Plasma-assisted atomic layer deposition of Ta₂O₅ from alkylamide precursor and remote O₂ plasma

Citation for published version (APA):

Heil, S. B. S., Roozeboom, F., Sanden, van de, M. C. M., & Kessels, W. M. M. (2008). Plasma-assisted atomic layer deposition of Ta₂O₅ from alkylamide precursor and remote O₂ plasma. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, 26(3), 472-480. <https://doi.org/10.1116/1.2905250>

DOI:

[10.1116/1.2905250](https://doi.org/10.1116/1.2905250)

Document status and date:

Published: 01/01/2008

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Plasma-assisted atomic layer deposition of Ta₂O₅ from alkylamide precursor and remote O₂ plasma

S. B. S. Heil

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

F. Roozeboom

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands and NXP-TSMC Research Center, High Tech Campus 4, 5656 AE Eindhoven, The Netherlands

M. C. M. van de Sanden and W. M. M. Kessels^{a)}

Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 18 December 2007; accepted 11 March 2008; published 21 April 2008)

Tantalum oxide (Ta₂O₅) films were synthesized by plasma-assisted atomic layer deposition from pentakis(dimethylamino)tantalum (Ta[N(CH₃)₂]₅), precursor and remote O₂ plasma as oxidation source. Film growth was monitored *in situ* by spectroscopic ellipsometry, and film properties were investigated for deposition temperatures between 100 and 225 °C. Saturated precursor dosing conditions and plasma exposure times were identified and growth rates ranging from 0.8 Å/cycle at 225 °C to 0.87 Å/cycle at 100 °C were obtained. The deposited films were found to be stoichiometric (Ta:O=2:5). Moreover, no N incorporation was detected, and the C content was below the detection limit of the Rutherford backscattering measurement (<2 at. %) for all films studied. The mass density of the films, ranging from 7.8 g cm⁻³ at 100 °C to 8.1 g cm⁻³ at 225 °C, was found to be close to the bulk Ta₂O₅ density. The deviation could partly be accounted for by the amount of H detected with elastic recoil detection analysis, varying from 2 at. % at 225 °C to 4.6 at. % at 100 °C. X-ray diffraction revealed that all films were amorphous, independent of deposition temperature. The reaction mechanisms, in particular, during the plasma step, were investigated by using quadrupole mass spectrometry and optical emission spectroscopy. During the plasma step, combustion products such as CO, CO₂, and H₂O were detected. This indicates that combustionlike processes occur, in which the alkylamide N(CH₃)₂ ligands are oxidized by the O radicals generated in the plasma. Additionally, the presence of excited C≡N* molecules in the plasma was observed in the plasma emission. © 2008 American Vacuum Society. [DOI: 10.1116/1.2905250]

I. INTRODUCTION

Tantalum oxide (Ta₂O₅) is an extensively studied material because of its interesting optical, chemical, and electrical properties. With a relatively high refractive index ($n \sim 2.2$) and a wide optical band gap (~ 4.35 eV), Ta₂O₅ is of interest for optical applications such as reflective coatings on mirrors and optical waveguides. Ta₂O₅ is also a very attractive material for use as a corrosion resistant coating due to its resistance to etching in various solutions.¹ Due to its high dielectric constant ($k \sim 25$, for amorphous films), low leakage current ($<10^{-6}$ A/cm² at ≤ 3 MV/cm), and voltage linearity, Ta₂O₅ has been investigated for electrical applications such as gate dielectric in metal-oxide-semiconductor field effect transistors,^{2,3} storage dielectric in dynamic random access memories (DRAMs), and insulating layer in thin film electroluminescent devices.⁴ Ta₂O₅ has proven to be especially suited as a dielectric in stacked metal-insulator-metal

(MIM) capacitor structures that can be found in applications integrated in the back-end-of-line (BEOL), such as embedded DRAM and rf decoupling capacitors in radio frequency integrated circuits.⁴⁻⁶

A common method for the deposition of Ta₂O₅ is metal-organic chemical vapor deposition (MOCVD) by using Ta(OC₂H₅)₅ [(pentaethoxide)tantalum (PET)] precursor and O₂ gas at temperatures around 400 °C.^{4,7} The deposited films, however, relatively contain large amounts of C and H impurities and need to be annealed at temperatures of >600 °C to obtain the appropriate film properties.⁷ For low-thermal budget applications, such as MIM capacitors embedded in the BEOL and corrosion resistant coatings on temperature sensitive materials, there is a desire to minimize the heat load during Ta₂O₅ processing, making the current annealing step less compatible. Furthermore, the importance of the deposition of Ta₂O₅ on demanding three-dimensional (3D) structures has increased. This is, for example, due to the miniaturization of devices which requires higher capacitance densities and, consequently, the deposition of MIM capacitor stacks in trenches and pores.⁸ Another example is the surface

^{a)}Author to whom correspondence should be addressed; electronic mail: w.m.m.kessels@tue.nl

finish of complex 3D objects by corrosion resistant Ta₂O₅. With MOCVD, it will become increasingly more challenging to grow thin, dense, and conformal Ta₂O₅ films at a low temperature on these structures once the aspect ratios employed increase. Therefore, alternative process techniques for the deposition of Ta₂O₅ are actively pursued.

Atomic layer deposition (ALD) has gained increasing interest for the growth of dielectric materials and is considered to be an attractive alternative technique to MOCVD for the growth of thin Ta₂O₅ films.⁴ In ALD, film growth is established through self-limiting surface reactions between alternately supplied gaseous precursors.⁹ The cyclic nature of ALD allows for excellent thickness control by the deposition of a single (sub)monolayer of film per cycle. Furthermore, the self-limiting surface reactions facilitate the growth of conformal and uniform films over large substrate areas with a challenging 3D topography. The possibility to deposit at relatively low temperatures is another major advantage of ALD.

