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In situ spectroscopic ellipsometry during atomic layer deposition of Pt, Ru and Pd

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Abstract

The preparation of ultra-thin platinum-group metal films, such as Pt, Ru and Pd, by atomic layer deposition (ALD) was monitored *in situ* using spectroscopic ellipsometry in the photon energy range of 0.75–5 eV. The metals' dielectric function was parametrized using a 'flexible' Kramers–Kronig consistent dielectric function because it was able to provide accurate curve shape control over the optical response of the metals. From this dielectric function, it was possible to extract the film thickness values during the ALD process. The important ALD process parameters, such as the nucleation period and growth per cycle of Pt, Ru and Pd could be determined from the thickness evolution. In addition to process parameters, the film resistivity in particular could be extracted from the modeled dielectric function. Spectroscopic ellipsometry thereby revealed itself as a feasible and valuable technique to be used in research and development applications, as well as for process monitoring during ALD.

Keywords: variable dielectric function, growth per cycle, nucleation

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last decade, nanometer-thin films have found myriads of applications for which atomic layer deposition (ALD) has become the prevalent technique when these films need to be deposited uniformly and conformally on complex 3D surfaces with sub-monolayer thickness accuracy [1]. In order to control and monitor the film thickness during the ALD process, the optical and non-invasive technique of spectroscopic ellipsometry (SE) is increasingly used [2–9], since it is able to detect changes in nominal film thickness as small as 0.01 monolayers [2]. This powerful tool has been widely employed *in situ* to extract thin film properties of metal oxide and metal nitride thin films, as previously reviewed by Langereis *et al* [4]. One of the most important parameters obtained by SE is the thickness increase per ALD cycle, known as *growth per cycle* (GPC), from which also saturation and nucleation behavior can be derived during the characterization of an ALD process. Furthermore, optical film properties such as refractive index, extinction coefficient, and band gap can be extracted from the

SE data; and for certain films also material crystallinity, composition and electrical properties [2, 4, 5, 10–15].

Recently, thin films (5–50 nm) of Pt-group metals, such as Pt, Ru and Pd, have attracted interest for a wide range of emerging applications mostly in nano-electronics [16–20], for which precise thickness control, uniformity and conformality are also required [1, 21]. Several studies have shown that the initial growth of Pt, Ru and Pd by ALD on non-metallic substrates suffers initially from a substrate inhibited growth mode [22] and is characterized by island formation [23–25]. The initial metal-island formation during ALD is so pronounced that ALD has also become a method to synthesize Pt-group metallic nanoparticles [26–31]. This gives rise to additional considerations in measuring and modeling the obtained SE data in order to be able to extract some of the above-mentioned parameters from the data.

ALD is relatively new for Pt-group metals compared to other deposition techniques, such as physical vapor deposition (PVD), including sputtering and evaporation. Therefore, such films deposited by ALD have hardly been characterized

optically [3, 6, 32, 33]. The material properties of Pt-group metal films are dependent on the deposition method which in turn affects the dielectric function of the metal, as was demonstrated in a comparative study of Pt deposited by evaporation and sputtering [34]. Therefore, it is important to study the optical properties of Pt, Ru and Pd films deposited specifically with ALD to obtain reference data for future ALD studies.

Furthermore, most PVD metal films studied by SE had thickness values at which the metals were opaque and showed bulk-like optical properties [35, 36]. Zollner showed that 50 nm Pt films exhibited optical properties that were almost the same as bulk Pt [36]. However, ALD generally yields films with thicknesses well below 50 nm of which the optical properties can be very different from those of bulk metals [37]. This holds especially for films with thicknesses below 10 nm [38, 39].

The thickness of a thin film is generally extracted from the SE data via an optical model which typically consists of a stack of layers, and each layer represents a material having its own dielectric function and thickness value. To parametrize the dielectric function of conductive materials, Drude–Lorentz oscillators are the most frequently used [4]. The Drude oscillator describes the absorption of light due to free carriers in the film, while the Lorentz term(s) describe the absorption of light due to interband transitions of bound charges in the material [40–42]. The absorption of light in the infrared region (<2 eV) is generally due to free carriers; however, in the case of Pt, Ru and Pd, interband absorptions also occur in this region. The absorption at low energies can therefore not solely be attributed to the absorption due to free carriers [43]. Therefore, the Drude–Lorentz parametrization of ultra-thin Pt-group metal films in the optical range studied (0.75–5 eV) cannot be applied unambiguously.

This work aims at extending the work described in the review by Langereis *et al* [4] with findings on Pt, Ru and Pd as representatives for Pt-group metals. To this end, we monitored the film thickness *in situ* during Pt, Ru and Pd ALD. In the optical model for the dielectric function of the film, a ‘flexible’ parametrization was investigated that accounts for the above-mentioned challenges:

- material properties which are significantly different from those obtained by deposition techniques other than ALD;
- effects due to the initial island-growth during ALD;
- thickness-dependent dielectric functions for films thinner than ~ 10 nm;
- light absorption due to both, free and bound, charges in the spectral region below 2 eV.

