On the nucleation of Pt & Pd during atomic layer deposition & temperature programmed desorption for thin film analysis

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Summary

Atomic layer deposition (ALD) has gained a lot of interest lately, due to its ability to deposit very thin and conformal films (<10 nm). During the nucleation phase of ALD also nano-sized particles can be created. The deposition of nano-sized particles is of interest for catalytic applications whereas the semiconductor industry relies on the creation of films as thin as possible.

In the first part of this work the nucleation of Pd and Pt on Al₂O₃ deposited by ALD is investigated to gain a better understanding of particle formation during the nucleation process. Transmission electron microscopy (TEM) and spectroscopic ellipsometry (SE) were used as the main analysis techniques. It was found that during the initial stages of the nucleation process both Pd and Pt form particles. Although both Pt and Pd showed the same behavior in the development of island density and coverage, several differences were observed. Pd has a longer nucleation phase (1000 ALD cycles) compared to Pt (300 ALD cycles). Furthermore the size distribution of the particles is broader for Pt than for Pd and the shape of the particles is different. Pd has circular particles throughout the nucleation phase. In the case of Pt the initial particles are circular but coalesced particles are without a distinctive shape. The differences are related to the different surface chemistry of both processes (such as the stability of the hfac ligand on Al₂O₃ in the case of Pd), differences in particle ripening and differences in the catalytic activity of the noble metal during the nucleation process.

From the analysis of the in situ SE data, using a B-spline parameterization, it was possible to make a distinction between a nucleation phase and linear growth phase during ALD. Qualitative information was obtained on the percolation threshold and particle coalescence. To obtain quantitative information on the percolation threshold a combination of ex situ SE and FTIR was required. This was necessary because the SE data could not be extrapolated to lower photon energies due to intraband transitions at the edge of its measurement range. The conductivity obtained from the combination of SE and FTIR was in agreement with the four point probe data in the case of thin films, but deviations occurred near the percolation threshold due to the capacitive coupling of the particles at the percolation threshold.

The second part of this thesis consists of the work performed on the Hiden Analytical TPD workstation, recently acquired by PMP. Temperature programmed desorption (TPD) is an analysis technique able to provide information about adsorbate coverage and desorption energy. This information is helpful to gain a better understanding of the surface chemistry, in the field of catalysis but it is also of interest for ALD. An introduction to TPD has been provided and several TPD analysis methods have been discussed. During measurements several issues of the TPD workstation became apparent. It was found that the heater assembly easily created shorts which could be prevented by the installment of a ceramic tube. The installed sample temperature measurement method proved to be inaccurate. Therefore a calibration method has been suggested using samples with known effusion maxima. Unfortunately this method could not be implemented during this thesis work. A basic analysis of several materials created within the PMP group (graphene, Al₂O₃ and SrTiO₃) has been performed to demonstrate the possibilities of the technique.
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PART I:

Nucleation of Pt and Pd during ALD
Chapter 1  Introduction

Atomic layer deposition (ALD) is a thin film deposition technique known for its good growth control, uniformity and conformality\textsuperscript{12}. It was introduced in the mid 1970’s by Suntola et al.\textsuperscript{3} Due to the inherently low growth rate of the technique the number of applications remained initially scarce. However, with the increased downscaling in semiconductor device manufacturing the interest in the technique has grown tremendously since the late 1990’s \textsuperscript{4}.

So far most research on ALD has been focused on the deposition of metal-oxides and metal-nitrides. These materials, such as HfO\textsubscript{2}, are used in the silicon device industry as a gate oxide in transistors. This process is implemented in industry by Intel since the introduction of its 45 nm node\textsuperscript{5}. Other applications of ALD materials include wear resistant coatings\textsuperscript{6}, transparent conductive oxides for displays\textsuperscript{7} and solar cells\textsuperscript{8}, and gas sensing applications\textsuperscript{9}.