By using H₂O as oxidant source, Ta₂O₅ has been deposited by the thermal ALD process from various Ta sources such as PET,^{10,11} and the metal halides TaCl₅ (tantalumpentachloride),^{12–14} TaF₅ (tantalumpentafluoride),¹⁵ and TaI₅ (tantalumpentaiodide).¹⁶ Deposition temperatures typically ranged from 200 to 400 °C. Alternatively, the growth of Ta₂O₅ from alternating exposures of PET and TaCl₅, i.e., without the use of an additional oxidant, has been demonstrated.^{17,18} By using a relatively high deposition temperature (>600 °C), it was also shown that films can be grown by using alternate exposures of TaI₅ and O₂ gas.¹⁹ Furthermore, the use of an O₂ plasma for oxidation (the so-called plasma-enhanced or plasma-assisted ALD) in combination with the PET precursor has been reported for both direct plasma^{20,21} and radical enhanced reactor configurations.²²

Recently, the use of the alkylamide-based precursor Ta[N(CH₃)₂]₅ [pentakis(dimethylamino)tantalum (PDMAT)] has attracted interest because of its high reactivity with surfaces during ALD, especially at low temperatures (<250 °C).²³ Moreover, it has a relatively high vapor pressure, and the absence of Cl- and O-containing ligands results in noncorrosive reaction products which are more compatible with processing of metals and organic materials and are considered more hardware friendly. The film growth of Ta₂O₅ by plasma-assisted ALD using PDMAT and a remote O₂ plasma has recently been demonstrated by Maeng *et al.*^{24,25} A constant, relatively high growth rate of 1.2 Å/cycle was reported for deposition temperatures ranging from 150 to 250 °C. The material properties obtained with plasma-assisted ALD were found to be better compared to thermal ALD grown Ta₂O₅ from PDMAT by using H₂O as oxidant.

In this article, we report on the deposition of Ta₂O₅ by plasma-assisted ALD by using PDMAT as Ta precursor and O₂ plasma as oxidant source. We have extended the analysis of the compositional, structural, and optical properties of Ta₂O₅ films to lower deposition temperatures, i.e., the

TABLE I. Typical operating settings during plasma-assisted ALD of Ta₂O₅. The ranges in which the settings were varied during the experiments are given between parentheses.

Parameter	Standard setting	Range varied
Ta[N(CH ₃) ₂] ₅ dose time	3.0 s	(0.5–8 s)
Ar partial pressure	30 mTorr	
Plasma exposure time	2.0 s	(0.5–5 s)
O ₂ partial pressure	7.5 mTorr	
Plasma power	100 W	
Deposition temperature	225 °C	(100–225 °C)
Wall temperature	85 °C	
Bubbler temperature	65 °C	

100–225 °C range. A major practical advantage of using a plasma as oxidant source is the possibility of keeping the cycle times short at low temperatures, since the reactivity is quickly removed when the plasma is switched off. In thermal ALD, the use of H₂O generally creates the necessity of applying a long purge period after the H₂O dose to maintain pure ALD film growth, i.e., without any chemical vapor deposition effect.²⁶ In addition, experimental insight is presented into the reaction mechanism of plasma-assisted ALD of Ta₂O₅. While Ta₂O₅ material properties and the performance of devices employing this dielectric are extensively discussed in the literature, such experimental insight into the reaction mechanisms, in particular, during the O₂ plasma exposure, is lacking. Earlier, we have demonstrated that combustionlike reactions occur during the plasma-assisted ALD of Al₂O₃ from the alkyl metal-organic precursor Al(CH₃)₃ (trimethylaluminum) and O₂ plasma.^{27,28} The production of CO, CO₂, and H₂O was detected by mass spectrometry and optical emission spectroscopy (OES). Here, we present a similar experimental investigation during the O₂ plasma exposure of Ta₂O₅ deposition. Unlike the situation in Al₂O₃ deposition, where prior to the plasma exposure, the surface is covered with –CH₃ groups resulting from the chemisorption of Al(CH₃)₃; in this case, –N(CH₃)₂ surface groups are expected to cover the surface due to the binding of the Ta[N(CH₃)₂]₅ precursor to the surface. In the literature, it has been speculated that during the plasma exposure the formation of reaction products occurs, such as CO₂ and H₂O and, specifically for the alkylamide metal-organic precursors, also NO.²⁴ These products have been experimentally investigated in this work.

II. EXPERIMENTAL

The experiments were carried out in a homebuilt remote plasma ALD reactor described in detail elsewhere.^{28,29} Briefly, it consists of a deposition chamber to which a precursor delivery system and remote inductively coupled plasma (ICP) source are attached. The chamber is pumped by a turbomolecular pump and has a base pressure of ~10^{–6} Torr. The typical processing conditions and experimental settings are summarized in Table I. The wall temperature was controlled at 85 °C. The solid metal-organic precur-

sor Ta[N(CH₃)₂]₅ (PDMAT, Sigma-Aldrich, purity of >99.99%), stored in a stainless steel bubbler, was heated up to a temperature of 65 °C to reach an adequate vapor pressure. To prevent condensation, the PDMAT vapor was delivered to the chamber through heated supply lines (>70 °C) by using a small Ar carrier gas flow controlled by a leak valve upstream. The Ar flow results in an operating pressure of ~30 mTorr in the reactor and is also used to purge the chamber after the precursor dosing by using a divert line. In addition, the chamber was briefly pumped down (<10⁻⁴ Torr) after purging with Ar to remove any remaining gaseous precursor and reaction by-products before switching on the O₂ flow through the plasma source. The ALD reaction was completed by exposure to an O₂ plasma generated in the ICP source (100 W), operated at a pressure of 7.5 mTorr.

