In Situ Mass Spectrometry Study on Surface Reactions in Atomic Layer Deposition of TiN and Ti(Al)N Thin Films

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Surface reactions in the atomic layer deposition (ALD) of TiN and Ti(Al)N films from titanium tetrachloride ($TiCl_4$), trimethylaluminum ($Al(CH_3)_3$), and deuterated ammonia (ND_3) were studied by using a mass spectrometer to determine the amounts of reaction products formed during each deposition step. Since the $Al(CH_3)_3$ dose has been noticed to have a considerable effect on the properties of the deposited Ti(Al)N films, the deposition was studied with low and high $Al(CH_3)_3$ doses. Deuterium chloride, DCl, was the most noticeable reaction byproduct during each deposition step, and the other byproducts increased to significant amounts merely with the high $Al(CH_3)_3$ dose. With the low $Al(CH_3)_3$ dose, most of the chlorine was eliminated during the ammonia pulse similarly to the TiN process. On the other hand, with the high $Al(CH_3)_3$ dose, most of the chlorine was removed during the $TiCl_4$ pulse. The detection of ethane during the Ti(Al)N deposition with the high $Al(CH_3)_3$ dose implied that $Al(CH_3)_3$ acts as an additional reducing agent releasing methyl radicals. During the deposition of AlN films, no ethane evolvement could be detected.

1. Introduction

Titanium nitride (TiN) is an important and widely studied material for example in microelectronics, where its most important application is as a diffusion barrier. For a long time TiN has been used between aluminum and silicon to prevent intermixing, and nowadays, when copper is replacing aluminum, it is also studied for ultra-large-scale integration (ULSI) devices. The requirements for both the materials and the deposition methods to be used in the future are very demanding because the device dimensions are continuously decreasing. The diffusion barrier should be as thin and conformal as possible in order not to decrease the cross sectional area of copper. Therefore, the deposition of the barrier film has to be strictly controllable. In addition, the films should preferably be deposited below 400 °C, considering the tolerance of other materials used in the circuits.

Atomic layer deposition (ALD) is maybe the most promising method to fulfill these high demands since the films grown by ALD exhibit excellent conformality,[1] thickness control, uniformity, and usually the deposition temperatures needed are reasonably low.[2,3] ALD is based on sequential saturative surface reactions which are accomplished by introducing the reactant vapors into the reactor in a cyclic manner, one at a time, separated by purging periods.[3] TiN films have been deposited by ALD from titanium halides and ammonia.[4,5] The deposition temperatures needed to achieve good quality films have, however, been quite high (∼500 °C). Therefore alternative approaches have been sought in order to reduce the deposition temperature.[6,7]

In a recent study we have deposited Ti(Al)N films by ALD from $TiCl_4$, $Al(CH_3)_3$, and NH_3. Already by using very low $Al(CH_3)_3$ doses in addition to $TiCl_4$ and NH_3, the film deposition took place at lower temperatures, the films contained less chlorine, and also the deposition rate was higher.[6] The positive effect of $Al(CH_3)_3$ was assumed to be due to its action as an additional reducing and chlorine removal agent. The growth rate could be increased by increasing the $Al(CH_3)_3$ dose, but then also more carbon, aluminum, and hydrogen were incorporated into the films. Unexpectedly, the increased $Al(CH_3)_3$ dose had no effect on the chlorine content and since more aluminum was incorporated into the Ti(Al)N films, the resistivity was also increased. Therefore, to achieve the best film properties it is recommendable to use just low $Al(CH_3)_3$ doses.

The purpose of this study is to find out what is the role of $Al(CH_3)_3$ in the ALD of Ti(Al)N films and what kind of an effect the $Al(CH_3)_3$ dose has on the deposition mechanism. We have used a recently developed quadrupole mass spectrometer−ALD reactor setup[8,9] for characterizing the titanium tetrachloride−trimethyl-

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aluminum−ammonia process. In the earlier Ti(Al)N growth studies,[6] the pulsing order of the reactants was noticed to have an effect on both the deposition rate and the composition of the films. In this paper, however, we will focus only on the pulsing scheme $TiCl_4$−$Al(CH_3)_3$−ND_3 where $Al(CH_3)_3$ is supplied onto the substrates after the $TiCl_4$ pulse.

2. Experimental Section

Reactor Setup. Experiments were carried out in a specially modified flow-type F-120 ALD reactor (ASM Microchemistry Ltd., Espoo, Finland). The reaction chamber was enlarged and loaded with glass substrates so that the total surface area was about 3500 cm^2.[8−12] The quadrupole mass spectrometer (QMS) used to detect the gaseous species was a Hiden HAL/3F 501 RC with an electron multiplier detector and ionization energy of 70 eV. The sampling and pressure reduction needed[8,9] for the measurements was accomplished through a 50 μm orifice. The pressure in the ALD reactor was about 1 mbar and in the QMS chamber below 10^{-6} mbar.

