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Citation for published version (APA):

Document status and date:
Published: 01/01/2010

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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Download date: 30. Dec. 2019
In Situ Spectroscopic Ellipsometry for Atomic Layer Deposition

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Presented at the 52nd SVC Technical Conference in Santa Clara, CA, in the Optical Coatings session on May 14, 2009

Abstract
The application of in situ spectroscopic ellipsometry during thin film synthesis by atomic layer deposition (ALD) is examined for results obtained on Al2O3, Ta2N, and TiN films with thicknesses ranging from 0.1 to 100 nm. By analyzing the film thickness and the energy dispersion of the optical constants of the films, the layer-by-layer growth and material properties of the ALD films can be studied in detail. The growth rate per cycle and the nucleation behavior of the films can be addressed by monitoring the thickness as a function of the number of cycles. It is shown that from the energy dispersion relation, insight into the conductive properties of metallic films can be derived. Moreover, the shape of the dispersion relation can be used to discriminate between different material compositions.

Introduction
With the optical, mechanical, electrical, and chemical properties of ultrathin films (<100 nm) being used in numerous applications, the synthesis of such functional thin films has become a key technology in present-day society. In this respect, the miniaturization and diversification in the semiconductor industry can be considered the main technological driver for developments in ultrathin film synthesis [1]. In particular for manufacturing steps where the emphasis lies on atomic scale thickness control and on conformal film growth in high-aspect ratio structures, atomic layer deposition (ALD) is currently the primary candidate to fulfill the strict requirements on ultrathin film growth [2,3].

By the virtue of separate self-limiting surface reactions, ALD has the ability to control film growth and material properties at the atomic level, as schematically illustrated in Figure 1. The amount of material deposited in an ALD cycle is determined by the amount of surface adsorption sites initially available and becomes at a certain point independent of the particle flux impinging on the surface. When sufficient precursor and reactant molecules are dosed to saturate the surface chemistry, a (sub)monolayer of material is deposited per cycle. ALD provides therefore "discrete" thickness control, i.e., the ability to increase the film thickness layer-by-layer by repeating ALD cycles. Moreover, ALD film growth is highly uniform and yields excellent conformality because at every available surface site (a maximum of) one precursor/reactant molecule can adsorb regardless the incoming particle flux or whether these surface sites are distributed over large surface areas or in demanding 3D topologies.

Over the years many ALD processes for thin films of inorganic materials have been developed, ranging from pure elements to compounds with oxygen, nitrogen, and sulphur, as reviewed by others [2,4]. Recently, an ALD scheme for organic materials was even designed using bifunctional monomers [5]. Well-established ALD processes have already been implemented for synthesis of ultrathin Al2O3, HfO2, and TiN films in industrial applications.

The successful integration of ultrathin films in industrial applications relies, however, not only on the development of methods to synthesize these ultrathin films, but also on the availability of accurate analytical or metrology techniques to determine the thickness and properties of these films. The ALD process lends itself particularly well for in situ studies, because the inherent cycle-by-cycle deposition process allows halting

![Figure 1. Atomic layer deposition (ALD) illustrated for two half-cycles of a typical deposition process. The first half-cycle consists of (a) self-limiting adsorption of the precursor molecules on the surface groups and (b) a purge step to remove the volatile reaction by-products and the excess of precursor dosed. After the first half-cycle, a submonolayer of precursor has chemisorbed on the surface. During the second self-limiting surface reaction (c), the surface is exposed to reactant molecules that react with the surface groups of the adsorbed precursor. The second half-cycle is completed by (d) another purge step to remove the volatile reaction by-products and the excess of reactant dosed. After the full ALD cycle, a submonolayer of material is deposited with the surface groups similar to those at the start of the cycle. Subsequently, the cycle can be repeated to deposit a film with the thickness targeted.](image_url)
the deposition for sensitive measurements in between the ALD cycles. Data acquisition in between the cycles provides, thus, the opportunity to monitor and address various aspects of the ALD growth process. Considering the amount of data that can easily be acquired, i.e., from cycle-by-cycle acquisition to, typically, acquisition after every 10-100 cycles, the influence of thickness on the material properties can be addressed in detail.

The majority of in situ studies have mainly focused on elucidating the fundamentals of the ALD reaction mechanism. Commonly employed techniques are infrared spectroscopy, mass spectrometry, and quartz crystal microbalance to provide insight into the surface species and volatile reaction by-products that are formed in the ALD half-cycles. Recently more emphasis has been put on in situ diagnostics that can be used online for process optimization, process monitoring, and for additional control of the deposition process at the atomic level.