This ‘flexible’ parametrization was introduced as a variational analysis method of optical spectra by Kuzmenko [44]. It can be regarded as a limiting case of a Drude–Lorentz parametrization, since it also uses pre-established shapes to fit optical data. The main difference lies in the number of these shapes, which can vary depending on the level of fitting accuracy desired. Due to a high number of these shapes, this variational fitting procedure allows for an accurate

shape control of the dielectric function, while at the same time being constrained to the Kramers–Kronig relationship, ensuring the physical meaning of the dielectric function [45]. This kind of variational parametrization has been used previously: (i) under the name of B-spline parametrization (see section 4.1) [45], to obtain the dielectric function of ‘optically challenging’ materials, such as SrTiO_3 films or Au particles [5, 9, 46], and (ii) under the name of variational dielectric function (VDF; see section 5) for superconductor materials [47–50].

This publication presents general accomplishments of SE which can be applied to any of the three metals (Pt, Pd and Ru) treated, such as the determination of film thickness and GPC using a B-spline model, and film resistivity by extending the VDF into a Drude–Lorentz model.

2. Preparation of the Pt, Pd and Ru films

The Pt and Pd thin films were deposited by ALD in a home-built ALD reactor [10] and the Ru films in an Oxford Instruments FlexALTM reactor [51]. The films were deposited by plasma-assisted ALD using MeCpPtMe_3 and an O_2 plasma for Pt, and $\text{Pd}(\text{hfac})_2$ and an H_2 plasma for Pd. A thick spacer film of 500 nm ALD Al_2O_3 was used to increase the optical contrast between the metallic films and the Si wafer, thereby enhancing the sensitivity of SE during the growth of Pt and Pd [52]. The Ru films were prepared by thermal ALD using $\text{CpRu}(\text{CO})_2\text{Et}$ and O_2 gas and they were directly deposited on Si wafers with native oxide, i.e. without the thick dielectric spacer film in-between. The set substrate temperature was 100 °C, 300 °C and 400 °C during Pt, Pd and Ru ALD, respectively. More details about the Pt and Pd ALD processes can be found elsewhere [3, 25]. With respect to the Ru process described in detail in a previous publication [24], the O_2 gas pressure for the films described in this work was increased to ~ 120 mTorr for 5 s to enhance the Ru nucleation on Si substrates. As a consequence, the overall GPC increased to ~ 1.6 Å/cycle, compared to the ~ 1 Å/cycle reported in [24].

The film properties obtained by ellipsometry were compared with the properties obtained by *ex situ* measurement techniques. The Pt and Pd film thickness values were studied by x-ray reflectometry (XRR) and the Ru thickness was measured by scanning electron spectroscopy (SEM) due to its high surface roughness. The resistivity of all the films was determined using a four point probe (FPP). Being still subjects of research, the processes did not yield optimized material properties in all cases. The Pt films were pure and smooth (0.4 nm roughness for a 30 nm film), but the Pd films contained $\sim 14\%$ C impurities [25] whereas the Ru films suffered from a high surface roughness (9 nm roughness for a 22 nm film) and delamination. The delamination is claimed to be due to the difficulty of Ru to wet non-metallic surfaces [32]. These effects are not uncommon for ALD metal films and can affect the film resistivity as will be discussed in section 5.

3. Optical characterization of the Pt, Pd and Ru films

3.1. In situ spectroscopic ellipsometry

SE is based on the change in polarization of incident polarized light upon its reflection from a sample material, as it is illustrated in figure 1. From the polarization of the reflected light the film thickness and dielectric function of the material can be deduced from the amplitude ratio ψ and the phase difference Δ . These two parameters are related to the complex Fresnel reflection coefficients, r_p and r_s , by the ellipsometry equation $\frac{r_p}{r_s} = \frac{E_{rp}/E_{rs}}{E_{ip}/E_{is}} = \frac{|E_{rp}|/|E_{rs}|}{|E_{ip}|/|E_{is}|} \exp[i(\delta_p - \delta_s)] \equiv \tan \psi \exp(i\Delta)$, where E represents the complex field amplitudes, the subscripts i and r represent the incident and reflected electric field, respectively, whereas s and p refer to the polarization of the electric field.

The ALD setups used in this work are equipped with optical viewports to monitor film growth by *in situ* SE. The silica windows are protected from film deposition by gate-valves, as illustrated in figure 1(b). The view port is designed to have an angle of $\theta = 70^\circ$ with respect to the substrate normal. This angle is close to the Brewster angle of Si (our most-commonly used substrate material) to ensure the highest sensitivity for the measurements for thin films. The data acquisition during the deposition was carried out by a J A Woollam, Inc. M2000U near-infrared (NIR) ellipsometer with an optical range of 0.75–5.0 eV, using the *CompleteEASE*® 4.48 software. The ellipsometer, equipped with a fixed polarizer, a rotating compensator and a fixed analyzer, is able to measure the four Stokes parameters in a single acquisition. The Stokes parameters relate the reflected polarized light intensity to the ellipsometric angles, ψ and Δ . The Stokes parameters are important for the evaluation of the fit and will be discussed separately in section 6.