Pulsing of the Reactants. $TiCl_4$ (99.9%, Aldrich), $Al(CH_3)_3$ (Witco Gmbh), and ND_3 (Cambridge Isotope Laboratories, Inc. D = 99%) were held outside the reactor and used without further purification. $TiCl_4$ and $Al(CH_3)_3$ vapors were generated in external reservoirs held at 22 °C and 20 °C, respectively, and pulsed into the reactor with the aid of solenoid valves. The $Al(CH_3)_3$ flow was controlled by a needle valve (Nupro SS-6BMG-MM), and in this study two different $Al(CH_3)_3$ doses with the needle opened either 0.1 (low dose) or 2 (high dose) turns were examined. ND_3 was introduced into the reactor through a mass flowmeter, a needle valve and a solenoid valve, and the flow rate was adjusted to 14 sccm during a continuous flow. ND_3 was used instead of NH_3 in order to distinguish hydrogens coming from $Al(CH_3)_3$ and ND_3. Nitrogen (99.999%) and argon (99.99%) were used as carrier gases.

Experimental Parameters in the Study of TiN Growth. When $TiCl_4$ reacts with ND_3, the expected reaction byproduct is DCl. The ion $D^{37}Cl^+$(m/z = 39) was followed instead of the more abundant $D^{35}Cl^+$(m/z = 37) because with $D^{35}Cl^+$ also $^{37}Cl^+$ would have contributed to the DCl signal. To study the reaction mechanisms of the TiN film growth, the amount of DCl released during each reactant pulse was examined in the temperature range of 300 to 400 °C. For both $TiCl_4$ and ND_3, a pulse length of 5 s was found to saturate the surface reactions since the use of longer reactant pulses did not increase the amount of the released DCl.

Experimental Parameters in the Study of Ti(Al)N Growth. During the deposition of Ti(Al)N films from $TiCl_4$, $Al(CH_3)_3$ and ND_3, ions at several m/z ratios were observed. However, many of these signals, namely, those ascribed to $Al(CH_3)_2Cl^+$, $CH_2Cl_2^+$, $CHCl_3^+$, $Al(CH_3)_2D^+$, and $Al(CH_3)D_2^+$, were quite minor, exhibited no clear trend, and were hardly measurable. Therefore, only the most abundant ions were measured:

$$m/z = 39\ D^{37}Cl^+$$

$$m/z = 30\ C_2H_6^+$$

$$m/z = 50\ CH_3{}^{35}Cl^+$$

$$m/z = 77\ Al(CH_3){}^{35}Cl^+$$

$$m/z = 17\ CH_3D^+$$

One problem with the mass spectrometric studies is the fragmentation. For example, if $Al(CH_3)Cl^+$ (m/z = 77) is observed by QMS, it can originate from any aluminum compound which contain both methyl and chloride ligands, and is therefore referred to generally as $Al(CH_3)_{3-x}Cl_x$ (x = 1,2). To examine the relative amounts of different reaction byproducts formed during each reactant pulse, the m/z signals were followed as a function of time, and the measured peaks corresponding to each pulse were integrated. Unfortunately, as already seen in the previous QMS-ALD studies,[8,10−12] an increase in the most m/z signals could be seen also when supplying subsequent pulses of only one precursor into the reactor. This background has to be taken into account by subtracting the reactant contributions from the integrated intensities measured for the corresponding m/z signals during the deposition sequences. Therefore, as a part of the overall experiment, 4−5 pulses of each reactant was supplied subsequently to measure the reactant contributions. During these reference pulses, the surface was fully covered with the given reactant which therefore contributed alone to the measured m/z signals. The deposition sequence consisted of 4−5 reaction cycles and the error bars in each figure represent the observed variation between these cycles.

The pulse length of 5 s was used for each reactant. It is possible that the surface reactions are not entirely saturated with these pulse lengths. On the other hand, because of the $Al(CH_3)_3$ decomposition possibility,[13] the growth of Ti(Al)N films from $TiCl_4$, $Al(CH_3)_3$ and NH_3 cannot be considered as an ideal ALD process with fully saturating surface reactions and therefore the use of longer pulse lengths is not reasonable.

