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Citation for published version (APA):

Heil, S. B. S., Langereis, E., Kemmeren, A., Roozeboom, F., Sanden, van de, M. C. M., & Kessels, W. M. M. (2005). Plasma-assisted atomic layer deposition of TiN monitored by in situ spectroscopic ellipsometry. *Journal of Vacuum Science and Technology A: Vacuum, Surfaces, and Films*, 23(4), L5-L8.
<https://doi.org/10.1116/1.1938981>

DOI:

[10.1116/1.1938981](https://doi.org/10.1116/1.1938981)

Document status and date:

Published: 01/01/2005

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.
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Plasma-assisted atomic layer deposition of TiN monitored by *in situ* spectroscopic ellipsometry

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(Received 3 December 2004; accepted 25 April 2005; published 22 June 2005)

In situ spectroscopic ellipsometry has been employed to determine the properties of titanium nitride (TiN) films during plasma-assisted atomic layer deposition by alternating TiCl_4 precursor dosing and $\text{H}_2\text{-N}_2$ plasma exposure. Besides monitoring the film thickness when optimizing the half reactions, it is shown that spectroscopic ellipsometry is a very valuable tool for *in situ* studies of (air-sensitive) film properties such as resistivity, and for investigating the nucleation phase during initial film growth. © 2005 American Vacuum Society. [DOI: 10.1116/1.1938981]

I. INTRODUCTION

The processing challenges in next-generation semiconductor device fabrication and integration make the self-limiting growth method of atomic layer deposition (ALD) a very innovative field from a scientific and technological perspective. For example, by the recent introduction of a low-temperature plasma step in the ALD reaction cycle, it is possible to deliver additional reactivity to the surface in the form of plasma-produced radical species. This opens up a processing parameter space that is unattainable by the strictly thermally driven process.¹ Plasma-assisted ALD (PA-ALD), therefore, is a bright prospect in terms of increased choice of chemistry and precursors as well as in improved film quality at lower substrate temperatures and higher growth rates.

A key factor in (PA-)ALD which still needs to be explored extensively is *in situ* monitoring of the film growth and on-line process control. Currently, for (PA-)ALD the most common techniques used for *in situ* studies are quartz crystal microbalance measurements and mass spectrometry.^{2–4} However, early insight into the growth of the film on the substrate material of interest and into the specific film properties obtained is also desired. This is especially relevant when information about the film properties during initial growth is required or when one cannot simply rely on *ex situ* film characterization, for example, for film properties that change under air exposure.

In this letter we will show that the optical technique of spectroscopic ellipsometry (SE) is a very valuable tool for *in situ* monitoring of the growth process and for determining

the film properties. We illustrate this for the PA-ALD process of titanium nitride (TiN) which is based on TiCl_4 precursor dosing and $\text{H}_2\text{-N}_2$ plasma exposure and which is an extension of the set of metals and their nitrides deposited by PA-ALD as recently reviewed by Kim.⁵ Thin metallic TiN films have widespread applications in the semiconductor industry, for example as diffusion barrier layers in interconnect technology (for W, Al, etc.), as a future replacement for the polysilicon gate electrode in metal-oxide-semiconductor field effect transistor (MOS-FET) gate stacks, and as metal electrode in high density MOS “trench” capacitors. From a comparison with *ex situ* techniques, we will show that SE gives accurate information on the TiN film thickness as well as on the resistivity of the films, even for very small film thicknesses (possibly as thin as 10 Å). Furthermore, it is revealed that SE also yields insight into the nucleation phase during initial film growth.