The dynamic measurement procedure starts with the automatic acquisition of (ψ, Δ) spectra as soon as the gate-valves are opened. The dynamic data were acquired every 5 ALD cycles with a measurement time of 40 s during Ru and Pd ALD and during the first 200 cycles of Pt ALD. For the remaining 800 cycles of Pt ALD, the data were collected every 10 ALD cycles. For each deposition all the spectra were appended into a single file. In doing so, the starting model of each (ψ, Δ) spectrum during the analysis (see below) was based on the model of the previously modeled spectrum. This increases the accuracy of the fit and makes it possible to obtain an accurate GPC value directly from the fit.

Prior to modeling the dynamic data of the metal films, the optical response of the substrates was carefully characterized in order to minimize the fitting error of very thin films. The film stacks and associated optical model used in this study are schematically described in figure 2. The single-sided-polished Si wafer (200 μm thick) was fitted by a model including the temperature-dependent response of the silicon [53] to account properly for the substrate temperature used during the ALD process. The optical properties of the native SiO_2 layer of $\sim 2\text{ nm}$ on top of the Si and of the alumina films were described

Figure 1. (a) Schematic representation of linearly polarized light incident on a sample and reflected as elliptically polarized light. The subscripts i and r represent the incident and reflected electric field E , respectively, whereas s and p refer to the polarization of the electric field. (b) Schematic configuration of the spectroscopic ellipsometer mounted on the ALD reactor. The reactor is equipped with gate valves to protect the SE windows from film deposition. The light from the light source of the ellipsometer passes through the fixed polarizer (P) and the rotating compensator (RC) and is reflected from the substrate through a fixed analyzer (A) into the detector.

by the Cauchy parametrization, yielding an Al_2O_3 thickness of $498 \pm 1\text{ nm}$ for the experiments with Pt and Pd. All of the fit parameters of the Cauchy parametrizations were then fixed for each metal film, and ψ and Δ were numerically inverted to ϵ_1 and ϵ_2 , as described in [38]. Due to this precise substrate characterization, any changes in ψ and Δ from subsequent data sets can be ascribed to adlayers only; in this case to the metal films deposited.

3.2. Ex situ Fourier transform infrared reflectance

In order to obtain an optical resistivity value of the films, it is desirable to extract the Drude contribution from the dielectric function. As it was mentioned in the Introduction, this is not straightforward from data in the NIR range. Therefore, it was necessary to extend the measured range in the infrared spectrum, where the absorption by free carriers in the metal is most prominent [54]. The combination of SE data and Fourier transform infrared (FT-IR) reflectance data has successfully been applied previously to metal films deposited by PVD and chemical vapor deposition to obtain a uniquely-defined Drude–Lorentz description of the dielectric constant [55–57].

Figure 2. Schematic representation of the film stacks used (in the case of Ru ALD no Al_2O_3 was present) and the associated optical model used. The film thickness of each layer was extracted from the data using a parametrization of the dielectric function of the layer. The Cauchy parametrization of the Al_2O_3 was numerically inverted prior to modeling the metal films. The metal films were modeled using a variational dielectric function (VDF).

Table 1. Models used for the substrates in the fitting software packages used in this study, *RefFit* and *CompleteEASE*[®], and the reference thereof. KK is the acronym for Kramers–Kronig consistent, VDF stands for variational dielectric function. The abbreviation Ntve stands for the native silicon oxide layer and Si_Temp is a temperature-dependant silicon optical model; and JAW is the acronym of J A Woollam Co., Inc.

	RefFit		CompleteEASE
Spectral range	0.04–0.86 eV	0.75–5 eV	0.75–5 eV
Al_2O_3 (500 nm)	KK VDF [44]	KK VDF [44]	Cauchy [39]
SiO_2 (1–2 nm)	—	—	Ntve_JAW [53]
Si (>200 μm)	KK VDF [44]	KK VDF [44]	Si_Temp_JAW [53]

As a proof-of-principle for metal films deposited by ALD, we applied this procedure to the Pt, Ru and Pd films after deposition, because they were sufficiently thick to show bulk-like properties.

To this end, a Bruker Tensor 27 spectrometer was employed *ex situ* in reflection mode at an angle of 12° covering the spectral range of approximately 0.04–0.86 eV ($7000\text{--}400\text{ cm}^{-1}$) with a resolution of 2×10^{-4} eV (2 cm^{-1}). The reflectance data and the SE data were modeled simultaneously using the software *RefFit* [44]. The metal films were first modeled using a VDF (see section 5) which was further parametrized with a Drude-term and Lorentz-oscillators over the range of 0.04–5 eV.