3. Results and Discussion

3.1. Deposition of TiN from $TiCl_4$ and ND_3. The release of DCl was observed during both $TiCl_4$ and ND_3 pulses (Figure 1) at all the studied temperatures. The evident reactions are thus

$$-TiCl_x(s) + ND_3(g) \rightarrow -TiND_{3-x}(s) + xDCl(g) \quad (1)$$

$$-ND_y(s) + TiCl_4(g) \rightarrow -NTiCl_{4-y}(s) + yDCl(g) \quad (2)$$

When ND_3 is pulsed into the reactor, it reacts with surface $-TiCl_x$ groups forming $-TiND_{3-x}$ surface species and gaseous reaction byproduct DCl (eq 1). DCl is also released during the following $TiCl_4$ pulse when $TiCl_4$ reacts with the surface groups left after the ND_3 pulse forming $-NTiCl_{4-y}$ surface species (eq 2). A similar mechanism has also been observed in FTIR studies on ALD deposition of tungsten nitride films from WF_6 and NH_3.[14]

Total amount of DCl produced during one cycle increased as a function of deposition temperature (Figure 2). At the same time, the relative amount of DCl released during ND_3 pulse increased. In the ALD growth of TiN films the dependence of deposition rate on temperature has not been studied in detail. In chemical vapor deposition (CVD), however, the deposition rate of TiN films has been noticed to be strongly dependent

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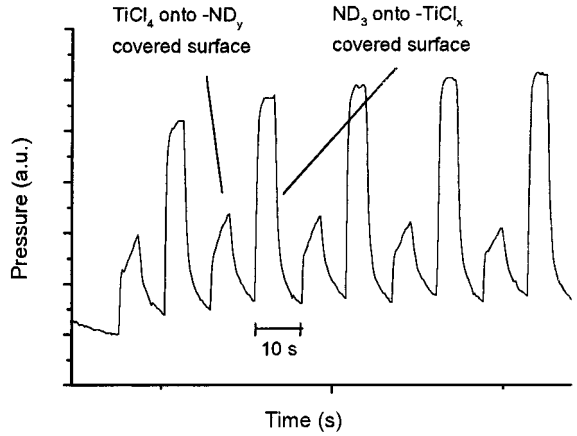

Figure 1. Time behavior of detected DCl ($m/z = 39$) during TiN growth from $TiCl_4$ and ND_3. The pulse length used for both reactants was 5.0 s.

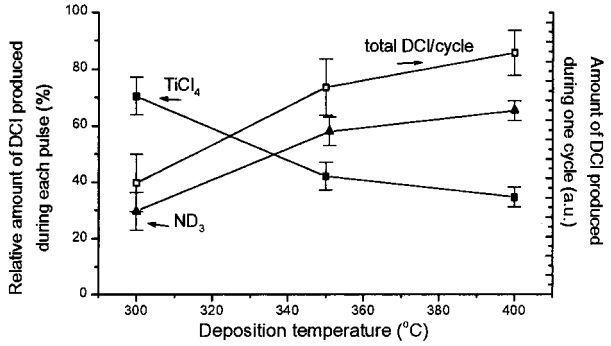

Figure 2. Amount of DCl produced during each reactant pulse divided by amount of DCl produced during one deposition cycle (left axis) and amount of DCl produced during one cycle (right axis) as a function of deposition temperature.

on the deposition temperature.[15,16] Therefore, it is understandable that more reaction products are formed at higher temperatures when the growth rate is higher. These results agree also with the suggested CVD reaction model where the reaction of NH_3 with the adsorbed $-TiCl_x$ species is considered to be the rate liming step with a significant activation energy.[17] The Ti atom in the adsorbed $-TiCl_x$ is coordinatively unsaturated and acts as an electron acceptor and the lone-pair orbital on the N atom of NH_3 (here ND_3) most likely interacts with this Ti site. The H (D) atom of NH_3 (ND_3), on its behalf, acts as an electron acceptor from the electron-rich Cl atom of $-TiCl_x$, thereby resulting in desorption of HCl (DCl).[17]

The relative amounts of DCl released during each reactant pulse show that at 300 °C more DCl is released during the $TiCl_4$ pulse than during the ND_3 pulse (Figure 2). At higher temperatures, less than 50% of DCl is released during the $TiCl_4$ pulse and thus the situation is inverse. In other words, it seems that when the temperature is increased the relative amount of chlorine left on the surface after the $TiCl_4$ pulse increases. According to these results, $TiCl_4$ adsorbs on the $-ND_y$ covered surface mainly as $-TiCl_x$, where x increases as a function of temperature. The main adsorbate species seem to be $-TiCl$, $-TiCl_2$, and $-TiCl_3$ at 300, 350, and 400 °C, respectively. This change in the adsorption chemistry may result from the loss of reactive $-ND_y$ surface groups or from their change from $-ND_2$ to $-ND$ groups,[18] i.e., the surface after the ND_3 pulse at low temperatures may contain more deuterium than at high temperatures. This kind of a behavior is typical also for ALD deposited oxide and sulfide films, where the losses of reactive $-OH$[10,11,19−21] and $-SH$[22,23] surface groups along with increasing temperature have been noticed to have an effect on the adsorption chemistry.