Recently, also the ALD of noble metal films has gained an increasing amount of interest. Using ALD both noble-metal nanoparticles and thin films can be deposited. The nanoparticles have shown to be efficient catalyst in various processes such as the oxidation of carbon monoxide\textsuperscript{10} or the decomposition of methanol for fuel cell applications\textsuperscript{11}. Depending on the application the typical size of the particles varies between 1 to 10 nm\textsuperscript{11–14}. Noble metal films are required for applications in micro-batteries, capacitors or fuel cells\textsuperscript{15,16}.

Since both particles and thin films can be deposited using the same ALD process, real-time monitoring is desired to gain control over the morphology of the deposits. In this work the nucleation of Palladium (Pd) and Platinum (Pt) on aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) is investigated using Transmission Electron Microscopy (TEM). Furthermore spectroscopic ellipsometry is investigated as a tool to provide real-time information on the nucleation of noble-metal ALD processes. The basic principle of ALD is discussed in Section 0 using Al\textsubscript{2}O\textsubscript{3} as the model system. In Section 1.2 ALD of noble metals is discussed in more detail. The motivation of this project, goal and outline of Part I of this thesis are discussed in Section 1.3

1.1 Atomic layer deposition

ALD consists of two steps, referred to as half-cycles, which are separated from each other by pump or purge steps. To further illustrate the ALD process the deposition of Al\textsubscript{2}O\textsubscript{3} is used as an example. Al\textsubscript{2}O\textsubscript{3} is one of the first materials to be deposited by ALD and the process is well understood\textsuperscript{2}. A schematic overview of the process is given in Figure 1.

For the deposition of Al\textsubscript{2}O\textsubscript{3} trimethylaluminum (TMA) is dosed in the ALD reaction chamber during the first-half cycle. TMA is called the precursor as it contains the Al to be incorporated into the film. The TMA reacts with the OH groups present on the surface as it adsorbs:

$$\text{Al-OH}_{(s)} + \text{Al(CH}_3)_3_{(g)} \rightarrow \text{Al-O-Al(CH}_3)_2_{(s)} + \text{CH}_4_{(g)}$$  \textsuperscript{1.1.1}
Where \((s)\) represents surface groups and \((g)\) represents gas species. TMA is dosed into the chamber until all surface groups have reacted. Because the precursor molecules do not react with the newly created surface groups, the reaction is self-limiting\(^{17}\). To remove the \(\text{CH}_4\) and the excess TMA the chamber is evacuated by a pump step or purged using an inert gas, for example Argon.

In the second half-cycle \(\text{H}_2\text{O}\) is dosed into the chamber. The \(\text{H}_2\text{O}\) (which is called the reactant) reacts with the surface groups created during the first half cycle. Leaving behind a (sub-)monolayer of the material to be deposited:

\[
\text{Al-CH}_3(s) + \text{H}_2\text{O}(g) \rightarrow \text{Al-OH}_3(s) + \text{CH}_4(g)
\]

Because the \(\text{H}_2\text{O}\) only reacts with the surface groups created during the first half cycle also this reaction is self-limiting, when sufficient reactant is dosed into the chamber. After the \(\text{H}_2\text{O}\) exposure again a pump or purge step is required to remove the \(\text{CH}_4\) and excess \(\text{H}_2\text{O}\) from the chamber. This prevents that the TMA reacts inside the chamber with \(\text{H}_2\text{O}\) in the next cycle and it eliminates a flux dependent growth contribution. During the second half-cycle the surface groups used in the first-half cycle are regenerated allowing for the process to be repeated until the desired thickness of the \(\text{Al}_2\text{O}_3\) is achieved. The complete process of precursor and reactant exposure is referred to as one ALD cycle. The thickness increase per cycle is referred to as the growth-per-cycle (GPC).

**Figure 1:** Schematic overview of the ALD process for \(\text{Al}_2\text{O}_3\). During the first half-cycle the substrate is exposed to TMA (the precursor), during the second half-cycle the surface is exposed to \(\text{H}_2\text{O}\) (the reactant). The half-cycles are separated from each other by purge or pump steps. The different molecules are also indicated Al (red), \(\text{CH}_3\) (green), \(\text{H}\) (white) and O (Blue).

