow -\mathrm{Ti(CH_3CH_2OD)(s)} \tag{5a}$$

Perhaps even more probably, CH_3CH_2OD would dissociate and combine with surface Ti and O atoms:

$$-\mathrm{Ti} + -\mathrm{O} + \mathrm{CH_3CH_2OD(g)} \rightarrow -\mathrm{Ti{-}O{-}CH_2CH_3(s)} + -\mathrm{OD(s)} \tag{5b}$$

In both cases, the next D_2O pulse would liberate the adsorbed or dissociated CH_3CH_2OD:

$$-\mathrm{Ti(CH_3CH_2OD)(s)} + \mathrm{D_2O(g)} \rightarrow -\mathrm{Ti(D_2O)(s)} + \mathrm{CH_3CH_2OD(g)} \tag{6a}$$

$$-\mathrm{Ti{-}O{-}CH_2CH_3(s)} + \mathrm{D_2O(g)} \rightarrow -\mathrm{Ti{-}OD(s)} + \mathrm{CH_3CH_2OD(g)} \tag{6b}$$

To examine the possibility of these reactions, TiO_2 film was grown on a QCM sensor at 250 °C. Ethanol was pulsed on top of the TiO_2 surface, and after a 60 s purge period D_2O was pulsed to the reactor. Indeed, a mass increment during the ethanol pulse and a mass decrement during the D_2O pulse were observed. At the same time, the gas-phase products were investigated with the QMS and ethanol was observed during the first three D_2O pulses. These observations support the ethanol adsorption mechanism suggested above.

At temperatures above 300 °C the thermal decomposition of the titanium precursor starts to contribute to the film growth:

$$\mathrm{Ti(OCH_2CH_3)_4(g)} \rightarrow \mathrm{TiO_2(s)} + 2\mathrm{CH_3CH_2OH\ (g)} + 2\mathrm{H_2C{=}CH_2(g)} \tag{7a}$$

$$\mathrm{Ti(OCH_2CH_3)_4(g)} \rightarrow \mathrm{TiO_2(s)} + 2\mathrm{(CH_3CH_2)_2O(g)} \tag{7b}$$

Figure 7 summarizes the effects of exchange reactions and the thermal decomposition of $Ti(OC_2H_5)_4$. The amount of exchange reactions is followed with CH_2OD^+ ($m/z = 32$) normalized to unity at 150 °C (solid circles) while the thermal decomposition of $Ti(OC_2H_5)_4$ is fol-

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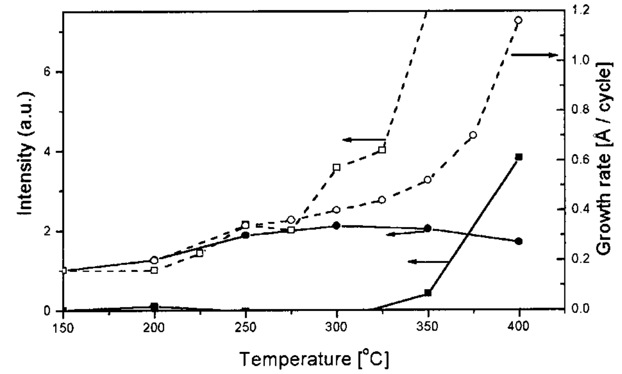

Figure 7. Temperature dependence of the amount of the product CH_3CH_2OD released during the D_2O pulse (solid circles) and the extent of thermal decomposition (solid squares). The amount of CH_3CH_2OD ($m/z = 32$) is from Figure 6, and the thermal decomposition is represented by the intensity ratio of the signal at $m/z = 28$ to the signal at $m/z = 183$ from Figure 4. Growth rates measured in the earlier studies optically[17] (open circles) and with QCM[18] (open squares) are shown also.

lowed with the intensity ratio of signals at $m/z = 28$ to $m/z = 183$ (solid squares). The thermal decomposition of $Ti(OC_2H_5)_4$ should be very low at 150 °C, so the $m/z = 28$ to $m/z = 183$ intensity ratio was first normalized and then vertically shifted to give zero at 150 °C. For comparison, the growth rates measured in the earlier thin film growth experiments[17] and in situ with QCM[18] (normalized to unity at 150 °C) are shown as well. In the QCM results the effect of thermal decomposition is observed at lower temperature. This is most probably due to differences in the reactor design. However, the overall consistency in the temperature dependence behaviors is remarkable.

