Reaction mechanisms of atomic layer deposition of TaN$_x$ from Ta(NMe$_2$)$_5$ precursor and H$_2$-based plasmas

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The reaction mechanisms of plasma-assisted atomic layer deposition (ALD) of TaN$_x$ using Ta(NMe$_2$)$_5$ were studied using quadrupole mass spectrometry (QMS). The fact that molecule dissociation and formation in the plasma have to be considered for such ALD processes was illustrated by the observation of 4% NH$_3$ in a H$_2$-N$_2$ (1:1) plasma. Using QMS measurements the reaction products during growth of conductive TaN$_x$ using a H$_2$ plasma were determined. During the Ta(NMe$_2$)$_5$ exposure the reaction product HNMe$_2$ was detected. The amount of adsorbed Ta(NMe$_2$)$_5$ and the amount of HNMe$_2$ released were found to depend on the number of surface groups generated during the plasma step. At the beginning of the plasma exposure step the molecules HNMe$_2$, CH$_4$, HCN, and C$_2$H$_2$ were measured. After an extended period of plasma exposure, the reaction products CH$_4$ and C$_2$H$_2$ were still present in the plasma. This change in the composition of the reaction products can be explained by an interplay of aspects including the plasma-surface interaction, the ALD surface reactions, and the reactions of products within the plasma. The species formed in the plasma (e.g., CH$_x$ radicals) can re-deposit on the surface and influence to a large extent the TaN$_x$ material composition and properties. © 2012 American Vacuum Society. [DOI: 10.1116/1.3625565]

I. INTRODUCTION

TaN$_x$ is one of the candidate materials for Cu diffusion barriers and for metal gates in the next semiconductor technology nodes. To deposit TaN$_x$ films, atomic layer deposition (ALD) is being investigated with ALD’s excellent conformality being of vital interest for the barrier application and ALD’s high uniformity and precise growth control being key for the deposition of metal gates. TaN$_x$ has many stable and metastable phases ranging from the conductive Ta metal to the semiconductive Ta$_3$N$_5$ phase. For the deposition of TaN$_x$, plasma-assisted ALD is considered to be very promising, since a highly reductive environment such as a H$_2$ plasma is required to obtain the conductive TaN$_x$ phase. However, with the use of H$_2$ plasma in ALD of TaN, a large variation in composition and resistivity of the films has been reported in the literature. To understand the relation between plasma processes and the material properties, a more detailed insight into the reaction mechanism is needed.

In general, there exist only a few reports on reaction mechanism studies of plasma-assisted ALD in the literature. Most of these studies concern O$_2$-plasma-based processes, i.e., Al$_2$O$_3$ (Refs. 14–16), TiO$_2$ (Ref. 17), and Ta$_2$O$_5$ (Ref. 18), and these studies mostly revealed combustion-like reactions during the plasma step. To our knowledge, only one extensive reaction mechanism study has been reported for the growth of metals or metal nitrides by plasma-assisted ALD, which was for the deposition of Ti using TiCl$_4$ and H$_2$ plasma. For many applications however, metal-organic precursors are preferred to exclude the possibility of introducing halide impurities in the deposited film. Kim et al. and Maeng et al. speculated on the reaction mechanism during the plasma-assisted ALD process of TaN$_x$ with Ta(NMe$_2$)$_5$ precursor and H$_2$ plasma and based their discussion on the TaN$_x$ film composition and on the results for thermal ALD of TiN from Ti(NMe$_2$)$_4$ and NH$_3$ (Ref. 9 and 20). They suggested that HNMe$_2$ is released during the precursor step and that HNMe$_2$ and CH$_4$ are released during the plasma step. Rayner et al. proposed a reaction between Ta(N’Bu)(NEt$_2$)$_3$ at the surface and incoming H radicals (generated by a hotwire source) forming HNEt$_2$ as reaction product. Moreover, it has to be realized that due to the presence of plasma, dissociation and recombination reactions should be considered as they could play an important role in the deposition process.

In this work the reaction mechanism of the plasma-assisted ALD process for TaN$_x$ with Ta(NMe$_2$)$_5$ precursor and H$_2$ plasma was investigated by quadrupole mass spectrometry (QMS). The process itself and the material properties obtained were described in our earlier work. First the TaN$_x$ ALD process is briefly reviewed, focusing on changes in the material and process properties with increase in plasma exposure time, i.e., the variation of the material composition, the change in resistivity, and the so-called soft saturation of the growth-per-cycle (GPC). Subsequently, the issues and considerations when using mass spectrometry for studying ALD are discussed and the measurement procedure is described. The aspect of molecule formation in plasmas is considered and illustrated by the observation of NH$_3$ in
H2-N2 plasmas. Using the described measurement procedure, the reaction products during growth of the conductive TaN phase were determined. Finally, the reaction mechanisms and growth processes are discussed, addressing the fact that the interaction of the material and the reaction products with the plasma plays an important role in the TaN growth process by plasma-assisted ALD.