If during both half-cycles sufficient precursor and reactant is dosed into the chamber, i.e. all the surface groups have reacted, the GPC is independent of the precursor and reactant flux. This has the advantage that the same amount of material is deposited everywhere on the substrate, independent of the surface area or aspect ratio of the substrate, resulting in a uniform and conformal film. Combined with the (sub)monolayer growth control this makes ALD a very interesting technique for a wide range of applications\(^{1,2}\).
1.2 ALD of noble metals

In contrast to the ALD of Al₂O₃ the reaction pathways of noble-metals ALD are more complicated and often not fully understood. This is partly because the noble-metals are catalytically active and able to break bonds present in the precursor molecules used (C-H, C-C, H-H etc. depending on the noble metal). To further illustrate the additional complexity of a metal ALD process, the ALD of Pt using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe₃) as the precursor and O₂ gas as the reactant is discussed in more detail. The Pt process described below is considered as a model system for noble-metal ALD ¹⁸–²⁰.

![Figure 2: Schematic representation of the reactions occurring during the ALD of Pt. (a) During the precursor exposure first the precursor reacts with the chemisorbed oxygen in combustion and dehydrogenation reactions. When the oxygen is depleted dehydrogenation reactions and incomplete combustion occur. (b) During the reactant exposure first the hydrocarbons are removed from the surface in combustion reactions after which oxygen chemisorbs dissociatively on the surface (adapted from Mackus et al. ²⁰).](image)

Similar to the ALD of Al₂O₃ the surface is exposed to repeating cycles of precursor and reactant separated from each other by pump and purge steps. However due to the catalytic nature of the Pt surface the reactions occurring are different ²⁰. The ALD process of Pt is schematically shown in Figure 2. Due to the catalytic activity of the Pt, oxygen is chemisorbed dissociatively during the O₂ half reaction and remains there after the pump and purge step. During the dosing of precursor the oxygen adsorbed on the surface combusts part of the precursor ligands. Furthermore, because of the ability of a Pt surface to break C-H bonds, dehydrogenation reactions occur during the precursor step, which continue...
until the surface is saturated with ligands of the precursor molecule. These are removed via combustion reactions in the subsequent $O_2$ dosing step, regenerating the initial surface with adsorbed $O$. This allows for the repetition of the process. In contrast to the ALD of $Al_2O_3$ it is not the completed reaction of the surface groups that leads to a self-limiting behavior of the growth but the saturation of the surface with precursor ligands. Furthermore the catalytic properties of the Pt surface play an important role in the reactions that occur, i.e. the dissociative chemisorption and dehydrogenation reactions.

As stated before also noble-metal particles can be grown using ALD. This occurs for example when noble-metals are to be deposited on metal-oxide surfaces. The formation of particles is the direct result of the inhibition of the ALD chemistry on the oxide surface, caused by a combination of several effects including, the inability of the precursor to react with adsorbed oxygen, the relation between the surface free energy of the metal and that of the metal-oxide and the absence of the catalytic activity of the noble metal during in the early stages of the ALD process$^{10,13,21}$. As an example, the thickness development of Pt during ALD as a function of the number of ALD cycles in given in Figure 3.

During the nucleation phase of ALD nanoparticles are formed, indicated in Figure 3. The particles continue to grow as the number of ALD cycles is increased. Eventually the particles coalesce and a closed film is formed after which growth continues in a layer-by-layer fashion. During island growth the particles can agglomerate and merge due to ripening processes. Ripening processes are spontaneous processes in which the particles minimize their total energy. Atoms present on the surface of a particle interact with less neighbor atoms and are bonded weakly compared to atoms present in the bulk. Since larger particles have less surface atoms compared to bulk atoms they are energetically favored and grow at the expense of smaller particles$^{22}$. 
When hydrogen gas is used as the reactant for the ALD of a noble metal, such as for Pd, it is not possible to deposit material on metal-oxide substrates. This is because hydrogen gas is unable to remove the ligands from the oxide surface. In this case a plasma, a partially ionized gas, can be used as a reactant. The ions and radicals (neutral atoms with an unpaired electron) present in the plasma are highly active in chemical reactions and therefore have the ability to remove the ligands from the surface, making it possible to deposit Pd on metal-oxide surfaces.