$Ta(OC_2H_5)_5$–D_2O and $Nb(OC_2H_5)_5$–D_2O Processes. In this study, no Ta-containing species appeared in the QMS spectra. Only species coming from the ligand were detected. This is most probably due to a low partial pressure of $Ta(OC_2H_5)_5$. It was shown earlier by QCM studies that the thermal decomposition of $Ta(OC_2H_5)_5$ on the growing film surface starts at 275 °C[43] and results in noticeable film growth without any water pulses at temperatures above 300 °C.[26] The general interrelation between the temperature dependencies of $Ta(OC_2H_5)_5$ decomposition and the growth rate of Ta_2O_5 measured earlier[26,43] resembles that obtained for $Ti(OC_2H_5)_4$–D_2O (Figure 7). According to the earlier growth experiments,[30] the best film properties were achieved in the $Ta(OC_2H_5)_5$–D_2O and $Nb(OC_2H_5)_5$–D_2O processes, and especially in the nanolaminate growth, in the reaction temperature range of 300–325 °C. For this reason, these processes were examined in more detail only at those temperatures.

In the $Ta(OC_2H_5)_5$–D_2O process, similarly to the $Ti(OC_2H_5)_4$–D_2O process, the main reaction product during the D_2O pulse was C_2H_5OD. However, differently from the $Ti(OC_2H_5)_4$–D_2O process, diethyl ether $(C_2H_5)_2O$ ($m/z = 74$) was released at 325 °C in higher amounts during the $Ta(OC_2H_5)_5$ exposure on water-exposed surface than on $Ta(OC_2H_5)_5$-exposed surface (Figure 8). Therefore, it could be suggested that the film grows during the $Ta(OC_2H_5)_5$ pulse mainly via the reaction 8, although some C_2H_5OD is also released (reaction 9).

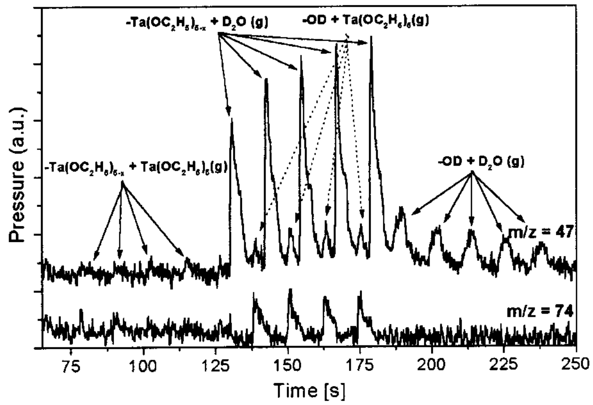

Figure 8. Time behavior of $(C_2H_5)_2O$ ($m/z = 74$) and C_2H_5OD ($m/z = 47$) in the $Ta(OC_2H_5)_5$–D_2O process at a reaction temperature of 325 °C. The data have been shifted vertically for clarity.