II. EXPERIMENT

The deposition system is similar to the one described by Rosnagel *et al.*¹ and consists of a $\text{H}_2\text{-N}_2$ operated plasma source connected through a gate valve to a deposition chamber. The radio frequency plasma power (100 W) is coupled inductively to the source that consists of a multiple-turn copper coil wrapped around a quartz tube. A resistively heated substrate holder is present in the chamber for depositing at elevated substrate temperatures (100–400 °C). TiCl_4 vapor from a bottle with liquid TiCl_4 , kept at room temperature, is injected into the wall-heated chamber (20–200 °C) using a timed leak valve. TiN films were deposited at 400 °C on ~2 nm native oxide and 1000 nm SiO_2 -covered *c*-Si sub-

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FIG. 1. Imaginary part of the dielectric function ϵ_2 of a TiN film deposited by the PA-ALD process. The Drude term and two Lorentz terms are indicated (dashed lines). The dielectric function ϵ_2 for this stoichiometric film is representative for all films reported in the letter. The inset shows a schematic representation of the optical model used, where the substrate is formed by the combination Si and SiO₂ (thermal or native oxide).

strates. One PA-ALD cycle typically consisted of 5 s exposure to TiCl₄ (3 mTorr), followed by 10 s Ar purge, 15 s plasma exposure (10 mTorr H₂ and 1 mTorr N₂ partial pressures), and 10 s pump-down of the reactor to base pressure (10⁻⁶ Torr).

The SE measurements were performed after every ten PA-ALD cycles using a J.A. Woollam, Inc. M2000U visible and near-infrared ellipsometer (0.7–5.0 eV) at a 68° angle of incidence.⁶ The ellipsometry data were analyzed by an optical model (see inset Fig. 1) using the Drude–Lorentz parameterization of the dielectric function of TiN:^{6–8}

$$\epsilon = \epsilon_{\infty} - \frac{\omega_{pu}^2}{\omega^2 - i\Gamma_D\omega} + \sum_j \frac{f_j\omega_{0j}^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j\omega}. \quad (1)$$

In this equation, the Drude term describes the conduction electrons and is characterized by the unscreened plasma energy $\hbar\omega_{pu}$ and the damping factor Γ_D ; the Lorentz oscillators take interband transitions into account and are characterized by their energy position $\hbar\omega_{0j}$, strength f_j , and broadening factors γ_j . The parameter ϵ_{∞} is a background constant larger than unity. Patsalas and Logothetidis have shown that Eq. (1) accurately describes ϵ when taking into account two Lorentz oscillators.^{7,8} A typical plot of the imaginary part of the dielectric function ϵ_2 for the PA-ALD films described in this letter is given in Fig. 1, which shows the Drude term at low energies and two Lorentz oscillators at ~ 3.1 and ~ 5.3 eV, respectively. This dielectric function is similar to the ones reported for magnetron sputtered TiN.^{7,8}

III. RESULTS AND DISCUSSION

Figure 2 shows the TiN film thickness as a function of the number of cycles monitored *in situ* by SE. The thickness increases linearly with the number of cycles, as expected for ALD growth. During deposition the TiCl₄ dosing was varied between 5.3×10^3 and 2.6×10^4 L (1 L = 10⁻⁶ Torr s) and the growth rate was determined from the gradient of the thickness as a function of the number of cycles. The experi-

FIG. 2. Thickness of the TiN film as a function of number of cycles as determined with *in situ* SE. The starting surface was a ~ 20 nm TiN film on native oxide covered Si. As indicated, during this deposition three different TiCl₄ doses have been used. The larger spread in the data at 140 and 160 cycles is caused by a significantly larger time interval between deposition and *in situ* SE measurement. The inset shows the growth rate as a function of TiCl₄ dosing.

ment was carried out on a ~ 20 nm thick TiN film deposited in a previous run. This procedure is followed to rule out any influence of the initial growth phase of the film on the substrate material (see below). The growth rate as a function of the TiCl₄ dosing (inset in Fig. 2) is found to be constant (~ 0.65 Å/cycle), indicating that the dosing is adequate enough to saturate the TiCl₄ surface coverage of the substrate.

To determine the influence of the plasma exposure on film growth, the plasma exposure time per cycle was varied between 0 and 120 s, while keeping the TiCl₄ dosing constant. The growth rate and TiN film properties were determined by *in situ* SE for the different exposure times in one single deposition run. In Fig. 3 the variation in growth rate as a function of plasma exposure time is shown and compared to growth rate data obtained from separate deposition runs. Both data sets are consistent with each other, which indicates the stability of the deposition process and the robustness of

FIG. 3. Growth rate as a function of plasma exposure time on native oxide covered Si. During the deposition run the plasma exposure time was varied and the growth rate was determined from the increase in thickness per deposition cycle. These values have been confirmed by measurements of the growth rate in separate depositions.