In this paper, the merits of the optical technique of spectroscopic ellipsometry are discussed for in situ monitoring the film growth of Al₂O₃, TaN, and TiN films by ALD. In this respect, it is mentioned that an extensive review has recently been published discussing the application of in situ spectroscopic ellipsometry to study various aspects of ALD of Al₂O₃, HfO₂, Er₂O₃, TiO₂, Ta₂O₅, TiN, and TaN films [6].

**Spectroscopic ellipsometry**

Over the years, spectroscopic ellipsometry (SE) was demonstrated to be a valuable diagnostic for determination of the thickness and (optical) properties of thin films. Because SE is an optical and non-intrusive technique detecting the change in polarization of light upon reflection from a surface, it has been commonly applied in situ to study the film

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**Figure 2.** Photograph of a J.A. Woollam, Inc., M2000 spectroscopic ellipsometers fitted on (a) the FlexAL™ and (b) the OpAL™ reactors of Oxford Instruments [11, 12]. Both commercial reactors are installed in the clean room facility of the Eindhoven University of Technology.
In Situ Spectroscopic Ellipsometry
continued from page 37

growth as reported for many physical and chemical vapor deposition
methods [7,8]. The most important requirement to employ in situ SE
during ALD is optical access on the reactor and the deposition on opti-
cally flat substrates that allow for specular reflection of the ellipsometer
light. The concept of in situ SE for thickness monitoring during an ALD
process was already reported by Klaus et al. [9], however, the application
of in situ SE did not settle in ALD research until approximately a decade
later [10]. The knowledge, accuracy, and also user-friendliness of ellip-
someter systems and related data analysis have improved in the recent
years, as can be expressed by the ability to detect changes in nominal
film thickness equivalent to 0.01 monolayer.
The in situ SE measurements described in this work were carried
The M2000U visible and near-infrared extended (0.75-5.0 eV) ellip-
someter was proven particularly powerful to study metallic films.
The M2000D visible and ultraviolet extended (1.2-6.5 eV) ellipsometer
was particularly suited to study (high) band gap materials. The typical
configuration of the ellipsometers on the ALD reactors used in this
work is shown in Figure 2. The angle of incidence of the light was fixed to 68
degrees with respect to the normal of the substrate.

From the ellipsometric data obtained over a certain photon energy
range, the film thickness and the dispersion relation of the optical
constants can be deduced. The optical constants can be expressed in
the refractive index and extinction coefficient, but they are often repre-
sented in terms of the real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the complex
dielectric function $\varepsilon$ [7]. From the optical constants, several material
properties of thin films can be derived such as the optical band gap of
dielectric materials and the conductive properties of metallic films.

The optical behavior of a material becomes immediately apparent
from its energy dispersion in optical constants. For the photon energy
range of 0.75-6.5 eV of the ellipsometers employed in this work, the
real and imaginary parts of the dielectric function of $\text{Al}_2\text{O}_3$, $\text{Ta}_2\text{N}_5$, and
$\text{TiN}$ films are shown in Figure 3. These ALD-deposited materials
clearly demonstrate the change in dielectric function when comparing
transparent ($\text{Al}_2\text{O}_3$), semi-transparent ($\text{Ta}_2\text{N}_5$), and fully absorbing
($\text{TiN}$) materials.

$\text{Al}_2\text{O}_3$ is non-absorbing ($\varepsilon_2 = k = 0$) over the whole range probed
and its optical constants can therefore be described by a Cauchy
relationship. The refractive index of this 109 nm thick $\text{Al}_2\text{O}_3$ film is
1.63±0.02 at 1.96 eV. $\text{Ta}_2\text{N}_5$ is a semiconducting material and has an
optical band gap that falls in the photon energy range of most common ellipsometers. Accordingly, the dielectric function can be parametrized using
(three) Tauc-Lorentz oscillators. The refractive index and Tauc
optical band gap for this 49 nm thick $\text{Ta}_2\text{N}_5$ film are 2.68±0.02 at
1.96 eV and 2.5±0.1 eV. The conductive properties of the $\text{TiN}$ film
are evident from the large intraband absorption in the infrared part
of the photon spectrum caused by free conduction electrons in the
material. Describing this absorption by a Drude oscillator allows to
extract electrical properties from the optical dielectric function, such
as electrical resistivity, electron mean free path, and electron density
[12,13]. Moreover, two Lorentz oscillators are added to the Drude term
to account for interband absorptions in $\text{TiN}$. The 12 nm thick $\text{TiN}$
film has a refractive index of 1.3±0.02 at 1.96 eV. More details on the
optical parametrizations employed and the method of direct inversion
in Figure 3 can be found in Ref. [6].