The ALD film growth experiments have shown that at these rather low temperatures large amounts of chlorine (over 10 at. % even at 400 °C) may be incorporated into the deposited TiN films.[24] In addition, in the TiN films deposited by low-pressure chemical vapor deposition (LPCVD) at 400 °C, even the crystalline TiNCl phase has been observed.[25] CVD[26] and ab initio calculation[27] studies have shown that $TiCl_4 \cdot xNH_3$ is formed during the reaction process at lower temperatures, which was found to change to TiClN after heating to 400 °C. It is therefore possible that part of ND_3 adsorbs molecularly as presented in eq 3 especially at lower temperatures where the amount of DCl evolved during the ND_3 pulse is low and more chlorine is incorporated into the film.[24]

$$-TiCl(s) + ND_3(g) \rightarrow -Ti(Cl)ND_3(s) \qquad (3)$$

Schulberg et al.[28] studied the interaction of NH_3 with a TiN surface and according to these studies NH_3 bonds to Ti through a dative bond, the dissociation energy of which was measured to be 100 kJ/mol. Further support to the molecular adsorption is obtained from the FTIR study on the ALD of tungsten nitride films where the presence of molecular NH_3 surface species was detected at lower temperatures (below 330 °C) indicating a formation of WF_x:NH_3 adduct.[14] Anyhow, since DCl is evolved at all the temperatures (Figure 2), most of the ND_3 adsorbed on the $-TiCl_x$-covered surface reacts with the $-Cl$ atoms and simultaneously some of the titanium-bound chlorine is liberated as gaseous DCl (eq 1).

During both reactant pulses DCl was the only reaction product observed. The reaction

$$6TiCl_4(g) + 8NH_3(g) \rightarrow 6TiN(s) + 24HCl(g) + N_2(g) \qquad (4)$$

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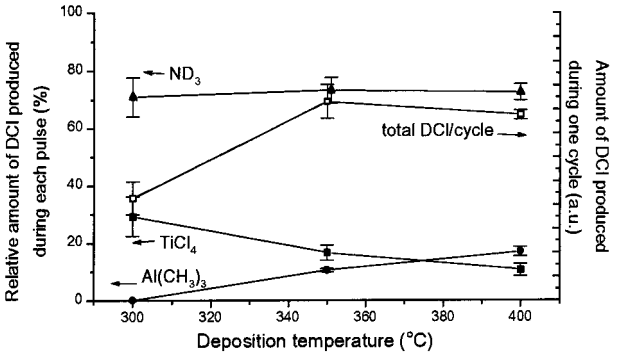

Figure 3. Amount of DCl produced during each reactant pulse divided by amount of DCl produced during one deposition cycle (left axis) and amount of DCl produced during one cycle (right axis) with the low $Al(CH_3)_3$ dose as a function of deposition temperature.

which has often been considered for the $TiCl_4-NH_3$ CVD process suggests that also N_2 should be formed, as is required to balance the formal reduction in the oxidation state from +IV to +III. However, no N_2 evolution has been documented and could not be observed in these studies either. Since the Ti−N bond strength is very high (over 335 kJ/mol), nitrogen desorption from a TiN surface is considered too slow to contribute to the actual deposition reactions at typical growth temperatures.[28]

3.2. Deposition of Ti(Al)N from $TiCl_4$, $Al(CH_3)_3$, and ND_3. Since the $Al(CH_3)_3$ dose has been noticed to have a profound effect on the quality of the deposited Ti(Al)N films,[6] the following reaction mechanism study has been divided into two categories: low ($Al(CH_3)_3$ needle valve open 0.1 turns) and high ($Al(CH_3)_3$ needle valve open two turns) doses. To simplify the discussion, the main focus is on the desorption of DCl, because among the possible volatile byproducts the amount of DCl was the most noticeable. In other words, the main aim is to clarify how $Al(CH_3)_3$ assists in decreasing the chlorine content and how it affects the reactions during each pulse. The amounts of the other measured byproducts became considerable merely with the high $Al(CH_3)_3$ dose, and therefore the mechanistic discussion on, for example, probable reductive chlorine desorption is carried out mainly in connection with the high $Al(CH_3)_3$ dose. Due to the overall complexity of the reaction mechanism, involving apparently many parallel reactions, the reactions suggested below are only elementary and unbalanced.

3.2.1. Desorption of Chlorinated Compounds with a Low $Al(CH_3)_3$ Dose. DCl was the main chlorine containing reaction byproduct also in the ALD growth of Ti(Al)N. The amounts of CH_3Cl and $Al(CH_3)_{3-x}Cl_x$ (where $x = 1$ and 2) detected during the reaction steps were either the same or even lower than those formed directly from the reactants (reference pulses).