TABLE I. Comparison of the TiN film properties determined with SE and *ex situ* FPP measurements, RBS, and ERD.

Plasma exposure time (s)	Resistivity		Composition		
	FPP ($\mu\Omega$ cm)	SE ($\mu\Omega$ cm)	[N]/[Ti]	[Cl] (at. %)	[H] (at. %)
5	174	137	0.93	0.27	4
15	141	129	1.0	0.25	4
60	144	134	1.15	0.20	9

thickness monitoring with SE. The growth rate saturates at higher plasma exposure times, indicating an almost complete surface reaction between the plasma-produced radicals and adsorbed TiCl_4 precursor.

An influence of the plasma exposure time on the film properties is the variation in $[\text{N}]/[\text{Ti}]$ ratio from understoichiometric at 5 s to overstoichiometric at 60 s (see Table I) as determined with Rutherford backscattering (RBS). The hydrogen content, determined by elastic recoil detection (ERD), is somewhat higher for the long plasma exposure of 60 s, but the value of 4% for the stoichiometric film is similar to other PA-ALD processes.⁹ The Cl impurity content of

FIG. 5. Initial growth on a 1000 nm thermal SiO_2 and on a native oxide covered Si substrate monitored by *in situ* spectroscopic ellipsometry.

0.2–0.3 at. % is low (even at an overexposure of $\text{TiCl}_4 > 10^6$ L) and is comparable to other ALD techniques.^{10,11} Oxygen, with a concentration of ~ 1.0 at. %, is mostly found in the top part of the film, suggesting postdeposition oxidation of the layer. These results on the film composition show that the films deposited can be analyzed properly by the optical model for TiN. The root-mean-square roughness of 0.45 nm, determined by atomic force microscopy (AFM) for a ~ 25 nm thick TiN film, shows that the films are also sufficiently smooth to omit a surface roughness layer in the optical model.

The thickness of the TiN films deduced from the SE analysis was confirmed *ex situ* by x-ray reflectometry and by transmission electron microscope (TEM) and scanning electron microscope (SEM) imaging. TEM and SEM micrographs are given in Fig. 4, which show a TiN film deposited on a wafer with 20:1 aspect-ratio macropores ($1.5 \mu\text{m}$ wide) used as the top electrode part in high-density MOS “trench” capacitors.^{12,13} The macropores, created using a Bosch-etch process, had large surface roughness and were covered with a SiO_2 – Si_3N_4 – SiO_2 (ONO) dielectric stack for the capacitor. A stoichiometric TiN metallic electrode film was deposited on top of the ONO stack using PA-ALD, and was subsequently covered by a polysilicon capping layer. The film thickness predicted on the basis of the SE measurements on silicon flats was 35 ± 3 nm, which is fairly close to the results from both the TEM and SEM analysis. With SEM the TiN film was also analyzed at the bottom of the macropores, which indicated the film conformality is reasonable but should be further optimized.

From the Drude term in the dielectric function ϵ deduced from the SE measurements, the resistivity ρ of the TiN films was determined by using the relation $\rho = \Gamma_D / (\epsilon_0 \omega_{pu}^2)$.^{7,8} As shown in Table I, the resistivity of the PA-ALD TiN films is low compared to other ALD techniques.^{5,10,11} Table I also gives a comparison between the resistivity found with SE and the resistivity determined *ex situ* by four-point probe (FPP) measurements. A fairly good agreement between the two techniques is found while the small difference can possibly be attributed to postdeposition oxidation of the TiN top layer before the *ex situ* FPP analysis (as also observed with

FIG. 4. Micrographs of a ~ 41 nm thick PA-ALD TiN film deposited on a SiO_2 – Si_3N_4 – SiO_2 stack on top of a Si wafer with 20:1 aspect-ratio macropores ($1.5 \mu\text{m}$ width). The TiN film is capped by a chemical vapor deposited poly-Si layer. (a) Cross-sectional TEM, (b) SEM image of the top surface, and (c) SEM image of the bottom of a macropore.