Each reflectance spectrum is the average spectrum of 1000 scans and the systematic error assigned to the reflectance data in the *RefFit* software was a fixed error of 1%. The reflectance data are, therefore, given a fitting weight of 10000 (compared to 1) during the simultaneous fit of reflectance and SE data. Due to this fixed systematic error and this high fitting weight, the χ_{red}^2 of the Drude–Lorentz parametrization also has a weight of at least 10000 and is therefore meaningless. For this reason, the χ_{red}^2 values will not be discussed in this publication for the Drude–Lorentz parametrization.

In the *RefFit* software, it is not possible to load tabulated optical constants; therefore, the Si substrate and the Al_2O_3 film were fitted using the VDF in each spectroscopic range used. In the case of the native SiO_2 , we assumed that the thickness of 2 nm was negligible with respect to the thickness of the metal film. The substrate characterization is summarized in table 1 for each software and spectroscopic range used.

From the *ex situ* SE measurements on a variable angle stage, it became apparent that the SE was most sensitive to the metal films deposited on Si wafers for an angle of incidence of 85° . Therefore, the SE data appended to the reflectance data of the thick Pt, Ru and Pd films was taken at this angle of incidence.

4. ALD film growth of Pt, Ru and Pd studied by *in situ* SE

4.1. Variational analysis of the *in situ* optical spectra (0.75–5 eV)

To accommodate the optical properties changing with metal film thickness in the optical range of 0.75–5 eV, we chose to apply the VDF available in the *Complete-EASE*[®] software called B-spline [45]. In that case, the imaginary part of the dielectric function as a function of photon energy, ϵ , is represented by the linear sum of B-spline polynomials over a given number of knots, n :

$$\epsilon_2 = \sum_{i=1}^n c_i B_i(\epsilon) \quad (1)$$

where c_i are the B-spline coefficients and B_i are the B-spline polynomials of degree 3. As mentioned in the Introduction, the B-spline dielectric function can be ‘physical’ by enforcing that $\epsilon_2 \geq 0$ and that ϵ_2 and ϵ_1 fulfill the causality requirement of Kramers–Kronig consistency [45]. Recently, the dielectric function of amorphous carbon films and graphene were parameterized accurately without making assumptions on the physical properties of the layers using a Kramers–Kronig consistent B-spline parametrization [58, 59]. For ALD prepared films, SrTiO_3 was also parameterized by B-splines [5, 9].

Figure 3 shows the imaginary part of the dielectric function, ϵ_2 , obtained by the B-spline parametrization of spectra selected from the dynamic data acquired during Pt (a), Ru (b) and Pd (c) ALD. For each metal, the dielectric function ϵ_2 can accurately describe the thickness dependent optical response. Clearly, for all three metals the absorption behavior in the NIR region is sensitive to changes in film thickness, especially below 10 nm thickness. From previous studies using non-metallic substrate materials [27, 30, 31, 60], it is

Figure 3. The imaginary part of the dielectric function, ε_2 , determined by the B-spline parametrization at different stages of the (a) Pt, (b) Ru and (c) Pd deposition. For each dielectric function, the thickness and number of cycles (abbreviated by ‘c.’) are given. The number of knots used for the B-spline parametrization (see equation (1)) was 11, 6 and 6 for Pt, Ru and Pd, respectively. The graphs show that the dielectric function significantly changes in the infrared region, especially during the initial cycles (up to ~ 10 nm film thickness).

known that metals deposited by ALD initially grow as islands rather than films. For the particular case of Au particles (not prepared by ALD) [46], the thickness values obtained by the B-spline parameterization was compared with transmission electron microscopy (TEM) images. This comparison suggested that the variational parametrization delivered an *effective* dielectric function and thickness value. Furthermore, other models (e.g. an effective medium approximation, or adding a gradient to the B-spline of the bulk-like films) were

considered to account for the initial surface roughness caused by the island-like growth of the Pt, Ru and Pd films. These approaches lead to high parameter correlation of the fit and did not provide satisfactory results. Therefore, we suggest that the B-spline is an adequate parametrization for the films throughout their growth and is able to account for the surface roughness by delivering an effective dielectric function.

For Pt and Pd in figure 3, ε_2 decreases monotonously with increasing photon energy, whereas for Ru an absorption peak ~ 4 eV can be observed, notably for very thin films. Since the optical response of the substrate was well described prior to deposition, it is not likely that this absorption peak is related to the underlying Si, but instead is a real absorption peak of the Ru. Furthermore, this feature at ~ 4 eV loses amplitude with increasing Ru thickness, but never vanishes completely, indicating that it is a feature intrinsic to the Ru metal. In section 5, we show that the most adequate oscillator-based model for the bulk-like Ru film includes a Lorentz oscillator at ~ 4 eV, very close to the one reported by Choi *et al* [35]. A similar absorption feature at ~ 2 eV has been previously reported for thin Au films, even during the initial growth of the films [57].