II. PLASMA-ASSISTED ALD OF TaNx

In previous publications we reported on the development of a plasma-assisted ALD process for TaNx using PDMAT [Ta(NMe2)5] and H2, H2-N2, and NH3 plasmas and showed that the resulting material depended on the plasma composition and the plasma exposure time. In short, the remote plasma ALD reactor consisted of a turbomolecular-pumped deposition chamber (base pressure of < 10^-5 Torr), an inductively coupled plasma (ICP) source, and a precursor dosing system. The plasma source could be separated from the deposition chamber by a gate valve in between. Ar was used as carrier gas at a working pressure of ~30 mTorr to adequately deliver the vapor from the solid Ta(NMe2)5 precursor which was heated to 75°C. The flow was controlled using a leak valve upstream. The Ar flow was also used for purging the chamber after precursor exposure using a divert line. The remote ICP plasma source was operated at 100 W rf power and 7.5 mTorr pressure of H2,H2-N2, or NH3 gas. In between the precursor and plasma step the chamber was pumped down (<10^-4 Torr).

At the typically used ALD exposure times with a 4 s exposure of Ta(NMe2)5 and 10 s exposure of H2 plasma at a deposition temperature of 225°C, conductive (1200 μΩ cm), cubic TaN3 films were obtained. By increasing the plasma exposure time to 30 s, the resistivity of the films decreased to 380 μΩ cm. A decrease in deposition temperature had a smaller effect on the resistivity leading to 1300 μΩ cm for depositing at 150°C. Figure 1 shows the change in resistivity and the number of Ta and N atoms deposited per cycle as a function of the plasma exposure time. The resistivity decreases about two orders of magnitude with the increase in plasma exposure time and the material becomes more Ta rich. The number of Ta atoms deposited per cycle increases while the number of N atoms deposited per cycle stays almost constant. Since each Ta atom comes from a Ta(NMe2)5 precursor molecule, more precursor molecules are apparently adsorbed per cycle when employing longer plasma exposure times. As commonly observed for TaN3 films deposited by ALD, O (~15%) and C (~10%) impurities are present in the films. The O content decreases slightly with plasma exposure time and the O probably originates from precursor impurities and post-deposition oxidation. The C content does not decrease with plasma exposure time and does not show a clear trend. The C content most likely originates from the Me groups in the precursor.

The evolution of the growth-per-cycle (GPC) is considered to better understand the large change in material properties with plasma exposure time. The precursor exposure shows normal saturation behavior (saturating in three seconds) and could be fitted with a single exponential function. The plasma exposure; however, showed a so-called soft saturation behavior characterized by a large increase in GPC in the first few seconds of the plasma exposure and a slow increase over longer time as shown in Fig. 2. Note, that this behavior is not caused by a parasitic CVD growth component, since thermal decomposition of the reactant (H2 plasma) cannot be an issue. The saturation behavior was fitted with a double exponential function with two time constants. These two time constants basically suggest that two processes play a role, one with a short time constant of 0.7 s, component “a”, and one with a long time constant of 8 s, component “b”. The two time constants and the accompanying change in material properties can be related to the reaction mechanism of the process and to the reaction products created. The latter will be shown by a systematic QMS study below.

When using plasmas consisting of H2-N2 (1:1 ratio) or NH3, amorphous Ta3N5 films with a high resistivity (> 5 × 10^4 μΩ cm) and low C content (< 2%) were obtained. Even when only a small amount of N2 was admixed to the H2 plasma (98:2 ratio), the N content increased (N/Ta = 1.0) and the resistivity of the films was high (1.1 × 10^4 μΩ cm). Therefore, the transition to the stable Ta3N5 phase is expected to be fast. Consequently, the dependence of the growth process on plasma exposure was not investigated.

III. MASS SPECTROMETRY STUDY FOR ALD

QMS is an excellent tool to study ALD processes. The most prominent merits of QMS are:

1. The technique is noninvasive. Because only a small amount of gas is extracted in the measurement, the ALD process is not influenced by it.

Fig 1. (Color online) Resistivity (a) and the number of Ta and N atoms per cycle per nm² (b) for TaN3 deposited by ALD as a function of the H2 plasma exposure time at a deposition temperature of 225°C. The data for a 10 s plasma exposure at 150°C were included for comparison.
(2) A relative high time resolution can be obtained when only a few masses are measured at the same time (e.g., 300 ms).
(3) It is easy to interpret when the cracking patterns of the parent molecules are known and/or do not overlap.
(4) It is sensitive as small concentrations of species can be measured especially when the background signals are low.
(5) A wide range of species can be detected, as basically any stable chemical species can be measured. For instance, a sensitive technique such as laser spectroscopy can typically only be used to probe a small selection of molecules due to the typical limited tuning range of the wavelength.