The films were deposited on 4 × 4 cm² native oxide covered monocrystalline Si (100) substrates (*p*-type, 10–30 Ω cm) placed on a heated substrate holder (100–225 °C). The substrates were exposed to an O₂ plasma for 5 min prior to the deposition. During this plasma oxidation step of the substrate, the SiO_x film growth was monitored *in situ* by spectroscopic ellipsometry (SE) by using a J.A. Woollam, Inc., M2000U visible and infrared extended ellipsometer (0.75–5.0 eV), mounted under a 68° angle relative to the substrate normal. During Ta₂O₅ processing, SE thickness measurements of the grown Ta₂O₅ film were taken after completion of a certain number of ALD cycles. To investigate the optical properties of the deposited Ta₂O₅ films near its band gap, an *ex situ* characterization was also performed by using a J.A. Woollam, Inc., M2000D visible and UV extended ellipsometer (1.2–6.5 eV), under an angle of 75°. A Tauc–Lorentz model was applied to fit the data by using the Woollam WVASE software.^{30,31}

The film composition was determined by Rutherford backscattering spectrometry (RBS), using a 2 MeV ⁴He⁺ beam under an 80° angle of incidence for determining the Ta, O, N, and C areal densities of the films. By using the same beam settings, elastic recoil detection (ERD) measurements were also performed to determine the H areal density. The mass density was calculated from the areal density by RBS, by using the thickness data obtained by SE. The microstructure of the deposited films was studied by using a PANalytical/Philips X'Pert Pro MPD diffractometer, equipped with a Cu Kα x-ray source and an X'Celerator detector.

A differentially pumped quadrupole mass spectrometer (QMS) (Pfeiffer QME 200, mass-to-charge ratio *m/z* = 0–200) was fitted to the side of the reactor. The gas sampling took place through a 150 μm orifice, keeping the pressure in the mass spectrometer within the working range (<10⁻⁵ Torr) for the secondary electron multiplier (SEM) to operate. The incoming molecules are ionized in the QMS through electron impact ionization by ~70 eV electrons. For most species, this leads to dissociative ionization of the incoming molecules. Therefore, the identification of the original incoming molecules was performed on the basis of their so-called cracking patterns. To achieve sufficient time reso-

lution, the time resolved measurements were carried out by monitoring only four mass-to-charge ratios (*m/z*) per deposition of typically ten ALD cycles. This experiment was repeated until data were obtained for all *m/z* ratios in the range of *m/z* = 15–45. In each deposition, the signal at *m/z* = 40 (Ar⁺) was included to serve as a reference while the other three *m/z* varied. On the basis of the Ar⁺ signal, the different measurements were synchronized afterwards. This procedure allowed for constructing a time resolved mass scan of all masses (*m/z* = 15–45), with an adequate time resolution.

OES was carried out by measuring the plasma emission just above the substrate holder by using an Ocean Optics USB2000 spectrometer, having a wavelength detection range of 250–870 nm and a resolution of approximately 1 nm. The emission by the plasma was coupled into the spectrometer by placing an optical fiber with a small aperture (~100 μm diameter) close to one of the glass windows (UV cutoff wavelength of ~350 nm) on the deposition chamber. Time dependent measurements were carried out by repetitively acquiring full spectra (350–870 nm) with an integration time of 100 ms. The spectral data of each spectrum were stored in separate files. For data reduction, the option in the software for selecting a single wavelength in the spectrum and acquiring the signal height as a function of time was used to monitor excited plasma species as a function of time during the plasma exposure step.

III. FILM GROWTH AND MATERIAL PROPERTIES

For optimizing the process, the precursor dose time and plasma exposure time were varied at a deposition temperature of 225 °C. Ta₂O₅ film growth was monitored by *in situ* SE, directly yielding the growth rate from the film thickness plotted versus the number of cycles during a single deposition run.³² Under all deposition conditions, the film growth was observed to linearly proceed with the number of cycles. In Fig. 1(a), the growth rate can be seen to vary with the PDMAT dose time, reaching a maximum of 0.81 ± 0.02 Å/cycle for dose times of 3 s or more. A similar trend can be observed when the plasma exposure time is varied while keeping the PDMAT dose at 3 s. Saturated film growth was found to occur when the plasma is applied longer than 1 s [Fig. 1(b)]. The presence of a saturated growth regime also proved that the combination of Ar purge, the intermittent pump down of the reactor, and the switching of the gases (Ar to O₂) is adequate to avoid the occurrence of residual CVD processes.

The saturated growth rate of ~0.8 Å/cycle obtained in our investigation considerably differs from the ~1.2 Å/cycle reported earlier by Maeng *et al.* for the use of PDMAT and a remote O₂ plasma in the temperature range of 150–250 °C.²⁴ The exact reason for this deviation remains unclear; the main difference is that they used a higher plasma power (300–500 W) compared to the 100 W plasma power used in the current experiments. Variations in growth rates are, however, not uncommon in the ALD processing of metal oxides and tend to depend also on the oxidant source, the Ta source, and the reactor configuration used in the experi-

FIG. 1. Ta₂O₅ growth rate as a function of (a) the precursor dosing time for a 5 s plasma exposure and (b) the plasma exposure time for a 3 s precursor dose.

ments. For instance, a more moderate growth rate of ~ 1.0 Å/cycle has been reported for plasma-assisted ALD of Ta₂O₅ involving the use of the PET precursor and a direct O₂ plasma.³³ At the same time, a considerable higher growth rate, even up to 2.0 Å/cycle, has been reported for radical enhanced ALD using PET and an O radical source by Niskanen *et al.*²²