4.2. Determination of film thickness and growth per cycle

As shown in the previous section, the film thickness can be extracted for each data set using a B-spline parametrization. These thickness values are plotted in figure 4 as a function of ALD cycles for Pt (a), Ru (b) and Pd (c). Initially, the thickness remains (almost) zero which represents the nucleation delay of the ALD processes. This nucleation delay is approximately 20, 20 and 100 ALD cycles for Pt, Ru and Pd, respectively. The film thicknesses determined at the end of the Pt and Pd deposition were 53.3 ± 0.4 nm and 40.9 ± 0.1 nm, respectively. These thickness values are in fair agreement with the values of 50 ± 2 nm for Pt and 36 ± 2 nm for Pd obtained by *ex situ* XRR. Between the nucleation delay and the final thickness value, the three plots exhibit a linear thickness increase which is characteristic for ALD film growth from which the GPC can be determined. For the Pt and Pd ALD processes, the GPC values are 0.55 ± 0.01 and 0.17 ± 0.01 Å/cycle, respectively. In this particular case, the error values represent the accuracy of the linear regression analysis of the thickness data points obtained by optical modeling. The Pt GPC is somewhat higher than the one reported previously (0.45 Å/cycle) [3], but such fluctuations in GPC have been observed occasionally for the plasma-assisted ALD process of Pt. For Pt films approaching 50 nm, it can be observed that the ‘noise’ in the thickness value increases. This can be attributed to the loss of sensitivity as the films become almost opaque.

In the case of Ru, the comparison is somewhat more complicated since Ru thickness values > 26 nm (i.e. for > 165 ALD cycles) cannot be extracted from the SE optical model due to the absence of the thick transparent (Al_2O_3) spacer in the film stack that can enhance the optical sensitivity. The slope of the linear thickness increase (figure 4(b)) delivers a GPC value of 1.6 ± 0.2 Å/cycle for Ru. From this value

Figure 4. Thickness increase of (a) Pt, (b) Ru and (c) Pd films determined by the B-spline parametrization of the *in situ* SE data. After the nucleation period, the thickness increases linearly with the number of cycles. The GPC of each deposition process is obtained by linear regression of the linear part of the plot.

it is possible to extrapolate the linear thickness increase and estimate the thickness value of the Ru film after 500 ALD cycles. On the basis of the GPC from the SE data, an expected thickness value at the end of the Ru deposition of ~ 77 nm could be estimated. The thickness was estimated to be ~ 90 nm using SEM, although this value is considered to be overrated due to the high surface roughness of the Ru film.

Figure 5. The imaginary part of the dielectric function, ϵ_2 , determined by the Drude–Lorentz dielectric function in the spectral range of 0.04–5.0 eV of rather thick (a) Pt, (b) Ru and (c) Pd films. The dotted lines represent the Drude contribution whereas the Lorentz oscillators are shown in the inset of each figure.

5. Drude–Lorentz parametrization for bulk-like films of Pt, Ru and Pd from the simultaneous fitting of ellipsometry and reflectance data (0.04–5 eV)

A variational parametrization is a very useful tool to extract the dielectric function of the Pt-group metals with proper curve shape control. Furthermore, it is much easier to add an oscillator-based description to features present in a dielectric function extracted by a VDF. Therefore, a VDF was performed in the *RefFit* software by fitting the ellipsometric and reflectance data simultaneously, using the final film thickness obtained from the B-spline parametrization. A VDF, like the B-spline parametrization, can be described by equation (1), in which

Table 2. Position, amplitude and broadening for the Drude–Lorentz parametrization of the Pt, Ru and Pd films shown in figure 5 compared to the parameters of earlier studies (indicated in italics). In the case of the Drude parameters, the amplitude is represented by $\hbar\omega_p$ and the broadening by $\hbar/\tau_D$, with ω_p and τ_D being the plasma frequency and the carrier scattering time, respectively. In the case of the Lorentz oscillators, the position is represented by $\hbar\omega_0$, the amplitude by $f\hbar\omega_p$ and the broadening by $\hbar\gamma$. The errors give the 90% confidence interval of the fitted value (which will be discussed below). When not stated specifically, the 90% confidence interval is equal to or less than 1% of the value.

	Position (eV)	Amplitude (eV)	Broadening (eV)	Position (eV)	Amplitude (eV)	Broadening (eV)	Ref.
Pt	0	7.18	0.09	0	7.54	n/a	[77]
	0.78	5.2 ± 0.1	0.6	0.7; 0.8; 0.9	5	0.9	[3, 35, 77, 78]
	1.2	6.5 ± 0.2	1.4	1.5; 1.7	4	2.2	[3, 35]
	3.1	12	6.7	2.2	10	4.3	[35]
				4.2	2.5	2.5	[35]
			$\varepsilon_\infty = 3.5$			$\varepsilon_\infty = 1.9$	[35]
Ru	0	3.0	0.04	0	n/a	n/a	
	0.4	3.3	1.04	0.6	4.1	1.1	[35]
	1.6	5.2	1.7	1.8; 1.5	9.3	1.7	[35, 61]
				2.9; 2.7	2.2	0.8	[35, 61]
	4.0	5.9	2.9	4.1	9.1	4.5	[35]
			$\varepsilon_\infty = 1.50$			$\varepsilon_\infty = 2$	[35]
Pd	0	4.8	0.21	0	3; 6.99	0.12; 0.21	[62, 78]
	1.27	7.5	2.76	1.16; 1.15	10	2.88	[62, 79]
	5.12	9.6	6.84	2.94	2.1	1.33	[62]
			$\varepsilon_\infty = 2.50$			$\varepsilon_\infty = 1$	[62]

case B_i are B-spline polynomials of degree 1. The obtained VDF over the extended photon energy range of 0.04–5 eV was then further parametrized by Drude–Lorentz oscillators for each metal film.