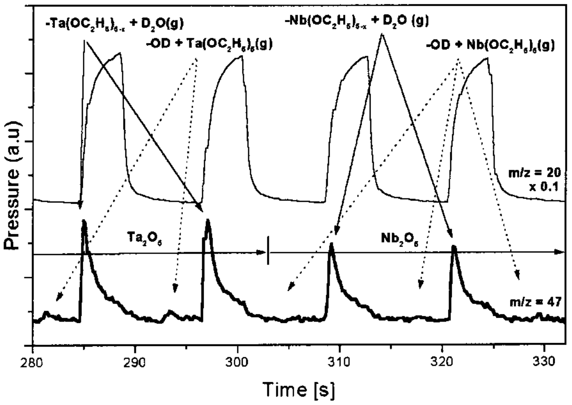

Figure 9. QMS data on the Ta_2O_5–Nb_2O_5 nanolaminate process from $Ta(OC_2H_5)_5$ and $Nb(OC_2H_5)_5$ at a reaction temperature of 325 °C.

$$Ta(OC_2H_5)_5(g) \rightarrow TaO_x(OC_2H_5)_{5-2x}(s) + x(C_2H_5)_2O(g) \quad (8)$$

$$x\ {-OD} + Ta(OC_2H_5)_5(g) \rightarrow TaO_x(OC_2H_5)_{5-x}(s) + xC_2H_5OD(g) \quad (9)$$

The qualitative features of the $Nb(OC_2H_5)_5$–D_2O process were essentially similar to those described above for the $Ta(OC_2H_5)_5$–D_2O process. However, the amount of C_2H_5OD released during the D_2O pulse was less than that in the $Ta(OC_2H_5)_5$–D_2O process. Thus the ALD growth of Ta_2O_5 and Nb_2O_5 can mainly be described as an alternate release of $(C_2H_5)_2O$ ($m/z = 74$) during the $Ta(OC_2H_5)_5$ or $Nb(OC_2H_5)_5$ pulses and C_2H_5OD ($m/z = 47$) during the D_2O pulse.

Figure 9 depicts a representative reaction sequence applied for the Ta_2O_5–Nb_2O_5 nanolaminate growth,[30] monitored by QMS in this study. It can be seen that, during the D_2O adsorption on the $Ta(OC_2H_5)_5$ treated surface, the reaction product $C_2H_5OD^+$ ($m/z = 47$) is released more intensely than in the case of $Nb(OC_2H_5)_5$, enabling the visualization of the multilayer growth with sharp transfer from the growth of one oxide to the other. It is expected that the lower the amount of the reaction products released, the lower the film growth rate.

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Indeed, according to the ex situ measurements by optical methods, the growth rate of Ta_2O_5 was 0.40 Å/cycle,[26] whereas the growth rate of Nb_2O_5 did not exceed 0.35 Å/cycle.[27]

Conclusions

The mechanisms of the ALD growth of TiO_2, Ta_2O_5, and Nb_2O_5 from the corresponding ethoxides and water were studied by QMS in the reaction temperature range of 150−400 °C. To distinguish between the reaction products (C_2H_5OD) and the thermal decomposition or fragmentation of the metal precursor, D_2O was used instead of water. The extent of the reactions was monitored by following the ions arising from the reaction products: $CH_3CH_2OD^+$ ($m/z = 47$) and CH_2OD^+ ($m/z = 32$).

In the case of titanium ethoxide the amount of the reaction product CH_3CH_2OD was the highest in the temperature range of 250−300 °C. Over 90% of the reaction products were detected during the D_2O pulse in the TiO_2 process. $Ti(OC_2H_5)_4$ probably adsorbs molecularly on the oxide surface, and the next D_2O pulse liberates the ethoxo ligands. The other possibility is that the reaction products produced during the ethoxide pulse are adsorbed on the oxide surface and are released during the next D_2O pulse.

At 325 °C the ALD growth of Ta_2O_5 and Nb_2O_5 can mainly be described as an alternate release of $(C_2H_5)_2O$ during the $Ta(OC_2H_5)_5$ or $Nb(OC_2H_5)_5$ pulses and C_2H_5OD during the D_2O pulse.

Above 300 °C all the metal precursors studied start to decompose. The growth is no longer controlled only by the surface exchange reactions.

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