Because of these merits, QMS has been used in a variety of studies of ALD in the literature.\(^{15,18,22–24}\)

Species detection by QMS occurs as follows: first a small fraction of the gas molecules are extracted from the reactor through the orifice into the QMS and are ionized through electron-impact ionization by electrons with typically an energy of ~70 eV. In typical QMS configurations only stable gas-phase species are detected since plasma radicals, which might be present in the reactor, will generally recombine while entering the QMS, i.e., before they can be ionized. Besides being ionized into parent molecule ions, i.e.,

\[
AB + e^- \rightarrow AB^+ + 2e^-,
\]
a significant part of the parent molecules will be ionized dissociatively into smaller fragments of the parent molecule:

\[
AB + e^- \rightarrow A^+ + B + 2e^-.
\]
The parent molecule ions and other ionized fragments will enter the quadrupole mass filter. This mass filter only allows ions within a narrow mass range to pass through on the basis of a properly controlled combination of dc and rf electric fields. The ions that pass through the filter are measured by the SEM detector. It is important to realize that it is not directly the mass of the ionized fragments that is measured, but the mass-to-charge ratio (m/z). Since most fragments have charge one at the used ionization energy of ~70 eV, m/z is in most cases the same as the mass of the ion. The mass spectrum resulting from the fragmentation of a particular molecule is referred to as the cracking pattern. The cracking pattern is a kind of fingerprint of the molecule and can be used to identify the parent molecules responsible for a measured spectrum. The NIST database can be used which contains a wide range of cracking patterns from a variety of sources.\(^{25}\) However, it should be realized that QMS setups can vary greatly in their sensitivity as a function of the m/z value depending on the configuration and on the parameter settings.

When following several m/z ratios, the time per m/z measurement is determined by the dwell time and the delay time. The dwell time is the time over which the SEM detector signal is integrated (e.g., 50 ms); the delay time is the dead time for changing between m/z values. The delay time should be sufficiently long for the mass filter to stabilize at a certain setting (e.g., 10 ms). Otherwise, also fragments other than those with the target m/z value will contribute to the signal. Moreover, it is advisable to measure m/z values in an order from low to high to minimize the magnitude of the changes in m/z value setting. When measuring from low to high m/z values contributions from fragments at unwanted m/z values can be avoided. Besides that, so-called pressure effects can also be present, i.e., changes in signal due to changes in pressure even when the measured signal is not from a species causing the pressure change. Therefore, comparison of signals should be done at similar reactor pressures. Furthermore, because the sensitivity of the QMS can vary over time, reference signals should be used to correct for this variation when different measurements have to be compared. For example a signal from Ar\(^+\) (m/z = 40) can be chosen as reference signal. In this case a known partial pressure of Ar gas should be present during the ALD process.

\[\text{A. QMS measurement procedure}\]

The QMS can operate in different modes, either measuring a wide mass range (e.g., m/z = 1 – 100) with low time resolution (also referred to as a mass scan) or a few masses with higher time resolution (also referred to as a time-dependent scan). The stepwise nature of ALD and the associated short time in which reaction products are released require a carefully considered measurement procedure to determine the reaction products. Measuring a large range of masses is desired to unambiguously attribute changes at certain m/z values to specific gaseous species. However, to achieve sufficient time resolution, the time resolved measurements should be carried out by monitoring only a few m/z values at the same time. Due to the cyclic nature of ALD in which the process is continuously repeated, the measurements at different m/z values during different cycles can be combined to form a mass spectrum for a single cycle. This

**Fig. 2.** (Color online) Growth-per-cycle for TaN, as a function of the plasma exposure time at a deposition temperature of 225°C. The solid line shows the double exponential decay fit with two time constants. The two contributions (a) and (b) with different time constants are shown separately in dashed lines. The growth-per-cycle for 10 s plasma exposure at 150°C was included for comparison.
mass spectrum represents the signals during a single cycle for of a wide range of masses with a high time resolution. To improve the signal-to-noise ratio the signals of multiple cycles can be used for averaging and the reference signal can be used to monitor the reproducibility of the measurements. To distinguish the signals caused by reaction products from the background signals properly chosen reference spectra are measured. Reaction products will not be formed when the surface reactions are already saturated so repeating a precursor or reactant exposure under saturated conditions will show their cracking patterns and can therefore serve as a reference. When plasma is used as reactant, a measurement under zero plasma power yields the signal for only the source gasses.

For the QMS measurements, a differentially-pumped quadrupole mass spectrometer (Pfeiffer QME 200, mass-to-charge ratio \( m/z = 0 – 200 \)) with a 150 \( \mu \)m orifice was fitted to the side of the reactor. In the measurement procedure for the TaN\(_x\) process, four \( m/z \) values were measured at the same time. The measurement per four \( m/z \) values consisted of five normal ALD cycles (“normal ALD”), five cycles with zero plasma power (“precursor only”), and five cycles with no Ta(NMe\(_2\))\(_3\) (“plasma only”). The “plasma only” cycles were performed by keeping the precursor valves closed (the Ar flow is not diverted through the Ta(NMe\(_2\))\(_3\) bubbler), and the “precursor only” cycles were performed by setting the plasma power to zero in the cycle. Therefore both “cycle conditions” have basically the same pressure changes as a normal cycle minimizing any “pressure effects” in the signal. The measurement per four \( m/z \) values was repeated until data were obtained for all \( m/z \) ratios in the range of \( m/z = 12 – 46 \). In each measurement, the signal at \( m/z = 40 \) (Ar\(^+\)) was included to serve as a reference while the other three \( m/z \) values varied. On the basis of the Ar\(^+\) signal, the different measurements were synchronized afterwards. Furthermore, the signal at \( m/z = 40 \) (Ar\(^+\)) during the precursor step was used to monitor the sensitivity of the QMS and was used to normalize the signal. The signal at each \( m/z \) value for each “cycle condition”, i.e., “normal ALD”, “precursor only”, and “plasma only”, was averaged over the last four cycles as the first cycle typically showed influences from the previous “cycle condition”.