RBS) and/or to the relatively large uncertainty in the FPP measurements due to the small thickness of the films (~ 20 nm). This proves that SE is a very valuable tool for an accurate and noninvasive determination of the resistivity of very thin ALD deposited TiN films *in situ*.

A key benefit of monitoring thickness with *in situ* SE is the ability to study the nucleation phase during initial film growth. As shown in Fig. 5, a region of low growth rate can clearly be observed for TiN deposited on thermal SiO₂ while such a nucleation delay is not observed when depositing on native-oxide covered c-Si. Similar observations have also been reported by others, for example by Satta *et al.* for TiN using an extensive set of *ex situ* RBS measurements.¹⁴ *In situ* SE allows the observation of this nucleation delay (attributed to differences in surface hydroxyl group coverage on different substrates¹⁴) in one single deposition run, without air exposure and on the substrate material of interest.

IV. CONCLUSIONS

We have used *in situ* spectroscopic ellipsometry as a tool to study the PA-ALD process of TiN films using TiCl₄ dosing and H₂-N₂ plasma exposure. We have corroborated the results using different *ex situ* diagnostics such as elastic recoil detection and Rutherford backscattering, SEM and TEM imaging, AFM, and four-point probe measurements. The *in situ* monitoring of the thickness has shown to be very valuable when optimizing the half reactions of the ALD process and for investigating the nucleation process during initial film growth. Moreover, it is shown that reliable values of the resistivity of the films can be extracted from the SE data,

even for very thin films and without air exposure.

ACKNOWLEDGMENTS

This work has been supported by the Netherlands Technology Foundation STW. The research of W.K. has been made possible by a fellowship from the Royal Netherlands Academy of Arts and Sciences (KNAW). The RBS measurements by Dr. Y. Tamminga and T. Dao and the TEM analysis by M. Verheijen (all Philips Research) are gratefully acknowledged.

- ¹S. M. Rossnagel, A. Sherman, and F. Turner, *J. Vac. Sci. Technol. B* **18**, 2016 (2000).
- ²M. Ritala, M. Juppó, K. Kukli, A. Rahtu, and M. Leskela, *J. Phys. IV* **9**, 1021 (1999).
- ³A. Rahtu, T. Alaranta, and M. Ritala, *Langmuir* **17**, 6509 (2001).
- ⁴R. Matero, A. Rahtu, and M. Ritala, *Chem. Mater.* **13**, 4506 (2001).
- ⁵H. Kim, *J. Vac. Sci. Technol. B* **21**, 2231 (2003).
- ⁶H. G. Tompkins and W. A. McGahan, *Spectroscopic Ellipsometry and Reflectometry: A User's Guide* (Wiley, New York, 1999).
- ⁷P. Patsalas and S. Logothetidis, *J. Appl. Phys.* **90**, 4725 (2001).
- ⁸P. Patsalas and S. Logothetidis, *J. Appl. Phys.* **93**, 989 (2003).
- ⁹H. Kim, A. J. Kellock, and S. M. Rossnagel, *J. Appl. Phys.* **92**, 7080 (2002).
- ¹⁰J. Kim, H. Hong, S. Ghosh, K.-Y. Oh, and C. Lee, *Jpn. J. Appl. Phys., Part 1* **42**, 1375 (2003).
- ¹¹H. Jeon, J.-W. Lee, Y.-D. Kim, D.-S. Kim, and K.-S. Yi, *J. Vac. Sci. Technol. A* **18**, 1595 (2000).
- ¹²F. Roozeboom, R. Elfrink, T. G. S. M. Rijks, J. Verhoeven, A. Kemmeren, and J. van den Meerakker, *Int. J. Microcircuits Electron. Packag.* **24**, 182 (2001).
- ¹³F. Roozeboom, A. Kemmeren, J. Verhoeven, F. van den Heuvel, H. Kretschman, and T. Frič, *Mater. Res. Soc. Symp. Proc.* **783**, 157 (2003).
- ¹⁴A. Satta, A. Vantomme, J. Schuhmacher, C. M. Whelan, V. Sutcliffe, and K. Maex, *Appl. Phys. Lett.* **84**, 4571 (2004).