Since ε_1 and ε_2 are correlated by the Kramers–Kronig relation, we mainly show and discuss ε_2 . For metals, it is common to describe the dielectric function of metals as containing an *intraband* (D , for Drude) and *interband* (i) contribution(s), i.e. $\varepsilon_2(E) = \varepsilon_2^D + \varepsilon_2^i$ [40–42], which is represented as shown in equation (2) in the case of a Drude–Lorentz model with n Lorentz oscillators.

$$\varepsilon_2(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\omega/\tau_D} + \sum_{j=1}^n \frac{f_j \omega_p^2}{\omega_{0j}^2 - \omega^2 + i\gamma_j \omega} \quad (2)$$

In this equation, ε_∞ accounts for contributions from ε_2 outside the measured range when $\varepsilon_\infty > 1$. The resistivity of the metal, ρ , can be extracted from the Drude parameters, i.e. from the unscreened plasma energy $\hbar\omega_p$ and the average lifetime of the free carriers τ_D by the expression $\rho = 1/\varepsilon_0 \omega_p^2 \tau_D$. Lorentz oscillators are located at the energy position $\hbar\omega_{0j}$ and have γ_j as damping factor.

In the case of Pt, Ru or Pd, strong absorption from bound and free carriers can both occur below 2 eV [43]. To separate these contributions, reflectance measurements in the optical range from 0.04–0.85 eV were performed for the films after deposition and modeled simultaneously with the SE data in the *RefFit* software as described in section 3.2. The imaginary part of the dielectric function resulting from the Drude–Lorentz model in the range of 0.04–5 eV is shown in figure 5 for the three metals. The thickness was fixed to the value found by the B-spline model, and for Ru at the SEM thickness

of 90 nm. The parameters of the fit are listed in table 2 using the fitting terminology *position*, *amplitude* and *broadening*.

To verify the validity of these models, the parameters of the Lorentz oscillators can be compared with those of other studies, as also summarized in table 2. Overall, the results of this study agree fairly well with previous work on Pt-group metals not prepared by ALD. Choi *et al* [35] specifically investigated interband transitions experimentally and theoretically. Amongst others, they considered Pt and Ru, deposited by PVD, for a spectral range of 1–10 eV, hence exceeding our measurement range. The Lorentz oscillators from our work are in relatively good agreement with theirs. In the case of Pt, the oscillator positioned at 3.1 eV shows the biggest discrepancy. Instead of an oscillator at ~3 eV, Choi *et al* found two oscillators, one at 2.2 eV and one at 4.2 eV. Replacing the 3.1 eV oscillator from our model with two oscillators at 2.2 eV and 4.2 eV led to a high fitting correlation of the two oscillators, i.e. the fit became worse. For Pt, a second difference with the work of Choi *et al* lies in the value of ε_∞ , which is likely due to the different spectral range covered in the two studies. The remaining small differences can possibly be assigned to the different material properties obtained by ALD and PVD.

In the case of Ru, our oscillator positions are shifted ~0.2–0.3 eV with respect to Choi’s oscillators at 0.6 and 1.8 eV. The most striking difference is the absence of an oscillator ~3 eV. Adding such an oscillator at 2.9 eV to our data resulted in a high fitting correlation of the fit parameter. Henrion *et al* [61] reported a dielectric function for Ru whose shape is very similar to the one we report. Moreover, they also found a Lorentz oscillator at 1.5 eV, as well as one at 2.7 eV.

The Drude parameters and the Lorentz oscillator at 1.2 eV of the Pd film are in good agreement with reports in the

Table 3. Comparison of the optical resistivity (in $\mu\Omega\cdot\text{cm}$) with the FPP resistivity of the Pt, Ru and Pd films, shown in figure 5. The error in the optical resistivity values is represented by the 90% confidence interval which is equal to or less than 1% of the value for the three metals, and is therefore not shown. The bulk resistivity values are given at 27 °C for Pt and Pd and at 20 °C for Ru [80].

	Optical resistivity ($\mu\Omega\cdot\text{cm}$)	FPP resistivity ($\mu\Omega\cdot\text{cm}$)	Bulk resistivity ($\mu\Omega\cdot\text{cm}$)
Pt (53 nm)	12.6	13.0 ± 0.2	10.4
Ru (90 nm)	32.8	18.0 ± 0.6	6.7
Pd (42 nm)	67.5	67 ± 1	10.5

literature, most particularly with the work of Yamada *et al* [62]. However, we also find an oscillator at 5.1 eV. The amplitude of this oscillator is much higher than the one reported at 2.94 eV in their work. No good fit to our data could be obtained with an oscillator at a position of ~ 3 eV. The reason for the discrepancy in oscillator positions is not yet clear.