Figure 3 shows the contributions in the QMS signal for the precursor and plasma step measured during the three “cycle conditions”. In this case \( m/z = 15 \) is used as an example. During the “normal ALD” cycle the precursor step has contributions from cracking of Ta(NMe\(_2\))\(_3\) precursor, from reaction products formed in ALD surface reactions, and from background signals including the Ar flow. The plasma step has contributions from plasma gas species, from reaction products and from background signals including the H\(_2\) flow. The “precursor only” and “plasma only” cycles represent situations for which extended Ta(NMe\(_2\))\(_3\) exposure or extended plasma exposure times have been employed, respectively. In the case of an extended Ta(NMe\(_2\))\(_3\) exposure time no contribution by reaction products is expected due to saturation of the precursor adsorption. Normally, also in the case of extended plasma exposure times no new reaction products are expected. However, due to the plasma-surface interaction, processes that cause a change in material properties can release gas-phase products. The reaction products for the Ta(NMe\(_2\))\(_3\) and plasma step can therefore be determined by comparing the signals measured during the “normal ALD” cycle with the signals for the cycles where either the Ta(NMe\(_2\))\(_3\) exposure or the plasma exposure was omitted. Possible reaction products after extended plasma exposure can be determined by comparing the plasma step of the “plasma only” cycle with the plasma step of the cycle with zero plasma power (“precursor only”). To be able to get a good overview of all the data, four mass spectra were constructed using all \( m/z \) values. In Fig. 3 the signals used for the mass spectra are indicated for \( m/z = 15 \) with vertical bars. Two mass spectra represent the signal for the reaction products during the precursor step (signal 1) and during the plasma step (signal 2) in the ALD cycle, while the other two mass spectra represent the reference signals which are the situations after extended precursor exposure (signal 3) or after extended plasma exposure (signal 4).

It should be noted that surface-generated species measured in the QMS can originate from all surfaces. Since reactor wall surfaces are typically large compared to the substrate size, species from the wall can contribute to a large extent to the measured signal. To ensure that all measured reaction products originate from reactions at the same temperature, both the wall and substrate temperature should be set to the same temperature. In this study the temperatures were set to 150°C. Therefore, reactions are representative for ALD growth of TaN\(_x\) at 150°C, which is fairly similar to ALD growth of TaN\(_x\) at 225°C as shown by the data in Figs. 1 and 2.

IV. RESULTS AND DISCUSSIONS

A. Dissociation and formation of molecules in plasmas

H\(_2\) and N\(_2\) plasmas are often used in plasma-assisted ALD since they generate H and N radicals. However, plasma
radicals can recombine and therefore H\textsubscript{2}–N\textsubscript{2} plasmas can also produce species such as NH\textsubscript{3}. Although dissociation reactions involving two species can occur in the gas phase at the pressures typically employed during plasma ALD, three body reactions in the gas phase are more unlikely and most of the molecule formation will therefore occur at surfaces.\textsuperscript{26} The formation of NH\textsubscript{3} will occur according to the net conversion reaction:

$$\text{N}_2 + 3 \text{H}_2 \leftrightarrow 2 \text{NH}_3.$$ 

Obviously, species generated by the plasma can again be dissociated and NH\textsubscript{3} dissociation can therefore lead to NH and NH\textsubscript{2} radicals.

To study the molecule formation in H\textsubscript{2}, H\textsubscript{2}-N\textsubscript{2}, and NH\textsubscript{3} plasmas, three mass spectra were measured for each plasma: (1) the mass spectrum during plasma operation (“plasma on”); (2) the mass spectrum of the plasma gas mixture (“plasma off”); and (3) the mass spectrum with the reactor at base pressure. The mass spectrum with the reactor at base pressure shows the baseline due to residual species in the reactor chamber and mass spectrometer.

As expected, in pure H\textsubscript{2} plasmas no molecules other than H\textsubscript{2} are produced. Figure 4 shows the mass spectrum of a H\textsubscript{2}-N\textsubscript{2} (1:1) gas mixture for the “plasma on” and “plasma off” case. Also the base signal level is indicated. The base pressure shows the presence of H\textsubscript{2}O in the background through its cracking pattern at m/z = 16, 17, 18. Comparing the mass spectrum of the “plasma off” case with the base spectrum, an increase in the masses for H\textsubscript{2} (m/z = 2) and N\textsubscript{2} (m/z = 7, 14, 28) is observed as expected. A comparison between the “plasma on” and “plasma off” case shows an increase for m/z = 15, 16, and 17. These m/z values and the relative intensities at which they are observed correspond with the cracking pattern of NH\textsubscript{3}, indicating the formation of NH\textsubscript{3} in the H\textsubscript{2}-N\textsubscript{2} plasma. The accompanied decrease of H\textsubscript{2} and N\textsubscript{2} is only small (especially on the logarithmic scale). This implies that only a small fraction of these molecules are converted in NH\textsubscript{3}.