The Ta₂O₅ film properties are presented in Table II for depositions at different temperatures under saturated growth

conditions, i.e., 3 s precursor dosing and 2 s plasma exposure. Stoichiometric films (Ta:O=2:5) were obtained at all deposition temperatures, as revealed by RBS. Possible C and N impurities are below the RBS detection limits of 2 and 0.5 at. %, respectively. ERD revealed a H content ranging from 4.6 at. % at 100 °C to 2 at. % at 225 °C. Although not directly measured here, it is conceivable that the H is incorporated in the form of –OH, which is typically reported for oxide films grown by ALD and CVD processes at low temperatures. The mass density of the films is calculated from the RBS elemental composition and the SE thickness and is found to increase with the deposition temperature from 7.8 g cm⁻³ at 100 °C to 8.1 g cm⁻³ at 225 °C. The latter value is close to the reported Ta₂O₅ bulk value of 8.24 g cm⁻³.³⁴ The growth rate shows a decrease from 0.87 ± 0.02 Å/cycle at 100 °C to 0.81 ± 0.02 Å/cycle at 225 °C. While the growth rate decreases with temperature, the number of Ta atoms deposited per cycle roughly remains the same ($\sim 0.18 \times 10^{15}$ at. cm⁻²/cycle) at all temperatures (cf. Table II). The variation of growth rate with temperature can, therefore, be largely explained by the difference in mass density of the deposited films. This is remarkably different from other plasma-assisted ALD processes, such as Al₂O₃, where the number of deposited Al atoms per cycle decreases with increasing deposition temperature.³⁵

In Fig. 2, x-ray diffraction (XRD) spectra are shown for the Ta₂O₅ films reported in Table II. Besides the large *c*-Si substrate peak at $2\theta=69^\circ$ for Si (400), a broad feature between 20° and 40° can be observed for all samples. The absence of sharp peaks in the XRD spectrum indicates that the Ta₂O₅ films are primarily amorphous when deposited in the temperature range of 100–225 °C. This kind of microstructure is typically found in XRD spectra of ALD Ta₂O₅ films in this temperature range for both metal-organic and metal-halide based Ta precursors used in combination with H₂O.^{14,36} For deposition temperatures above 300 °C, the hexagonal δ -Ta₂O₅ phase is typically found in films deposited from metal-halide Ta precursors (i.e., TaCl₅, TaF₅, and TaI₅) in combination with H₂O.^{14–16} At increased deposition temperatures or upon annealing, the Ta₂O₅ films tend to be-

TABLE II. Film properties as determined by Rutherford backscattering spectrometry, elastic recoil detection, and spectroscopic ellipsometry for Ta₂O₅ films grown by using 700 ALD cycles at different deposition temperatures. The optical band gap E_g has been determined from the spectroscopic ellipsometry data by using the Tauc formalism.

Properties	Deposition temperature		
	100 °C	150 °C	225 °C
Thickness (Å)	607 ± 2	559 ± 2	568 ± 2
Growth rate (Å/cycle)	0.87 ± 0.02	0.80 ± 0.02	0.81 ± 0.02
Ta (10 ¹⁵ at. cm ⁻²)/cycle	0.185 ± 0.007	0.173 ± 0.007	0.180 ± 0.007
O (10 ¹⁵ at. cm ⁻²)/cycle	0.462 ± 0.007	0.434 ± 0.007	0.449 ± 0.007
H (10 ¹⁵ at. cm ⁻²)/cycle	0.031 ± 0.007	Not measured	0.014 ± 0.007
Ta:O	2:5 ± 0.1	2:5 ± 0.1	2:5 ± 0.1
H (at. %)	4.6 ± 1	Not measured	2.0 ± 1
Mass density (g cm ⁻³)	7.8 ± 0.05	8.0 ± 0.05	8.1 ± 0.05
E_g (eV)	4.31 ± 0.05	4.29 ± 0.05	4.26 ± 0.05
n (at 2.0 eV)	2.20 ± 0.03	2.20 ± 0.03	2.23 ± 0.03

FIG. 2. XRD spectra of plasma-assisted ALD Ta₂O₅ at different deposition temperatures. The data have been normalized and vertically offset for clarity.

come more crystalline and changing toward the orthorhombic β -Ta₂O₅ phase with the undesirable effect of causing a higher leakage current.³⁶ At all deposition temperatures and even after annealing, the films are reported to contain a large fraction of amorphous material.¹⁶

The refractive index (n) and extinction coefficient (k) of the deposited Ta₂O₅ were determined from the fit of the ellipsometric data of the films described in Table II. In Fig. 3, the n and k of the Ta₂O₅ film deposited by plasma-assisted ALD at 225 °C are shown over a range of 0.75–6.5 eV (1700–193 nm). The data have been generated by using the Tauc–Lorentz parametrization of the combined data as obtained by the infrared (down to 0.75 eV) and UV (up to 6.5 eV) extended ellipsometers. The Tauc–Lorentz fit parameters at 225 °C were found to be $A=330.2$, $E_n=4.950$ eV, $C=1.769$ eV, $E_g=4.216$ eV, and $E_{inf}=2.312$ eV, and these values were found to be very similar for all films. At a photon energy of 2 eV (~ 633 nm), the refractive index is found to range from $n=2.20$ at 100 and 150 °C to $n=2.23$ at 225 °C. The refractive index is close to the highest reported values ($n \approx 1.9$ – 2.2) for Ta₂O₅ ALD using various Ta precursors and H₂O as oxidant in the same temperature range.^{10,14,16,17,36} The high refractive index can be correlated

FIG. 3. Refractive index and extinction coefficient for Ta₂O₅ deposited at 225 °C.