The resistivity values for the 53 nm Pt, 90 nm Ru and 40 nm Pd films calculated from the Drude parameters extracted from the model are in good agreement with the values obtained by *ex situ* FPP measurements, as shown in table 3. For Pt, the optical resistivity and FPP values coincide very well, and the optical resistivity is very close to the bulk resistivity of single crystal Pt. Since the ALD Pt films are polycrystalline, this slight discrepancy can mainly be attributed to scattering effects of conduction electrons at grain boundaries of the polycrystalline film [63, 64] and at the film surface [65, 66].

For the ALD Ru and Pd films, the resistivity is somewhat higher than the bulk resistivity. The Ru film delamination and the high Ru film roughness deteriorate electronic transport by phenomena which are complex to take into account in the SE model may be responsible for the discrepancy in optical resistivity and FPP values. In the case of Pd, the films of this study contained 14% of C impurities (see section 2), potentially leading to scattering of the conduction electrons at these C impurities [67], thereby increasing the measured resistivity values compared to the bulk resistivity of Pd. Nevertheless, the optical resistivity and FPP values, show a very good agreement.

6. B-spline fit reproducibility and goodness of the fit for Pt, Ru and Pd

The previous sections did not include a discussion on the goodness of the fit, which is crucial in order to select a given parametrization over another. To evaluate the goodness of the fit, the most commonly used parameters include mean squared error, the error bars, the uniqueness of a fit parameter, and the correlation of fit parameters. In this section, these fit parameters will be presented and discussed for the B-spline-based models obtained for the Pt, Ru and Pd films prepared by ALD. As mentioned in section 3.2, the χ_{red}^2 values obtained during the simultaneous fitting of the reflectance-FTIR and SE data are affected by the high fitting weight attributed to the FTIR data. Therefore, only data from SE will be discussed which was fitted using the B-spline parametrization over the spectral range of 0.7–5 eV.

The experimental data used to extract the ellipsometric angles, ψ and Δ , are the Stokes parameters mentioned in section 2; defined as follows: $S_0 = 1$; $S_1 = -\cos 2\psi$; $S_2 = \sin 2\psi \cos \Delta$; $S_3 = -\sin 2\psi \sin \Delta$. To obtain the best possible match between the experimental data and the model, *CompleteEASE*[®] and *RefFit* use the iterative Marquardt–Levenberg regression algorithm to minimize χ^2 , expressed in equation (3) [44, 68].

$$\chi_{\text{red}}^2 = \sum_{j=1}^p \frac{1}{N_j - M} \sum_{i=1}^N \omega_i \left(\frac{X_i^{\text{exp}} - X_i^{\text{mod}}}{\sigma_i^{\text{exp}}} \right)^2 \quad (3)$$

where N is the number of data points, M is the number of fit parameters, p is the number of datasets fitted simultaneously, X a data set (ψ , Δ , reflectance, etc.), w_i the weighting coefficient of the dataset X and σ the standard deviation of the normally dispersed N datapoints [44]. As ellipsometry uses the three Stokes parameters to extract ψ and Δ , *CompleteEASE*[®] uses S_1 – S_3 as datasets with a fixed standard deviation of ~ 0.001 . In *CompleteEASE*[®], the parameter χ_{red}^2 in equation (3) is commonly called mean squared error (MSE) for historical reasons, but strictly speaking an MSE does not include the first summation, i.e. the division by the number of degrees of freedom [69].

In general, there are three main parameters used to assess the quality and validity of a fit: (i) the reduced chi-square χ_{red}^2 (ideally ~ 1), (ii) the 90 % confidence interval which in our study has been represented by the error bars of the fit parameter value obtained and (iii) the uniqueness of the value of a fit parameter [70]. In figures 6(a)–(c), each (grey) data point shows the χ_{red}^2 value obtained for the Pt, Ru and Pd thickness values extracted from the *in situ* SE measurements. Starting from the thickest Pt film (figure 6(a)) to the thinnest, χ_{red}^2 is close to unity, remains (almost) constant until it starts to increase below ~ 20 nm film thickness, and finally peaks at a value of $\chi_{\text{red}}^2 \sim 6$ for a thickness value of ~ 6 nm. A similar behavior can be observed for Pd (figure 6(c)). Starting from the thickest Pd film to the thinnest, χ_{red}^2 increases until a thickness of ~ 7.5 nm is reached when it peaks at a value of $\chi_{\text{red}}^2 \sim 13$. According to Tompkins and McGahan [39], a χ_{red}^2 value around 10 is acceptable in the case of metal films. The rise in χ_{red}^2 as the films become thinner may indicate that around these thickness values, phenomena caused by the increasingly granular nature of the metal films due to the island formation might play a role [71, 72]. In the case of Au particles studied using SE and TEM, it was shown that the optical thickness obtained from the B-spline parametrization corresponds to the Au particle height measured by TEM [46]. From this study on Au particle, we conclude that effects due to metal-island formation are accounted for in the B-spline parametrization, thereby delivering an *effective* dielectric function and thickness value. Nevertheless, the thickness values extracted from the dielectric function are accurate from a modeling perspective, and this will be discussed in more details below by scrutinizing the 90% confidence interval and the uniqueness of the thickness value.