To investigate the amount of NH\textsubscript{3} formed in the H\textsubscript{2}-N\textsubscript{2} plasma, the NH\textsubscript{3} m/z signals were calibrated by introducing gas mixtures with known partial pressures of NH\textsubscript{3} in the reactor. The volume fraction of NH\textsubscript{3} was varied and the total pressure was kept constant at the same value used for the other measurements to minimize any “pressure effects.” With these known partial pressures for NH\textsubscript{3}, the relations between the measured ion currents at m/z = 16 and 17 and the partial pressure were determined. Using this calibration the volume fraction of NH\textsubscript{3} in the plasma was calculated.

Figure 5 shows the volume fraction of NH\textsubscript{3} in an H\textsubscript{2}-N\textsubscript{2} plasma as a function of the volume fraction of H\textsubscript{2} with respect to the total H\textsubscript{2}-N\textsubscript{2} gas mixture. All volume fractions are expressed as a percentage of the original gas mixture. The maximum in NH\textsubscript{3} production is obtained at around 60% H\textsubscript{2} resulting in about 4% of NH\textsubscript{3}. Our results relate well to a similar study by Van Helden et al. on expanding thermal plasma reactors (with different geometries and volumes), the maximum in NH\textsubscript{3} production was found to occur in the same range, i.e., 60% – 70% H\textsubscript{2}, and had the same magnitude, i.e., 2% – 10% NH\textsubscript{3} produced.\textsuperscript{27}

Instead of a H\textsubscript{2}-N\textsubscript{2} plasma also an NH\textsubscript{3} plasma can be employed during ALD. When employing such plasma, a large part of the NH\textsubscript{3} is dissociated into H\textsubscript{2} and N\textsubscript{2} which leads to an increase in the total number of particles. Corresponding to the net conversion reaction it was found that roughly 40% of the NH\textsubscript{3} is dissociated, giving 60% H\textsubscript{2} and 20% N\textsubscript{2}. Together with the remaining 60% NH\textsubscript{3} this reveals that the particle number density increases to 140% of the initial amount. This is in rough agreement with the observed pressure increase to 170% of the initial pressure. The difference is likely caused by heating of the gas.

As addressed earlier, both the use of H\textsubscript{2}-N\textsubscript{2} and NH\textsubscript{3} plasmas in ALD of TaN\textsubscript{x} basically result in the same material, Ta\textsubscript{3}N\textsubscript{5}. This is not surprising considering the fact that these plasmas have similar compositions, i.e., a combination of H\textsubscript{2}, N\textsubscript{2}, NH\textsubscript{3}, and N\textsubscript{2}H\textsubscript{y} radicals. Although the relative

![Fig 4. (Color online) Mass spectra measured for: a H\textsubscript{2}-N\textsubscript{2} plasma (1:1), a H\textsubscript{2}-N\textsubscript{2} gas mixture (1:1), and with the reactor at base pressure. The main parent molecules of the fragments are indicated.](image)

![Fig 5. (Color online) NH\textsubscript{3} production in a H\textsubscript{2}-N\textsubscript{2} plasma as a function of the volume fraction of H\textsubscript{2} with respect to the total H\textsubscript{2}-N\textsubscript{2} gas mixture. The NH\textsubscript{3} amounts were calculated from the m/z = 16 and 17 signal measured by the QMS. The percentages are given with respect to the original H\textsubscript{2}-N\textsubscript{2} gas mixture.](image)
concentrations of these species will be different in these plasmas, this apparently does not significantly affect the resulting material composition. When discussing the reaction mechanisms during the plasma step it will be shown that molecule formation can also occur using pure H2 plasmas when ALD reaction products are released from the surface.

### B. Cracking pattern of Ta(NMe2)5

The cracking pattern of the Ta(NMe2)5 precursor was determined to be able to distinguish signals due to the precursor from signals due to reaction products. An Ar flow was used to transport the Ta(NMe2)5 into the chamber in the same way as during the precursor exposure step in the ALD cycle. To determine the cracking pattern of Ta(NMe2)5, the spectrum for pure Ar measured at the same pressure was subtracted from the Ta(NMe2)5 + Ar spectrum. Fragments containing Ta were not detected, most probably due to the reduced sensitivity of the QMS in the high m/z range (m/z = 181 for Ta+). Figure 6 shows the Ta(NMe2)5 cracking pattern. The HNMe2 pattern from the NIST database is included for comparison. The two spectra show good overlap in the m/z values. Violet et al. have shown that during mass spectrometry of Ta(NMe2)5, fragments from the molecule HNMe2 are measured, which explains the agreement between the cracking pattern of Ta(NMe2)5 and HNMe2 in this mass range. They suggested that HNMe2 is formed in the mass spectrometer by NMe2 detachment from Ta(NMe2)5 and subsequent reaction of the detached NMe2 with hydrogen adsorbed on the mass spectrometer walls.

Assuming that also in the present case the Ta(NMe2)5 cracking pattern is dominated by HNMe2-related species, the observed intensity difference between the experimental Ta(NMe2)5 and the NIST HNMe2 spectrum as a function of m/z value can be explained by a difference in sensitivity and/or transmission for different m/z values, as often observed for different QMS systems in the literature.29 The signal at m/z = 17 and 18 can be attributed to fluctuations in the H2O levels present in the background during the measurements.