About 70% of the DCl detected is produced during the ND_3 pulse at all the deposition temperatures (Figure 3). The deposition temperature affects, on the other hand, the relative amounts of DCl desorbed during the $TiCl_4$ and $Al(CH_3)_3$ pulses. When the deposition temperature is increased the relative amount of DCl produced during the $Al(CH_3)_3$ pulse increases whereas it exhibits a decreasing trend during the $TiCl_4$ pulse. As compared to the TiN process, chlorine seems to be released from the surface quite similarly since at temperatures of 350 °C and higher chlorine is eliminated in both processes mostly during the ND_3 pulse. Hence, according to these results a use of a low $Al(CH_3)_3$ dose between the $TiCl_4$ and ND_3 pulses does not essentially change the basic surface mechanism of DCl desorption. The chlorine content of the Ti(Al)N films is, however, much lower than that of the TiN films (2 vs >10 at. % at 400 °C)[6,24], and thereby, the use of the low $Al(CH_3)_3$ dose has a profound positive effect on the chlorine desorption though $Al(CH_3)_3$ itself does not seem to form chlorine containing species. Because DCl is the only Cl containing reaction byproduct detected, gaseous $Al(CH_3)_3$ has to interact with both $-ND_y$ and $-TiCl_x$ groups resulting in the desorption of DCl. It is interesting that even after the $TiCl_4$ pulse some unreacted $-ND_y$ sites are present on the surface to react with the incoming $Al(CH_3)_3$ molecules. Therefore, it can be concluded that $TiCl_4$ does not react with all the ($-ND_y$) adsorption sites. Quite probable reaction pathway can be presented with the following equation:

$$-Ti(Cl_x)ND_y(s) + Al(CH_3)_3(g) \rightarrow -TiNDAl(CH_3)_z(s) + -CH_3(s) + DCl(g) \quad (5)$$

The Al atom in the $Al(CH_3)_3$ molecule acts as an electrophile toward the lone-pair orbital on the N atom of the $-ND_y$ surface group forming a bond between N and Al atom. As a result, the N−D bond weakens and gaseous DCl is produced (eq 5). It is also possible that some $Al(CH_3)_3$ originated radicals, such as $\cdot Al(CH_3)_z$ and $\cdot CH_3$, interact with the adsorbed electron deficient Ti surface sites by donating some electron density, and thereby reduce titanium and assist in desorbing chlorine (eqs 6 and 7).

$$-Ti(ND_y)Cl_x(s) + \cdot Al(CH_3)_z(g) \rightarrow -TiNAl(CH_3)_z(s) + DCl(g) \quad (6)$$

$$-Ti(ND_y)Cl_x(s) + \cdot CH_3(g) \rightarrow -TiNCH_3(s) + DCl(g) \quad (7)$$

According to both possible explanations DCl desorbs during the $Al(CH_3)_3$ pulse.

The amount of DCl produced during one cycle increases as a function of temperature (Figure 3). However, this can be ascribed largely to the increase in the growth rate: at 400 °C the growth rate was found to be almost two times higher than at 300 °C.[6] Clearly, the efficiency of the ND_3 reactions (eq 1) leading to the growth of Ti(Al)N film increases with the temperature. This is also reflected in film purity as it was observed in the earlier studies where the Ti(Al)N films deposited at 400 °C contained less chlorine and hydrogen than the films deposited at 300 °C (Cl, 2 vs 7 at %, and H, 2 vs 5 at. % at 400 and 300 °C, respectively).[6]

3.2.2. Desorption of Chlorinated Compounds with a High $Al(CH_3)_3$ Dose. The most abundant desorption product including chlorine was again DCl. The amounts of the other measured chlorine containing species ($Al(CH_3)_{3-x}Cl_x$ and CH_3Cl) during the ALD growth were comparable or even lower than during the reference pulses. This was noticed especially at low (300−350 °C) temperatures.

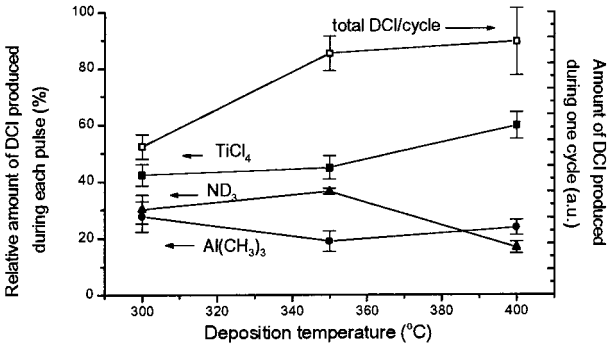

Figure 4. Amount of DCl produced during each reactant pulse divided by amount of DCl produced during one deposition cycle (left axis) and amount of DCl produced during one cycle (right axis) with the high $Al(CH_3)_3$ dose as a function of deposition temperature.