ALD Studied by In Situ SE
Monitoring ALD film growth

The film thickness is among one of the most important parameters for
the application of ALD films. The thickness can be precisely controlled
by selecting the appropriate number of ALD cycles. Monitoring the
ALD process by in situ SE allows determining the film thickness at any
stage during the process and to calculate the ALD growth per cycle
during the film growth. Moreover, SE provides the opportunity to con-
trol the process such that the film deposition can be actively stopped
when the thickness targeted has been reached.

The film thickness as a function of ALD cycles as determined by
in situ SE is shown in Figure 4 for the ALD processes of $\text{Al}_2\text{O}_3$ [14],
$\text{Ta}_2\text{N}_5$ [15], and $\text{TiN}$ [13]. As generally expected for an ALD process,
the thickness increases linearly with the number of cycles; although in
some cases a (pronounced) film nucleation effect can occur.

In the linear region, the growth rates, i.e., the amount of material
deposited per cycle, can be obtained from linear regression analyses
of the data. For the data in Figure 4 this resulted in growth rates of
0.118±0.005, 0.054±0.005, and 0.041±0.005 nm/cycle for the $\text{Al}_2\text{O}_3$,
$\text{Ta}_2\text{N}_5$, and $\text{TiN}$ films, respectively. It is noted that the growth rates of ALD
processes typically are (considerably) smaller than one monolayer
(2-3 Å) per cycle. Among others, this can be related to the number of
adsorption sites available on the surface and to steric hindrance effects
during precursor adsorption.

The increase in film thickness during the first deposition cycles
reveals that the ALD growth of $\text{Al}_2\text{O}_3$ proceeds immediately on an
H-terminated Si substrate. Similarly, ALD of $\text{Ta}_2\text{N}_5$ on a native oxide
covered Si substrate shows immediate linear growth. These two growth
curves demonstrate that these metal-organic precursor molecules
readily react with the substrates employed. A completely different
nucleation behavior is observed for ALD of $\text{TiN}$ on a thermally grown
$\text{SiO}_2$ surface. A distinct nucleation delay is observed and the growth
Film thickness as a function of number of ALD cycles for growth of (a) $Al_2O_3$ from $Al(CH_3)_3$ precursor and $O_2$ plasma on a H-terminated $Si$ substrate, (b) $Ta_3N_5$ from $Ta[N(CH_3)_2]$ precursor and $NH_3$ plasma on a native oxide covered $Si$ substrate, and (c) $TiN$ from $TiCl_4$ precursor and $H_2$-$N_2$ plasma on a thermally grown $SiO_2$ substrate. The film thicknesses are calculated using the optical parameterizations shown in Figure 3.

starts only after ~20 ALD cycles. This behavior is consistent with the inability of the $TiCl_4$ precursor molecules to react with the siloxane bridges mainly present on the thermal $SiO_2$ substrate. The slow nucleation is caused by the limited surface density of defect sites and OH groups on which the $TiCl_4$ can absorb and nucleate to start film growth.

These results demonstrate the ability of in situ SE to accurately determine the film thickness of the nanometer thick ALD films. Moreover, cycle-by-cycle data acquisition enables to monitor the film nucleation and linear growth region in detail. In this respect it is mentioned that the determination of the growth rate during deposition allows for fast optimization of the ALD process, where the influence of deposition parameters on the growth rate can easily be obtained from a single deposition run [6].

Monitoring electrical film properties
Insight into the electrical properties of conductive films can be derived from the dielectric function by adopting the Drude parameterization. Therefore, monitoring the ALD film growth by in situ SE provides the opportunity to investigate the influence of ALD process conditions on the electrical film properties obtained [6,11,13].

The resistivity of the TiN films as determined from in situ SE and ex situ four-point probe (FPP) measurements is shown in Figure 5 as a function of deposition temperature in the range from 100 to 400 °C. In order to make a proper comparison with the FPP resistivity determined at room temperature, first the in situ SE resistivity values obtained at the deposition temperature were corrected to values representing room temperature [13]. The resistivity values obtained by in situ SE and ex situ FPP were in good agreement, especially for films deposited at substrate temperatures above 200 °C. Both techniques show that the resistivity of the TiN films increases for depositions at lower temperatures. This effect can be related to the increase in chlorine impurity content of the films, as was determined by Rutherford backscattering spectroscopy (RBS) and shown in the inset of Figure 5. In turn, the increase in impurity content causes the electron mean free path to decrease due to more pronounced electron-impurity scattering in the film [4]. In addition, the discrepancy between the resistivity values determined by SE and FPP at low temperatures (100 °C) can also be related to the impurity content.