1.3 Motivation, Goal and outline

In this work the nucleation of Pd and Pt on $\text{Al}_2\text{O}_3$ as deposited by ALD is investigated to gain a better understanding of the nucleation process. Two different noble metals are analyzed to identify the differences and similarities between noble-metal nucleation. For the analysis of the nucleation phase transmission electron microscopy (TEM) is used, which provides direct information on the particle size, shape and coverage.

TEM is time consuming and expensive to use. Furthermore TEM is difficult to implement in situ or real time, which is required to monitor and detect variations in the deposition process. A means to monitor the nucleation process in situ is required because the nucleation phase described in the previous section is strongly dependent on the process conditions. For this reason the nucleation process is also investigated using spectroscopic ellipsometry (SE). SE is a non-contact and non-destructive optical technique that is able to determine multiple material properties from a single measurement such as the dielectric function and thickness of a film with monolayer sensitivity. Therefore it can possibly be used to study nanoparticles and their properties as well. SE has the advantage that it can be implemented relatively easy in situ and has proven to be a viable optical technique for the study of ALD processes.

The goal of this work is thus twofold; a characterization of the Pd and Pt nucleation process using TEM and an investigation of the (additional) information that can be obtained from SE. The work performed is therefore divided into two research steps:

1. The investigation of the nucleation of Pt and Pd using TEM to gain information on particle size, density and shape. Special attention will be given to the differences and similarities between the two processes.

2. SE data (both in and ex situ) are combined with other ex situ techniques such as Fourier transform infrared spectroscopy (FTIR) and four point probe (FPP) measurements to correlate the data obtained by TEM and in-situ SE.

1.3.1 Outline of the Thesis Part I

In Chapter 2 the theory related to the optical analysis of the samples using SE and FTIR is discussed. A description of the ALD reactor and the different ALD processes is given in Chapter 3 together with an introduction on the different measurement techniques used. Chapter 4 contains the results on the growth study of Pd and Pt. In this chapter the TEM data and the SE data are discussed and a library linking the two techniques is established. Chapter 5 contains the conclusions together with an outlook.
Chapter 2  Theory

In this chapter the theory of metal light interaction is discussed together with the procedure followed to analyze the optical data obtained from the SE and FTIR measurements. The theory of SE and FTIR is presented in Section 2.1. In Section 2.2 the interaction between a metal (both particles and films) and an electromagnetic wave is described in more detail. How to determine the optical properties from the SE and FTIR data is described in Section 2.3 and 2.4 where the layer parameterizations and optical models used in this work are discussed. How the ‘goodness’ of the model is determined is described in Section 2.5. In Section 2.6 the similarities and differences of the B-spline parameterization used in this work are compared to the effective medium approximation (EMA) often used in literature.

2.1 Optical Analysis
The ALD growth of the as deposited Pd and Pt films starts with the formation of nanoparticles and eventually a closed film is formed. In literature both metal particles and films have been studied extensively and their optical properties have been characterized using various techniques, such as absorption measurements and spectroscopic ellipsometry \(^{24}\). The optical properties of particles and metal films are however dependent on the deposition method, i.e. the optical properties of sputtered films can differ from ALD grown films. Furthermore most studies focus on the characterization of either particles or films \(^{25,26}\). The optical analysis in this work is performed using \textit{in situ} SE and a combination of \textit{in situ} and \textit{ex situ} SE and \textit{ex situ} FTIR.