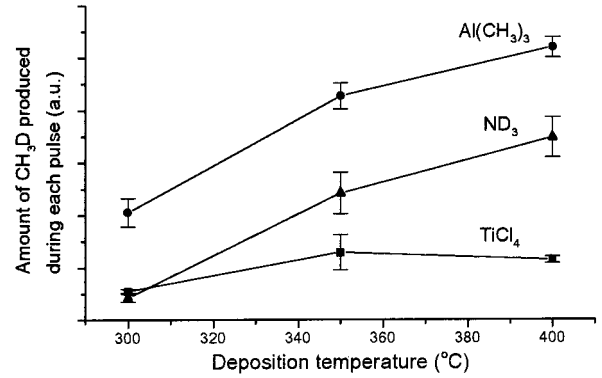

Figure 5. Amount of produced CH_3D during each reactant pulse with the high $Al(CH_3)_3$ dose as a function of deposition temperature.

The total amount of DCl produced during one ALD growth cycle increased as a function of temperature (Figure 4) and was about the same as with the low $Al(CH_3)_3$ dose. This is in agreement with the ALD growth experiments, where the increase of the $Al(CH_3)_3$ dose did not have any effect on the chlorine content of the deposited Ti(Al)N films.[6] Importantly, with the high $Al(CH_3)_3$ dose, the desorption of DCl is the most noticeable during the $TiCl_4$ pulse (eq 2) and thus differs from both the low $Al(CH_3)_3$ dose and the $TiCl_4-ND_3$ processes where most of the DCl was released during the ND_3 pulse. The relative amount of DCl released during the $TiCl_4$ pulse increases as a function of temperature from approximately 40 to 60% (Figure 5). So about half of the chlorine is eliminated during the $TiCl_4$ pulse and therefore it appears that gaseous $TiCl_4$ reacts with the $-ND_y$ species producing mainly $-TiCl_2$. Because the amount of DCl released during the ND_3 pulse is much lower than that with the low $Al(CH_3)_3$ dose (cf. Figure 3), more deuterium seems to be left on the surface after the ND_3 pulse with the high $Al(CH_3)_3$ dose. In light of these results it seems that after the ND_3 pulse the surface consists mainly of $-ND$ sites with the low $Al(CH_3)_3$ dose, and of $-ND_2$ sites with the high $Al(CH_3)_3$ dose. This difference may be attributed to a more effective chlorine removing capacity of the high $Al(CH_3)_3$ dose: as there is less chlorine on the surface, the adsorbing ND_3 molecules react mostly with only one chlorine and thus produce $-ND_2$ groups.

Approximately the same amount of DCl is released during the $Al(CH_3)_3$ and ND_3 pulses at 300 and 400 °C. At 350 °C DCl is more effectively removed from the surface during the ND_3 pulse than during the $Al(CH_3)_3$ pulse. A reason to this is not clear, but it may somehow be associated with the $Al(CH_3)_3$ decomposition, which begins at this temperature range.[29−31] For example, in the surface studies of trimethylaluminum adsorbed on porous alumina the decomposition of $Al(CH_3)_3$ was reported to begin above 300 °C.[29]

The amounts of $Al(CH_3)_{3-x}Cl_x$ and CH_3Cl desorbed during the $TiCl_4$ pulse seemed to increase as a function of temperature. This refers to ligand exchange reactions between the adsorbing $TiCl_4$ and some unreacted $-Al(CH_3)_x$ groups left on the surface after the ND_3 pulse. During the $Al(CH_3)_3$ pulse, on the other hand, the amount of CH_3Cl decreased as a function of temperature and the amount of $Al(CH_3)_{3-x}Cl_x$ exhibited a minimum at 350 °C. During the ND_3 pulse no CH_3Cl or $Al(CH_3)_{3-x}Cl_x$ was desorbed at any temperature.

3.2.3. Desorption of Aluminum and Methyl-Containing Species. The reactions desorbing methyl and aluminum species during different pulses were more clear with the high than low $Al(CH_3)_3$ dose, since the amounts detected were much higher. Therefore, more insight into the supposed reductive behavior of $Al(CH_3)_3$ can be gained from the studies made with the high $Al(CH_3)_3$ dose, and thus this case is discussed first.

With the high $Al(CH_3)_3$ dose the desorption of $Al(CH_3)_{3-x}Cl_x$ was the slightest at 350 °C. Interestingly, the deposition experiments with the low $Al(CH_3)_3$ dose have shown that the amount of Al incorporated into the deposited films is the highest at 350 °C.[6] No $Al(CH_3)_{3-x}Cl_x$ was desorbed during the ND_3 pulse, which is understandable since AlN films have actually been deposited by ALD from $Al(CH_3)_3$ and NH_3 [13] and also from $AlCl_3$ and NH_3,[32] although from the latter only above 450 °C.