### C. Reaction products: precursor step

In Fig. 7, the spectra during Ta(NMe2)5 exposure for a “normal ALD” cycle (signal 1 in Fig. 3) and for a “precursor only” cycle (signal 3 in Fig. 3) are shown. The spectrum during a “normal ALD” cycle is the result of cracking of Ta(NMe2)5 and cracking of reaction products, and the spectrum during a “precursor only” cycle is the result of Ta(NMe2)5 cracking only. Interestingly, the m/z values at which a signal is observed are the same for the two spectra. This can be explained by a main contribution to the signals by Ta(NMe2)5 and HNMe2 for the “normal ALD” cycle since the cracking pattern for HNMe2 is very similar to the cracking pattern for Ta(NMe2)5 in this m/z range as shown in Fig. 6 (Ref. 28). The spectrum intensity level cannot be explained by precursor cracking only because the measured intensity for the “normal ALD” cycle is higher than for the Ta(NMe2)5 spectrum. Therefore, it can be concluded that HNMe2 is present as a reaction product. The resulting intensities of the signals during ALD are therefore a combination of Ta(NMe2)5 which is partially consumed and HNMe2 which is produced. The amount of HNMe2 produced per consumed Ta(NMe2)5 could be quite high since in the literature it has been reported that for thermal ALD most of the ligands are released during the precursor adsorption. For ALD with Ta(NBu)(NEt2)3 and N2H4 it was reported that three out of four ligands were removed during precursor adsorption.30 However, no quantitative conclusions on the number of ligands released can be drawn from the intensity difference. For example, the higher measured intensity level in this m/z range could be simply due to a relatively higher signal per measured HNMe2 molecule than the signal per measured Ta(NMe2)5 molecule. For instance, ionization of...
Ta(NMe2)5 could in principle result predominantly in ionized fragments containing Ta which would have higher masses and would cause a relative low intensity for Ta(NMe2)5 in the measured m/z range.

D. Reaction products: plasma step

Figure 8 shows the mass spectrum representing the reaction products during the beginning of the plasma step (signal 2 in Fig. 3). The spectrum can be accounted for by a combination of cracking patterns representing different molecules. The used cracking patterns represent the following molecules: HNMe2, CH4, C2H2, and HCN. Cracking patterns that span a wide m/z range such as the cracking pattern for HNMe2 show more difference between different QMS setups and therefore it is better to use a cracking pattern obtained using the same QMS setup than to use the one from the NIST database. To this end, the measured Ta(NMe2)5 cracking pattern (signal 3 in Fig. 3) can be used as a cracking pattern for HNMe2 as discussed in the previous section. The cracking patterns for CH4, C2H2, and HCN were obtained from the NIST database.25 The cracking patterns were scaled such that their linear combination roughly corresponds with the measured spectrum. Due to the high background of H2O in the QMS only large signals can be detected at m/z = 17 and 18. Therefore, small amounts of H2O and/or NH3 as reaction product could be present, despite the fact that no clear difference in signal was observed at these m/z values. The respective levels of C2H2+ at m/z = 26 and HCN+ at m/z = 27 were about equal in the linear combination used. This implies that the concentrations of C2H2 and HCN are roughly similar, since the ionization cross-sections of C2H2+ to C2H2+ and HCN to HCN+, are expected to be similar as in both cases it concerns ionization of the parent molecule without dissociation.

Figure 9 shows the spectrum of the reaction products during the beginning of the plasma step, and the spectrum after extended plasma exposure. After extended plasma exposure a few signals which were also present at the beginning of the plasma are still observed. These are the signals which can be attributed to CH4 and C2H2. Apparently, these products are present in the plasma for a longer time (roughly equivalent to 30 s plasma exposure). Although the signal for C2H2 at m/z values 24, 25, and 26 is low, the signal can be clearly distinguished due to the low background signals at these m/z values.

E. Reaction products: time dependence

Apparently, besides a decrease in reaction product concentration during the plasma exposure due to the reaching of saturation also the composition of the reaction products changes over time. To obtain more insight into this time dependence a few specific masses were followed during an extended plasma exposure time. Furthermore, optical emission spectroscopy (OES) was used to measure emission from excited species in the plasma. Optical emission spectroscopy measurements were carried out by measuring the plasma emission just above the substrate holder by using an Ocean Optics USB2000 spectrometer.31 Besides emission from excited H and H2 species, the emission from CN radicals was observed.10,31 The excited CN radical can for example be produced from HCN by the following reaction:

\[ \text{HCN} + e^- \rightarrow \text{CN} + \text{H} + e^- . \]

Note, that although no emission from CH4 and NH3 radicals was observed, these radicals were expected to be present as well. CH4 and NH3 radicals might simply not be excited to energy levels resulting in optical emission. Figure 10 shows the CN emission at 388 nm and the QMS signal at m/z = 15, 27, and 45 for three subsequent plasma exposures. For the
first plasma exposure, power was applied for 5 seconds followed by a 10 s interruption. This was followed by a second plasma exposure by applying power for 10 s, again a 10 s interruption and finally an exposure by applying power for 25 seconds. In total the plasma exposure was therefore 40 s. All lines have a higher intensity at the start of the first plasma exposure after the Ta(NMe2)5 exposure. This is not a plasma start-up effect since this effect is not present for the second and third plasma exposure step. As was shown in the previous section, during this initial period the reaction products HNMe2, CH4, C2H2, and HCN were present in the gas phase. The intensity increase in OES emission shows that also excited CN was present. The OES emission at 388 nm was measured with OES, and the m/z values 15, 27, and 45 were monitored by QMS. The periods with the plasma power applied are indicated in gray.