FIG. 4. QMS signals of key fragments ($m/z=18, 28, 32, 44$, and 45) during the two cycles of the Ta₂O₅ plasma-assisted ALD process. The periods during which the Ar flow and O₂ flow are active, have been indicated, as well as the precursor dosing time and the plasma exposure time.

to the relatively high density of the Ta₂O₅ material obtained in this work. From the SE data, the Tauc band gap was determined.³⁷ Tauc band gap values ranged from $E_g=4.31$ eV at 100 °C to $E_g=4.24$ eV at 225 °C. These values are close to typical values reported for thermal ALD Ta₂O₅ films.^{14,31}

IV. REACTION MECHANISM STUDIES

To investigate the reaction mechanisms governing Ta₂O₅ film growth by plasma-assisted ALD, QMS and OES were employed. In particular, the reactions occurring during the O₂ plasma exposure are of interest since a clear difference with the thermal ALD process exists in the form of the chemical reactivity of the oxidant source. The deposition temperature during the QMS and OES experiments is set by the wall temperature (85 °C) of the deposition chamber. Saturated dosing conditions were used (3 s PDMAT dose and 5 s plasma exposure), unless otherwise stated.

QMS data of the mass-to-charge (m/z) ratios in the range of $m/z=15$ – 45 were obtained by using the experimental procedure described in Sec. II. In Fig. 4(a), time dependent scan over the two ALD cycles is shown. The periods during which the Ar flow and the O₂ flow active have been indicated, as well as the introduction of PDMAT and the plasma exposure. The mass-to-charge ratios shown in Fig. 4 were selected on the basis of the cracking patterns of the reactants (O₂ and PDMAT) and expected reaction products: $m/z=18$ (H₂O⁺), $m/z=28$ (CO⁺/NCH₂⁺), $m/z=32$ (O₂⁺), $m/z=44$ [CO₂⁺/N(CH₃)₂⁺], and $m/z=45$ [HN(CH₃)₂⁺]. It should be noted that the switching of gases during the ALD cycle from Ar during PDMAT dose (30 mTorr) to O₂ during plasma exposure (7.5 mTorr) introduces changes in (background) pressure inside the mass spectrometer. The baselines of the m/z signals, therefore, shift in height, whereas spikes associated with the sudden pressure increase induced by the start of Ar and O₂ flows can be observed. In Fig. 4, these effects are most pronounced for $m/z=32$ (O₂⁺).

During the precursor dose, no response was observed at any of the m/z signals shown in Fig. 4. As a matter of fact, no response to the PDMAT precursor introduction was seen

at any of the m/z signals in the range of $m/z=15$ –45. This is remarkable since this would imply that there is no production of $\text{HN}(\text{CH}_3)_2$ which would suggest that another chemisorption mechanism other than the commonly presumed ligand exchange reaction would be occurring. A lack of detection sensitivity of the QMS for the measurements carried out could be another explanation for the absence of a signal due to $\text{HN}(\text{CH}_3)_2$. However, in a similar investigation of plasma-assisted deposition of TaN from PDMAT and H_2 plasma,³⁸ where the same mass spectrometer was used and under similar experimental conditions, a clear response was observed during the precursor dosing at $m/z=28$, 44, and 45. Under these conditions the response closely matched the cracking pattern of $\text{HN}(\text{CH}_3)_2$ [$m/z=44$ (100%), 45 (64%), and 28 (18%)].³⁹ In the case of plasma-assisted ALD of TaN, the chemisorption of PDMAT most likely involves binding to NH_x surface groups by splitting off volatile $\text{HN}(\text{CH}_3)_2$ reaction products.³⁸ A lack of sensitivity of the mass spectrometer in the Ta₂O₅ experiments is, therefore, not likely. In addition, we would like to note that the chemisorption of metal alkylamides has not been as extensively studied as for metal-alkyl or metal-halide precursors. On the basis of quartz-crystal microbalance measurements, Hausmann *et al.* speculated about the chemisorption of PDMAT on a hydroxylated surface during thermal ALD of Ta₂O₅; however, the limited experimental data prohibited the exact identification of the surface reactions.²³ For plasma-assisted ALD processes of metal oxides from metal alkylamides, even less literature data have been reported and even no information is available about the surface composition of amorphous Ta₂O₅ after the oxidation step. This is contrary to the Al₂O₃ case, for which evidence has been presented that $-\text{OH}$ groups are the main reactive surface sites both in thermal ALD with H_2O as oxidant and plasma-assisted ALD using an O₂ plasma.^{27,28,40} Thus, the exact precursor chemisorption mechanism occurring during the deposition of Ta₂O₅ remains an open question.

During the O₂ plasma step of the plasma-assisted ALD process of Ta₂O₅, clear peaks can be observed at $m/z=18$ and 44. These signals indicate the formation of H_2O and CO_2 , respectively. Their formation can be attributed to combustionlike reactions during the plasma exposure induced by O radicals. Also, a clear peak can be distinguished at $m/z=28$, which is associated with the presence of CO that can be formed either via incomplete combustion reactions or through the electron impact dissociation of CO_2 in the plasma. Furthermore, from the dip in the $m/z=32$ (O_2^+) signal, the consumption of oxygen due to the oxidation of the Ta surface layer and simultaneous formation of H_2O , CO_2 , and possibly CO can be deduced.

From the peak intensities of the signals shown in Fig. 4 and the other m/z ratios measured in the range of $m/z=15$ –45, the gas composition during the plasma exposure (at $t \sim 200$ ms after ignition of the plasma) was determined. The result is shown in Fig. 5 as a bar graph of the signals that increased during the plasma exposure compared to the QMS background. For some of the signals, the most likely contrib-

FIG. 5. QMS peak intensities for mass-to-charge ratios (m/z) between 10 and 50 as observed during the O₂ plasma exposure.