Figure 6. The χ^2_{red} value (left y-axis, light) corresponding to the fit of the experimental data and the confidence interval (right y-axis, dark) for each thickness value of the (a) Pt, (b) Ru and (c) Pd metal films. The graphs in (d)–(f) represent the uniqueness plot for a thin and thicker film.

The 90% confidence interval is a useful parameter to assess how reliable the Pt, Ru and Pd thickness values are. By definition, it means that the fit provides a 90% confidence that the true value of the fit parameter lies within the given interval. Based on this definition, if the interval is small, the value of the fit parameter is close to the true value and can therefore be regarded as accurate [72, 73]. The confidence intervals for each thickness value of Pt, Ru and Pd are also shown in figures 6(a)–(c). For all of the three metals the confidence interval is small for all thickness values.

The uniqueness plots for Pt, Ru and Pd for a thinner and a thicker film are shown in figures 6(d)–(f). They were obtained by varying the thickness values, and for each thickness value the other fit parameters are fitted. The extracted thickness is regarded as unique when it clearly has the lowest χ^2_{red} value of all the thickness values scanned. As indicated by the narrow confidence interval for Pd, the uniqueness of the thickness value is well defined for all thickness values, even for thicker films. The Pt thickness is uniquely defined for thin films, not for thicker ones, which is related to the decrease in sensitivity as the films are almost opaque. In the case of Ru, the evolution of χ^2_{red} and the uniqueness plots as a function of thickness behave differently from those of Pt and Pd. The reason does not lie in the material itself, but in the poorer optical contrast between Si and Ru due to the absence of a thick transparent spacer material. Nevertheless, the values of χ^2_{red} remain well under the value of 10 which is regarded as acceptable for metal films. In addition, while the uniqueness of the 7 nm-thin Ru film is not well-defined, the χ^2_{red} values for films of <8 nm are low (~2) and the 90% confidence interval is small. Overall, on the basis of this evaluation, the thickness values for Ru films are also regarded as fairly well-defined.

From figure 6, it is possible to conclude that the thickness values and the fit are reliable. However, it is also important to test the reproducibility of a fit. The uniqueness of a fit consists of the uniqueness of every individual fit parameter. For each fit parameter, the regression algorithm can converge to a local minimum of χ^2_{red} , and yet yield incorrect parameter values, even if the fit is good overall. It is therefore essential to probe the reproducibility of the graphs shown in figure 4 by employing different starting values. For example, the dynamic fit can once be started from the data at cycle number 200, and another time at cycle 500, etc. Selecting different starting values after the nucleation delay reproduced the graphs shown

in figures 6(d)–(f) quite well with only minor differences (i.e. <2 nm in final film thickness). This and the fact that none of the fit parameters were correlated yield strong support for the fact that the thickness determination using the B-spline approach is unique in the case of Pt, Ru and Pd films deposited by ALD.

The thickness values retrieved from the fit during the metal nucleation exhibit the largest χ^2_{red} in the case of Pt and Pd, and in the case of Ru the thickness values are not unique in this region. Therefore, the thickness values below the linear growth increase are indicative rather than absolute. Optical phenomena due to the initial island growth of the metal can arise and make the interpretation of the data very challenging, such as capacitive behavior of the islands, scattering due to size effects or phonon emission to name a few [67, 74–76].

7. Conclusion

ALD has gained considerable interest over the last decade as a technique able to deposit nanometer thin films of platinum-group metals, such as Pt, Pd and Ru. We monitored the evolution of the thickness and the dielectric function of the films using *in situ* SE in the range of 0.75–5 eV. Using a Kramers–Kronig consistent variational parametrization to account for the thickness-dependent dielectric functions, we were able to obtain accurate film thickness values at almost any stage of the ALD process. Based on this model, we found the nucleation delay and the GPC values to be 40, 20 and 100 cycles and 0.55 Å/cycle, 1.6 Å/cycle, 0.17 Å/cycle for Pt, Ru, and Pd, respectively. To study the films' electrical properties specifically, we performed reflectance-FTIR and modeled the resulting data simultaneously with *ex situ* SE data. The variational parametrization of the metal films over the large photon energy range not only provided important process-related information but also served as a basis for the more traditional Drude–Lorentz parametrization of the metals in the range of 0.04 eV–5 eV. The resistivity values from the Drude parameter and four-point-probe values were in good agreement, especially in the case of the Pt and Pd films, and the parameters of the Lorentz oscillators were in line with previous ellipsometry reports on Pt, Ru and Pd.

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