Similar to the two timescales present in the soft saturation behavior of the GPC, there seem to be two timescales present in the decay of the reaction products. Fitting an exponential decay to the OES signal reveals that it has a similar timescale as the fast process in Fig. 2 (time constant is 0.8 s compared to 0.7 s). Although the signal for m/z = 15 is quite noisy, the signal can be fitted with a single exponential decay function to obtain a time constant for the process with the long timescale. Although the accuracy of the data does not allow a precise comparison, the resulting time constant (~16 s) and the long time constant in Fig. 2 (8 s) are both in the order of 10 s. Note that the data in Fig. 2 refer to a “local” measurement (ellipsometry on the substrate) whereas the data in Fig. 10 refer to a “global” measurement (mass spectrometry probing the species present in the whole reactor). Nonetheless, the similarity between the time constants might indicate a relation between the processes which are responsible.

V. DISCUSSION ON THE REACTION MECHANISMS

Reaction mechanisms taking place during plasma-assisted ALD of TaNₓ using Ta(NMe2)5 and H2 plasma can be postulated by considering the measured reaction products and by considering the dependence of the material properties on plasma composition and exposure. The main observations by QMS are:

1. During the Ta(NMe2)5 exposure step, the reaction product HNMe2 is detected.
2. During the plasma exposure step, immediately after striking the plasma, the molecules HNMe2, CH4, C2H2, and HCN are measured. After an extended plasma exposure time the reaction products CH4 and C2H2 are still observed in the plasma.

These observations can be related to the dependence of the TaNₓ material properties on plasma exposure time shown in Figs. 1 and 2.

A. Ta(NMe2)5 exposure

The incoming precursor adsorbs by reacting with H at the surface. The reaction between an x number of surface species containing H and precursor ligands results in the formation of an x number of HNMe2 molecules:

\[
x \text{surf-H} \rightarrow \text{surf-Ta(NMe2)}_x \rightarrow x \text{HNMe2}
\]

The reactive hydrogen at the surface is most likely present in the form of –NHₓ and –TaH. Also the presence of –OH from O impurities cannot be excluded. Hydrogen in the form of –CHₓ is expected to be unreactive towards the precursor. Whether the ligands are removed directly during adsorption or by hydride elimination reactions after adsorption, cannot be concluded from the present data.

To estimate how many ligands are removed per precursor molecule (x), the maximum amount of ligands on the surface due to steric hindrance is first estimated. To this end the GPC for the Ta2O5 process using Ta(NMe2)5 and O2 plasma is considered. For this process, the GPC does not change in the temperature window, which suggests that kinetic processes are not the limiting factor. Furthermore, the constant GPC suggests that additional hydroxylation or dehydroxylation processes do not play a significant role since those would also be temperature-dependent processes. Therefore, the assumption can be made that steric hindrance determines the GPC in this case. Another assumption is that during the reactant step for each removed ligand one new surface group is created on which a ligand can adsorb in the next half-cycle. Together with the fact that the precursor is homoleptic, this assumption leads to the conclusion that the average amount of ligands on the surface after precursor adsorption is 2.5 per precursor molecule (i.e., half of the ligands). Assuming that the precursor adsorption per cycle is...
The number of precursor molecules adsorbed for the TaN$_x$ process with 30 s plasma is 2.1 nm$^{-2}$ as indicated in Fig. 1. If 2.5 ligands would remain per adsorbed precursor, the NMe$_2$ coverage would be higher than the maximum coverage due to steric hindrance reasons as just calculated (5.3 versus 4.5 nm$^{-2}$). This suggests that more than 2.5 ligands have to be removed during precursor adsorption ($x > 2.5$). This implies, therefore, that to remove these ligands additional surface groups have to be created during the 30 s plasma exposure besides the ones created for each removed ligand. Similar conclusions have been drawn for Al$_2$O$_3$ at low temperature, where additional OH groups are created resulting in removal of more than 1.5 ligands (i.e., half of the total number of ligands of AlMe$_3$) during AlMe$_3$ adsorption. Burton et al. also suggested that more than half of the ligands are removed for thermal ALD of TaN using Ta(NBu)(NMe$_2$)$_3$ and N$_2$H$_4$. They also suggested creation of additional surface groups for precursor adsorption during the reactant step.

### B. H$_2$ plasma exposure

Unlike the reaction products during the precursor step, not all detected molecules in the plasma have to be directly related to ALD reactions. Molecules created through surface reactions, which enter the plasma, can be dissociated by electron impact dissociation, leading to the formation of reactive fragments of the molecules (i.e., radicals) and the generation of new molecules. This dissociation of reaction products has also been observed in plasma-assisted ALD using O$_2$ plasmas where CO$_2$ can be dissociated by the plasma into CO (Ref. 15). Due to the low pressure and the associated unlikelihood of three-body reactions in the gas phase, recombination of the plasma radicals into new molecules will mostly occur at surfaces. HNMe$_2$ is expected to be a direct product of ALD reactions, but the other products (CH$_4$, C$_2$H$_2$, and HCN) can also be formed by the dissociation of HNMe$_2$ in the plasma and subsequent surface-mediated molecule formation from the fragments.