Most of the carbon is probably desorbed from the surface as deuterated methane (CH_3D) or ethane (C_2H_6), since their intensities were much higher than those of CH_3Cl or $Al(CH_3)_{3-x}Cl_x$. Figure 5 depicts how the amount of CH_3D increases as a function of temperature during all the reactant pulses. The reactions producing CH_3D during each reactant pulse may be presented with the following equations:

$$-NDAl(CH_3)(s) + TiCl_4(g) \rightarrow -NAl(Cl)_xTi(s) + CH_3D(g) \quad (8)$$

$$-TiND_y(s) + Al(CH_3)_3(g) \rightarrow -TiNAl(CH_3)_{3-y}(s) + yCH_3D(g) \quad (9)$$

$$-TiNAl(CH_3)(s) + ND_3(g) \rightarrow -TiNAlND_2(s) + CH_3D(g) \quad (10)$$

In eq 8, part or all of the chlorines are bridging between aluminum and titanium as the formation of a metallic Ti−Al bond is improbable. The amount of CH_3D is the

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most noticeable during the $Al(CH_3)_3$ and ND_3 pulses. When ND_3 is pulsed onto the surface after the $Al(CH_3)_3$ pulse, it forms AlN, and methane is released. The growth rate of AlN films was found to strongly increase as a function of temperature[13] and thereby also the amount of methane should increase. Also according to the chemisorption studies of ammonia on trimethylaluminum modified silica, ammonia reacts with the adsorbed methyl groups more effectively at high temperatures.[18]

It has been suggested that the function of $Al(CH_3)_3$ in the deposition of Ti(Al)N from $TiCl_4$, $Al(CH_3)_3$ and NH_3 is to act as an additional reducing agent and thereby reduce titanium from the oxidation state +IV to +III.[6] An indication of this reductive behavior is the formation of ethane during the $Al(CH_3)_3$ pulse in the deposition of Ti(Al)N. As already presented in eq 5, $-CH_3$ species are formed on the surface during the $Al(CH_3)_3$ pulse. If two of these methyl groups react with each other gaseous ethane is formed. Recognizing the instability of titanium alkyls the formation of $Ti-CH_3$ is quite unlikely.[33] Ethane could form also with the following radical mechanism, either in a gas phase or on a surface. The homolytic bond cleavage of $Al(CH_3)_3$ produces $\cdot Al(CH_3)_z$ (where $z = 1$ and 2) and $\cdot CH_3$ radicals (eq 11a). $\cdot Al(CH_3)_z$ can react with the adsorbed $-TiCl_x$ groups producing reduced titanium and gaseous $Al(CH_3)_{3-x}Cl_x$ while methyl radicals can combine with each other to form gaseous ethane. This can be represented with the following reaction equations:

$$Al(CH_3)_3(g) \rightarrow \cdot Al(CH_3)_2(g) + \cdot CH_3(g) \quad (11a)$$

$$-TiCl_x(s) + \cdot Al(CH_3)_z(g) \rightarrow Ti\cdot(s) + Al(CH_3)_{3-x}Cl_x(g) \quad (11b)$$

$$2\cdot CH_3 \rightarrow C_2H_6 \quad (11c)$$

Naturally not all the ethane correlates with the reduction reactions since whenever the temperature is high enough, $Al(CH_3)_3$ decomposition occurs and ethane is produced. However, when the AlN growth from $Al(CH_3)_3$ and ND_3 was studied separately, it could be seen that the reaction of $Al(CH_3)_3$ with the surface $-ND_y$ groups did not increase the amount of C_2H_6 as compared with the reference pulses. During the AlN growth the most important reaction byproduct is methane and no reduction of aluminum is needed since it already is at the right oxidation state +III. On the other hand, since the amount of C_2H_6 increased during the deposition of Ti(Al)N where a reduction is needed, $Al(CH_3)_3$ most likely acts as an additional reducing agent.

The amount of C_2H_6 increased also during the $TiCl_4$ and ND_3 pulses as a function of temperature. The reactions taking place during the $TiCl_4$ and ND_3 pulses may be represented with the following equations where part or all of the chlorines are probably bridging between aluminum and titanium:

$$-NAl(CH_3)_2(s) + TiCl_4(g) \rightarrow -NAl(Cl)_xTi(s) + C_2H_6(g) \quad (12)$$

$$-Ti(Cl)_xAl(CH_3)_2(s) + ND_3(g) \rightarrow -Ti(Cl)_xAlND_3(s) + C_2H_6(g) \quad (13)$$

In these reactions, $TiCl_4$ and ND_3 adsorb onto surface sites previously occupied by $-CH_3$ groups. These combine and form ethane.