uting gas species have been indicated. Besides the increase at $m/z=28$ due to ionization and dissociative ionization of CO and CO_2 in the mass spectrometer, respectively, a clear increase can also be observed at $m/z=27$, 29, and 30. On the basis of the cracking patterns, we suggest that the main candidates contributing to the signals are HCN^+ ($m/z=27$), $\text{N}(\text{CH}_3)^+$ ($m/z=29$), and NO^+ ($m/z=30$), respectively.³⁷ From the gas composition, we can speculate that the $-\text{N}(\text{CH}_3)_2$ surface groups after PDMAT chemisorption appear to be not completely combusted by the O radicals. Possibly, a combination of different surface processes simultaneously occurs. The latter was also observed in the plasma-assisted ALD process of Al₂O₃ from $\text{Al}(\text{CH}_3)_3$. In this process, both combustionlike reaction products (CO, CO_2 , and H_2O) as well as hydrocarbon species (CH_4 , C_2H_x , etc.) were observed during the O₂ plasma exposure. One reaction mechanism for hydrocarbon generation was a secondary reaction pathway in which the produced H_2O reacted with the $-\text{CH}_3$ surface groups through ligand exchange to form CH_4 and $-\text{OH}$ groups.^{27,28}

OES was used to investigate the excited species in the gas phase during the plasma exposure. The light emissions which are observed during the first 200 ms of the plasma exposure in the plasma-assisted ALD processing of Ta₂O₅ and during a regular O₂ plasma in continuous operation are shown in Figs. 6(a) and 6(b), respectively. A clear difference can be observed between both spectra. The difference is related to the presence of reaction products in the plasma during the oxidation step of plasma-assisted ALD of Ta₂O₅. From an identification of the spectral lines, the broadband emission in Fig. 6(a) was found to be predominantly originating from excited CO^* molecules. The bands from the Angström ($B^1\Sigma^+-A^1\Pi_i$), Herzberg ($C^1\Sigma^+-A^1\Pi_i$), and third positive ($b^3\Sigma^+-a^3\Pi_r$) systems of CO^* as well as the Comet tail ($A^2\Pi_i-X^2\Sigma^+$) and Baldet–Johnson ($B^2\Sigma^+-A^2\Pi_i$) systems of the CO^{+*} ion were identified, as indicated in Fig. 6(a). Several atomic oxygen lines (777 and 845 nm) could also still be clearly identified in the spectrum during the Ta₂O₅ ALD process.

For comparison, the spectrum recorded during the plasma-assisted ALD of Al₂O₃ is shown in Fig. 6(c).²⁷ The

FIG. 6. Optical emission spectrum taken during (a) the first 200 ms of the plasma exposure in the Ta₂O₅ plasma-assisted ALD process, (b) a regular O₂ plasma in continuous operation, and (c) the emission spectrum during the first 200 ms of the plasma exposure in the Al₂O₃ plasma-assisted ALD process (Ref. 27). The identification of the different emission lines has been indicated in the spectrum recorded during plasma-assisted ALD of Ta₂O₅.

spectra for Ta₂O₅ and Al₂O₃ show similarities, but a clear difference is, besides the higher broadband background, the presence of peaks at around 388 and 358 nm. These peaks have been identified to originate from the Violet system ($B^2\Sigma-X^2\Sigma$) of C $\equiv$ N*, and they are clearly related to the presence of alkylamine ligands in PDMAT.⁴¹ The emission of excited nitric oxide (NO*) could not be observed in the spectra, although the formation of NO was indicated by the QMS measurements. The reason for this is that NO* mostly radiates in the UV region (γ system: 195.61–345.85 nm), which is below the UV cutoff of the optical emission window.

Since the reaction products are continuously pumped away, their characteristic emission can also be used to gain information on the progress of the surface reactions, thus serving as an indicator for the completion of the plasma step. Furthermore, since the number of reaction products is limited to the number of surface sites that underwent reactions, the OES measurements can also be used to investigate the actual film growth by varying one of the growth parameters such as precursor dose. From the emission spectra shown in Fig. 6, the wavelengths of several peaks related to the reaction products were selected and monitored as a function of time during the plasma exposure. In Fig. 7, the time dependent signals at 777 nm (O*), 656 nm (H*), 519 nm (CO*), and

FIG. 7. Time resolved OES measurements of (a) O* (777 nm), (b) H* (656 nm), (c) CO* (519 nm), and (d) CN* (388 nm). The signals are given for precursor dosing times of 0 s ($\blacktriangle$), 0.5 s ($\blacktriangledown$), 2.0 s ($\blacklozenge$), and 4.0 s ($\blacktriangleleft$). The plasma exposure time was 5 s.

388 nm (CN*) are given for different precursor dose times. Figure 7(a) shows that when no PDMAT dose ($t=0$ s) preceded, the plasma exposure signal at 777 nm immediately shows a stable O* emission after plasma ignition. When the precursor has been introduced for a relatively brief period of time ($t=0.5$ s) prior to plasma exposure step and, consequently, surface reactions have taken place, the O* emission is observed to be slightly lower at the start of the plasma exposure. Subsequently, it reaches its steady state level again after a certain period. With the introduction of more precursor ($t=2$ and 4 s), this effect is becoming increasingly pronounced. The decrease in intensity of the O* radical emission at the start of the plasma exposure correlates with the sharp increase seen in the CO*, CN*, and H* emissions shown in Figs. 7(b)–7(d). The increase in emission is followed by a decrease to its steady state level after some time. The shape of this transient signal depends on the production and removal rate of the excited reaction products. For all species, the transient signal becomes more pronounced with increasing precursor dose which indicates that more reaction products have been generated at larger precursor doses up to a precursor dosing time of 4 s.