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continued on page 40
In Situ Spectroscopic Ellipsometry
continued from page 39

The higher impurity content and the related lower film density make the films more susceptible to post-deposition oxidation when the films are exposed to air. This directly affects the ex situ measurements.

Figure 5. Electrical resistivity of plasma-assisted ALD TiN films as a function of deposition temperature. The resistivity is determined by in situ spectroscopic ellipsometry and ex situ four-point probe (FPP) measurements. The change in resistivity with deposition temperature can be related to the chlorine impurity content of the films as shown in the inset.

The agreement in the electrical resistivity deduced from the optical model and obtained by the FPP validates the optical Drude-Lorentz model employed to describe the dielectric function of these thin TiN films. Moreover, these results demonstrate that in situ SE provides an accurate means to investigate electrical properties of conductive films and their dependence on the deposition conditions.

Distinction of different material phases
The dispersion in the optical constants gives immediate insight into the optical properties of the films and, therefore, on the material properties. The influence of the ALD deposition parameters on the material properties can therefore be deduced by monitoring the dispersion in optical constants by in situ SE. This is demonstrated for tantalum nitride (TaN) that can exist in different crystalline phases and for which it was shown that the TaN phase and film properties can be tailored by varying the plasma step in the remote plasma ALD process [15].

Figure 6 shows the imaginary part ($\varepsilon_2$) of the dielectric functions of the TaN films that were deposited using different plasma conditions in the ALD cycle. The inset shows the film composition as determined by Rutherford backscattering spectroscopy. Adding more nitrogen into the plasma, result in a transition from conductive, cubic TaN, to semi-conductive Ta$_3$N$_5$ films. This transition is clearly visible in the dielectric function of the TaN films acquired by SE.

The dielectric function of the TaN film obtained using a pure H$_2$ plasma in the ALD process contains a prominent Drude absorption that is related to the free conduction electrons in the film. Moreover, it is observed that the strength of the Drude absorption, i.e., the measure of the conductivity, can be increased by extending the H$_2$ plasma exposure time used in the ALD cycle. Admixing little N$_2$ (2%) to the H$_2$ plasma strongly reduces the magnitude of the Drude absorption in the film and the two Lorentz oscillators become clearly visible. The dielectric function of the Ta$_3$N$_5$ film deposited using a H$_2$-N$_2$ (1:1) plasma clearly differs in shape. This dielectric function is best described by a parametrization employing a Tauc-Lorentz oscillator and an additional Lorentz oscillator, which is added to account for the small absorption below the optical band gap. The dielectric function of the Ta$_3$N$_5$ film deposited using a NH$_3$ plasma clearly shows an optical band gap and is best described by a parametrization consisting of three Tauc-Lorentz oscillators.

From the above mentioned, it is evident that by monitoring the dielectric functions by in situ SE, the change in film composition and crystalline phase can already be probed during the ALD process when the film is being deposited.

Conclusions
In this paper, the versatility of in situ spectroscopic ellipsometry to study atomic layer deposition processes has been exemplified. It has been shown that:

- Monitoring the thickness as a function of number of ALD cycles enables calculation of the growth rate during the ALD process;
- Insight into the nucleation behavior of the ALD films can be obtained by acquiring cycle-by-cycle data during initial film growth;
- Optical film properties, such as refractive index, extinction coefficient, and optical band gap, can be obtained from the energy dispersion of the optical constants;
- Electrical properties of conductive films can be calculated from the Drude absorption by conduction electrons in the film;
- For certain materials, insight into film composition can be derived from the “shape” of the optical dispersion in the dielectric function;

The value of SE in monitoring the film growth has recently been recognized by researchers and ALD tool manufacturers and has led to the development of commercial ALD reactors with integrated in situ spectroscopic ellipsometry capability (cf. Figure 2). It is, therefore, anticipated that in situ SE has a bright application prospect in the field of ALD.

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Erik Langereis is a postdoctoral researcher at the Department of the Applied Physics of the Eindhoven University of Technology in the Netherlands. He has held a PhD degree from the same university since 2008. In his work he focuses on the development of atomic layer deposition processes as well as the study of the underlying reaction mechanisms by a variety of in situ diagnostics. He initiated the application of in situ spectroscopic ellipsometry during atomic layer deposition.

Erwin Kessels is an associate professor at the Department of Applied Physics of the Eindhoven University of Technology in the Netherlands. He obtained his PhD degree at the same university in 2000. His research covers the field of (plasma-based) synthesis of thin films and nanostructures using methods such as plasma-enhanced chemical vapor deposition and atomic layer deposition. The main application areas considered are photovoltaics and nanoelectronics. The research is complemented by fundamental studies of thin film growth mechanisms by advanced diagnostics including non linear surface spectroscopy.

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