The mass spectrometry results with the low $Al(CH_3)_3$ dose differed from the results with the high $Al(CH_3)_3$ dose. The amount of CH_3D produced with the low $Al(CH_3)_3$ dose increased slightly as a function of temperature during the $Al(CH_3)_3$ pulse, but exhibited a slight decrease during the ND_3 pulse. The decrease during the ND_3 pulse disagrees with both the deposition and surface reaction studies where it has been found that at high temperatures ammonia reacts with the adsorbed methyl groups more effectively.[13,18] These contradictory results are most likely due to the consumption of ND_2H, since our ammonia was not entirely deuterated and NDH^+ is at the same $m/z = 17$ value as CH_3D^+. The consumption of ND_3, and hence of ND_2H, is more considerable at high temperatures when the deposition rates are higher. Therefore especially at higher temperatures the actual amount of CH_3D produced during the ND_3 pulse may be higher than detected. On the other hand, with the high $Al(CH_3)_3$ doses the amount of CH_3D produced during the ND_3 pulse in the deposition cycle was higher than during the reference ND_3 pulses at all the temperatures. This resulted most likely from the much higher amount of surface methyl groups after the high $Al(CH_3)_3$ dose. Thereby the amount of CH_3D produced during the ND_3 pulse was much more noticeable and overrode the effect of the ammonia consumption. During the $TiCl_4$ pulse with the low $Al(CH_3)_3$ dose, on the other hand, the production of CH_3D was not significant. Ethane, C_2H_6, was evolved in meaningful amounts only during the ND_3 pulse exhibiting an increase as a function of temperature.

With the both $Al(CH_3)_3$ doses the total amounts of CH_3D and C_2H_6 increased as a function of the deposition temperature. In the first place, this can be related to an increased growth rate and increased Al content, but at the same time it may also indicate more efficient methyl group desorption and thus fewer carbon residues. According to the IR and NMR surface studies on trimethylaluminum adsorbed on porous silica, all methyl groups bonded to aluminum could be removed with ammonia at temperatures higher than 300−350 °C but at lower temperatures some methyl groups were left on the surface.[18] These surface studies were, however, made by using much longer reactant exposure times than used in this study and therefore the results are not straightforwardly comparable. Therefore, it is understandable that even at temperatures higher than 350 °C carbidic carbon, but not necessarily methyl groups, is left in the films. Anyhow, interestingly the carbon content of the Ti(Al)N films seemed to exhibit a decreasing trend as a function of the deposition temperature (16 at. % at 300 °C and 11 at. % at 400 °C) with the low $Al(CH_3)_3$ dose,[6] which agrees well with both the surface[18] and current mass spectrometry studies. However, also the opposite temperature effect has been

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noticed in the $Al(CH_3)_3$ based AlN[13] and Ta(Al)N(C)[34] ALD processes. This has been attributed to the $Al(CH_3)_3$ decomposition which is more significant at higher temperatures where methyl groups are supposed to decompose to carbidic residues already during the $Al(CH_3)_3$ pulse. Apparently, these carbidic residues cannot be removed by the subsequently dosed ammonia.

4. Conclusions

The surface reactions occurring during the ALD deposition of TiN and Ti(Al)N thin films from $TiCl_4$, $Al(CH_3)_3$, and ND_3 were studied by means of in situ mass spectrometry. The reactions were studied by measuring the amounts of reaction byproducts during each reaction step in the temperature range of 300−400 °C. The main focus was on the reactions releasing chlorine containing desorption products, of which the most abundant was DCl.

During the TiN growth DCl was the only observed reaction byproduct and it was released during both $TiCl_4$ and ND_3 pulses. The deposition temperature had an effect on the amount of DCl produced during the ND_3 pulse so that at higher temperatures more DCl was released. It seems that $TiCl_4$ adsorbs on the $-ND_y$ covered surface mainly as $-TiCl_x$ where x increases as a function of temperature. This change in the adsorption chemistry is attributed to the loss of reactive $-ND_y$ surface groups or their change from $-ND_2$ to $-ND$ groups.

When studying the deposition of Ti(Al)N films two different; low and high $Al(CH_3)_3$ doses, were used since according to the earlier growth studies the dose had a noticeable effect on the film properties, such as growth rate, resistivity, and impurity contents. The reactions were not fully saturating but left unreacted surface groups which lead to a complicated behavior. The use of a low $Al(CH_3)_3$ dose in the deposition of Ti(Al)N films did not seem to have an effect on the basic surface reaction mechanism, since most of the chlorine was still desorbed during the ND_3 pulse as in the deposition of TiN films. However, the reaction mechanism seemed to change when the Ti(Al)N films were deposited with the high $Al(CH_3)_3$ dose. Then approximately half of the chlorine was removed during the $TiCl_4$ pulse at all the studied temperatures. This change was related to a more effective chlorine removing capacity of the high $Al(CH_3)_3$ dose.

Reaction byproducts other than DCl were released in slighter amounts and were dependent on the $Al(CH_3)_3$ dose. Most interestingly, with the high $Al(CH_3)_3$ dose ethane was produced during the deposition of Ti(Al)N, but not during the deposition of AlN. This is an implication of $Al(CH_3)_3$ acting as an additional reducing agent releasing methyl radicals.

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