The completion of the plasma step can be determined from the decay of the transient emissions of H*, CO*, and CN*. Typical $1/e$ decay times of ~ 0.5 s are found for the

FIG. 8. Integrated intensity of the time resolved OES measurements of CN* and CO* during the plasma step of the ALD cycle (cf. Fig. 7) as a function of the precursor dosing time used in the cycle.

transient signal of all species, revealing that the plasma step is completed within ~ 2 s (i.e., several $1/e$ decay times). A similar result is obtained from the O* emission when estimating the time in which it reaches its steady state value. A saturation time of < 2 s correlates well with the SE film growth data, as presented in Fig. 1. The total light emission by the reaction product species can be determined by integrating the time dependent signals displayed in Fig. 7. The result is shown in Fig. 8, where the integrated emission signals of CO* and CN* are shown as a function of precursor dose. Some initial differences at low precursor doses can be observed between the integrated CO* and CN* emission signals, but a clear saturation of the amount of emission can be observed for both CO* and CN* for precursor doses larger than 3–4 s. The saturation of both CN* and CO* emissions at higher precursor dose is induced by the fact that during the plasma exposure, only a limited amount of surface groups enters the gas phase due to the self-limiting adsorption reactions of the precursor. When compared to the growth rate measured by SE shown in Fig. 1, the OES results for CO* and CN* show a very similar trend, reaching a saturated value when a precursor dose of 3–4 s and longer is applied. The comparison between the SE film thickness and the QMS and OES gas phase measurements forms a check. It correlates the gas phase measurements, to which all surfaces on which film growth occurs contribute to the local measurement of film growth on the substrate by SE. This check indicates that, due to the uniform temperature throughout the reactor and the deposition of a fresh Ta₂O₅ layer prior to this experiment, the film growth occurs at the same rate and most likely in the same fashion on all reactor surfaces. The difference in emission between CN* and CO* at a low precursor dose ($t < 3$ –4 s) could be related to the amount of surface groups that is present due to the chemisorption of the precursor at the surface. We can assume that the plasma produces the same number of O radicals in any condition and, therefore, the following explanation can be suggested. At low precursor dose ($t < 3$ –4 s), the number of surface groups is relatively small compared to the number of O radicals, such that the C atoms in the surface groups are mainly converted

into CO and/or CO₂. With increasing precursor dose, however, the density of surface groups increases and the ratio between the O radicals and surface groups decreases. In this case also, CN starts being formed due to the lower amount of O radicals available, although the combustion and the formation of CO and CO₂ might still be the dominant process.

V. CONCLUSIONS

The Ta₂O₅ film growth by plasma-assisted ALD using PDMAT precursor and an O₂ plasma has been investigated. The process was proven to exhibit true ALD-like properties showing saturated film growth at a rate of 0.81 Å/cycle at 225 °C. The films were stoichiometric (Ta:O=2:5) and N and C impurities were below the detection limit of the RBS analysis. The mass density was high and close to the bulk value of crystalline Ta₂O₅ ($> 98\%$), whereas the as-deposited films were found to be predominantly amorphous. While the growth rate in terms of thickness increase per cycle was found to slightly vary with deposition temperature, increasing to 0.87 Å/cycle at 100 °C, the number of Ta atoms deposited per cycle was found to remain independent of temperature. The difference in growth rate could be explained by the decrease in mass density. The H content in the film was found to vary from 4.6 at. % at 100 °C to 2.0 at. % at 225 °C. The optical properties in terms of refractive index and extinction coefficient were determined in the range of 0.75–6.5 eV by using SE. From these data, the Tauc band gap values were determined to range from $E_g = 4.31$ eV at 100 °C to $E_g = 4.24$ eV at 225 °C.

The associated reaction mechanisms of the ALD process have been studied by using QMS and OES. During the precursor dose, remarkably, no HN(CH₃)₂ and associated cracking products in the range of $m/z = 15$ –45 were detected. This might suggest a different chemisorption mechanism from simple ligand exchange. For example, an association reaction of the complete precursor could take place during the PDMAT step. In such an association reaction, the precursor remains intact when it chemically adsorbs without the release of reaction products into the gas phase.⁴⁰ However, further investigations are necessary to settle this issue. During the plasma exposure, the occurrence of combustionlike reactions was established through the detection of CO, CO₂, and H₂O. The Ta₂O₅ plasma-assisted ALD process from the alkylamide-based Ta[N(CH₃)₂]₅ precursor, therefore, showed many similarities with the deposition of Al₂O₃ from the alkyl-based Al(CH₃)₃ precursor previously reported.^{27,28} Specifically for the Ta₂O₅ process, however, the production of NO was found by mass spectrometry, indicating the presence of alkylamide surface groups [–N(CH₃)₂] after chemisorption of PDMAT. Furthermore, the detection of signals due to HCN⁺, NCH₂⁺, and C≡N* by mass spectrometry and OES suggests that during the plasma exposure, other processes also occur at the surface, in addition to combustion reactions. On the basis of the investigation on Ta₂O₅ presented here and the earlier work on Al₂O₃, it can be concluded that the occurrence of combustionlike reactions during the plasma exposure appears to be generic for plasma-

assisted ALD processes of metal oxides from metal-organic precursors when using an O₂ plasma for oxidation.

ACKNOWLEDGMENTS

The authors acknowledge the skillful technical assistance of J. F. C. Jansen, M. J. F. van de Sande, and J. J. A. Zeebregts. A. J. M. Mackus is thanked for his help with the OES measurements and spectrum analysis. The authors also acknowledge T. Dao and Dr. P. C. Zalm for the RBS measurements and R. Bakker for the XRD measurements (all Philips Material Analysis). This work was financially supported by the Dutch Technology Foundation STW. The research of W.K. was made possible by a fellowship from the Royal Netherlands Academy of Arts and Sciences (KNAW).