Ta is in the 5$^+$ oxidation state in the precursor and has to be reduced to the 3$^+$ oxidation state to form conductive TaN. H radicals can reduce the Ta atom, and react with the NMe$_2$ surface groups to form HNMe$_2$:

$$\text{H} + \text{Ta}^{5+} \rightarrow \text{H}^+ + \text{Ta}^{4+},$$

$$\text{H}^+ + \text{surf} - \text{NMe}_2 \rightarrow \text{HNMe}_2.$$

For these reactions also the oxidation state has to be taken into account, since the oxidation state changes during the plasma step. If the growth process only consists of the removal of complete ligands by H radicals, the resulting material from the plasma-assisted ALD process should be pure Ta metal. However, TaN$_x$ is deposited with N being one of the major constituents of the film. Removal of the Me groups by CH$_4$ formation has been proposed as a reaction leading to N in the film:

$$4\text{H} + \text{surf} - \text{NMe}_2^- \rightarrow \text{surf} - \text{NH}_2 + 2\text{CH}_4.$$
paper the interpretations do not conflict with each other. To
determine the exact reaction pathways and confirm the sug-
gested mechanisms, sensitive in situ surface diagnostics such
as infrared spectroscopy would be needed.

To summarize, in the plasma step the reaction products
can be dissociated in the plasma and the dissociated products
can redeposit and influence the ALD growth process.

Because these plasma reactions and redeposition processes
differ for different species, the composition of the reaction
products can change in time for the plasma step. This knowl-
edge can be used to optimize the ALD process. For instance,
by decreasing the residence time of the gas in the reactor the
interaction of the reaction products with the plasma can be
reduced. Another possibility would be on-off modulation of
the plasma on the time scale of the residence time.

VI. CONCLUSIONS

The reaction mechanisms of plasma-assisted atomic layer
deposition (ALD) of TaN using Ta(NMe2)5 precursor were
studied using quadrupole mass spectrometry (QMS). Molecu-
lar formation in plasmas was addressed and exemplified by
NMe2 ligands at the surface. These products interact with the
cules HNMe2, CH4, C2H2, and HCN are measured, while af-

amount of precursor adsorbed.

This change in the composition
in the plasma. In general, it can therefore be concluded that
the material composition and properties are determined to a
large extent by the plasma-surface interaction and by the reac-
tions of products with the plasma.

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1International Technology Roadmap for Semiconductors, 2009 ed.,
www.itrs.net.

1K. S. Chang, M. L. Green, I. Levin, J. R. Hattrick-Simpers, C. Jaye, D. A.
Fischer, I. Takeuchi, and S. De Gendt, Appl. Phys. Lett. 96, 192114
(2010).
Lett. 4, C17 (2001).
6J. S. Park, H. S. Park, and S. W. Kang, J. Electrochem. Soc. 149, C28
(2002).
7H. Kim, C. Detavenier, O. van der Straten, S. M. Rossnagel, A. J. Kellock,
8E. Langereis, H. C. M. Knoops, A. J. M. Mackus, F. Roozeboom, C. M.
van de Sanden, and W. M. M. Kessels, J. Appl. Phys. 102, 083517
(2007).
9H. C. M. Knoops, L. Baggetto, E. Langereis, C. M. C. van de Sanden,
J. H. Klootwijk, F. Roozeboom, R. A. H. Niessen, P. H. L. Notten, and W.
15S. B. Heil, F. Roozeboom, C. M. M. van de Sanden, and W. M. M.
17J. H. van Helden, R. A. B. Zijlmans, D. C. Schram, and R. Engeln,
19P. Viole, I. Nuta, C. Chatillon, and E. Blanquet, Rapid Commun. Mass
Spectrom. 24, 2949 (2010).
21B. B. Burton, A. R. Lavoie, and S. M. George, J. Electrochem. Soc. 155,
D508 (2008).
22A. J. M. Mackus, S. B. S. Heil, E. Langereis, H. C. M. Knoops, C. M. C.
van de Sanden, and W. M. M. Kessels, J. Vac. Sci. Technol. A 28, 77
(2010).
24E. Langereis, J. Keijmel, C. M. C. van de Sanden, and W. M. M.
25D. P. Liu, I. T. Martin, J. Zhou, and E. R. Fisher, Pure Appl. Chem. 78,
27J. Perrin, M. Shiratani, P. Kae-Nune, H. Videlot, J. Jolly, and J. Guillon,
29M. F. A. M. van Hest, A. de Graaf, C. M. C. van de Sanden, and D. C.
30G. Lombardi, K. Hassouni, G. D. Stancu, L. Mechold, J. Ropcke, and A.
(2010).
32H. C. M. Kim, K. M. Song, and S. W. Rhee, J. Electrochem. Soc. 157,
H652 (2010).