- ¹P. M. Natishan, E. McCafferty, P. R. Puckett, and S. Michel, *Corros. Sci.* **38**, 1043 (1996).
- ²G. B. Alers, D. J. Werder, Y. Chabal, H. C. Lu, E. P. Gusev, E. Garfunkel, T. Gustafsson, and R. S. Urdahl, *Appl. Phys. Lett.* **73**, 1517 (1998).
- ³G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.* **89**, 5243 (2001).
- ⁴C. Chaneliere, J. L. Autran, R. A. B. Devine, and B. Balland, *Mater. Sci. Eng., R.* **22**, 269 (1998).
- ⁵E. Gerritsen *et al.*, *Solid-State Electron.* **49**, 1767 (2005).
- ⁶M. B. Yu *et al.*, *IEEE Electron Device Lett.* **26**, 793 (2005).
- ⁷E. Deloffre, C. Wyon, and M. Gros-Jean, *Proc.-Electrochem. Soc.* **2005-1**, 510 (2005).
- ⁸M. Thomas *et al.*, *Microelectron. Eng.* **83**, 2163 (2006).
- ⁹M. Ritala and M. Leskelä, *Handbook of Thin Films Materials*, edited by H. S. Nalwa (Academic, San Diego, CA, 2002), Vol. 1, p. 103.
- ¹⁰K. Kukli, M. Ritala, and M. Leskelä, *J. Electrochem. Soc.* **142**, 1670 (1995).
- ¹¹K. Kukli, J. Aarik, A. Aidla, H. Siimon, M. Ritala, and M. Leskelä, *Appl. Surf. Sci.* **112**, 236 (1997).
- ¹²H. Kattelus, M. Ylilampi, J. Saarilahti, J. Antson, and S. Lindfors, *Thin Solid Films* **225**, 296 (1993).
- ¹³J. Aarik, A. Aidla, K. Kukli, and T. Uustare, *J. Cryst. Growth* **144**, 116 (1994).
- ¹⁴K. Kukli, J. Aarik, A. Aidla, O. Kohan, T. Uustare, and V. Sammelselg, *Thin Solid Films* **260**, 135 (1995).
- ¹⁵C. W. Hill, G. J. Derderian, and G. Sandhu, *J. Electrochem. Soc.* **152**, G386 (2005).
- ¹⁶K. Kukli *et al.*, *Chem. Mater.* **13**, 122 (2001).
- ¹⁷K. Kukli, M. Ritala, and M. Leskelä, *Chem. Mater.* **12**, 1914 (2000).
- ¹⁸M. Ritala, K. Kukli, A. Rahtu, P. I. Raisanen, M. Leskela, T. Sajavaara, and J. Keinonen, *Science* **288**, 319 (2000).
- ¹⁹J. Sundqvist, H. Högberg, and A. Härsta, *Chem. Vap. Deposition* **9**, 245 (2003).
- ²⁰D. F. Gu, J. Li, S. K. Dey, H. de Waard, and S. Marcus, *J. Vac. Sci. Technol. B* **24**, 2230 (2006).
- ²¹H.-J. Song, C.-S. Lee, and S. W. Kang, *Electrochem. Solid-State Lett.* **4**, F13 (2001).
- ²²A. Niskanen, U. Kreissig, M. Leskelä, and M. Ritala, *Chem. Mater.* **19**, 2316 (2007).
- ²³D. M. Hausmann, P. de Rouffignac, A. Smith, R. Gordon, and D. Mon-sma, *Thin Solid Films* **443**, 1 (2003).
- ²⁴W. J. Maeng, S. J. Park, and H. Kim, *J. Vac. Sci. Technol. B* **24**, 2276 (2006).
- ²⁵W. J. Maeng and H. Kim, *Electrochem. Solid-State Lett.* **9**, G191 (2006).
- ²⁶M. D. Groner, F. H. Fabreguette, J. W. Elam, and S. M. George, *Chem. Mater.* **16**, 639 (2004).
- ²⁷S. B. S. Heil, P. Kudlacek, E. Langereis, R. Engeln, M. C. M. van de Sanden, and W. M. M. Kessels, *Appl. Phys. Lett.* **89**, 131505 (2006).
- ²⁸S. B. S. Heil, J. L. Van Hemmen, M. C. M. van de Sanden, and W. M. M. Kessels (unpublished).
- ²⁹S. B. S. Heil, E. Langereis, F. Roozeboom, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Electrochem. Soc.* **153**, G956 (2006).
- ³⁰B. von Blanckenhagen, D. Tordova, and J. Ullmann, *Appl. Opt.* **41**, 3137 (2002).
- ³¹N. V. Nguyen, C. A. Richter, Y. J. Cho, G. B. Alers, and L. A. Stirling, *Appl. Phys. Lett.* **77**, 3012 (2000).
- ³²S. B. S. Heil, E. Langereis, A. Kemmeren, F. Roozeboom, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Vac. Sci. Technol. A* **23**, L5 (2005).
- ³³E. Deloffre *et al.*, Presentation at the Seventh AVS Topical Conference on Atomic Layer Deposition, San Diego, CA, 2007.
- ³⁴D. R. Lide, *CRC Handbook of Chemistry and Physics*, 87th ed. (CRC, Boca Raton, 2007).
- ³⁵J. L. van Hemmen, S. B. S. Heil, J. H. Klootwijk, F. Roozeboom, C. J. Hodson, M. C. M. van de Sanden, and W. M. M. Kessels, *ECS Trans.* **3**, 67 (2007).
- ³⁶K. Kukli, M. Ritala, R. Matero, and M. Leskelä, *J. Cryst. Growth* **212**, 459 (2000).
- ³⁷J. Tauc, R. Grigorov, and A. Vancu, *Phys. Status Solidi* **15**, 627 (1966).
- ³⁸E. Langereis, H. C. M. Knoop, A. J. M. Mackus, F. Roozeboom, M. C. M. van de Sanden, and W. M. M. Kessels, *J. Appl. Phys.* **102**, 083517 (2007).
- ³⁹NIST/EPA/NIH mass spectral Library, data version NIST05, software version 2.0d.
- ⁴⁰R. L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).
- ⁴¹R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (Chapman and Hall, London, 1976).