2.1.1 Spectroscopic Ellipsometry
Spectroscopic Ellipsometry (SE) is an optical analysis technique which measures the change in polarization of linearly polarized light reflecting from a surface. The change in the polarization state is caused by the different reflection coefficient of s- and p-polarized light on the sample. These reflection coefficients depend on thickness and dielectric function of the different layers composing the sample. SE determines two parameters, \(\Psi\) and \(\Delta\), as a function of the photon energy. \(\Psi\) represents the angle between the reflected waves of the s- and p-polarized light \((E_{rs} \text{ and } E_{rp}\) respectively, where \(E\) represents the amplitude of the electric field of the wave). \(\Delta\) represents the phase difference between \(E_{rs}\) and \(E_{rp}\), schematically shown in Figure 4.
The principle of an SE measurement, due to interactions with the sample the linearly polarized light is converted into elliptically polarized light. The parameters $\Psi$ and $\Delta$ contain information about the thickness and optical constants of the material. The angle of incidence is $\theta$.

The detection of a phase difference makes SE very sensitive to changes in the thickness, variations as low as 0.1 Å can be detected. $\Psi$ and $\Delta$ are related to the complex Fresnel reflection coefficients of the p- and s-polarized light, $R_p$ and $R_s$ respectively:

$$\rho \equiv \frac{R_p}{R_s} = \tan\Psi e^{-i\Delta}$$  \hspace{1cm} 2.1.1

With $\rho$ the ellipsometric parameter. The Fresnel reflection coefficients contain the information about the dielectric function and thickness of a sample. Because SE measures the ratio of the Fresnel reflection coefficients it is insensitive to changes in the light intensity. This results in a high measurement accuracy and good reproducibility of the measured data.

### 2.1.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is an optical analysis technique in which infrared (IR) light incident on a sample is measured, in transmission or reflection mode. The transmission and reflection depend on the thickness and dielectric function of the different layers of a sample. FTIR measures the intensity of the transmitted or reflected light as a function of the photon energy using a broadband light source and a Michelson interferometer. Because the light intensity is measured a reference measurement is required to take into account the intensity of the source. The transmittance ($T$) of the sample under investigation can be determined using the following formula:

$$T = \frac{I_s}{I_0}$$  \hspace{1cm} 2.1.2

Where $I_s$ is the intensity transmitted through the sample and $I_0$ the intensity of the source, measured without a sample in the beam path. The reflectivity ($R$) can be determined in a similar way. However, in this case the reference measurement ($R_{\text{ref}}$) consists of measuring the reflection of an Au mirror. This Au mirror is also part of the beam path during the measurement of the sample ($R_{\text{meas}}$), a schematic overview is given in Figure 5. To calculate reflectivity the following formula is used:

---

* Transmission is the passing of a light beam through the sample, the transmittance describes how much of the incoming light passes through the sample. The same is true for reflection and reflectivity.
In this formula $R_s$ is the reflectivity from the sample and $R_{Au}$ the reflectivity of the gold mirror. The square root is required because the beam reflects of the sample two times. Equation 2.1.3 assumes that no backside reflections occur. To ensure that this assumption holds, the backside of the samples used in this work was painted black using spray-paint. The black paint absorbs the infrared beam preventing any backside reflections.

2.2 Metal light interaction
The optical properties of a material are dependent on the frequency of the applied electromagnetic wave. This frequency dependency is described by the dielectric function $\varepsilon(\omega)$:

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2$$

Where $\varepsilon_1$ is the real part of the dielectric function, $\varepsilon_2$ the imaginary part and $\omega$ the frequency of the incident electromagnetic wave. $\varepsilon_1$ describes the polarizability of the material and $\varepsilon_2$ is a measure for the absorption in a material\textsuperscript{24}. $\varepsilon_1$ and $\varepsilon_2$ contain the same information as the refractive index ($n$) and absorption coefficient ($k$) and are related via:

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2nk$$

It should be noted that $\varepsilon_1$ and $\varepsilon_2$ are not independent of each other. To ensure the system satisfies the causality principle, i.e. a material can only respond to an electromagnetic field after the field has been applied, $\varepsilon_1$ and $\varepsilon_2$ are related through the Kramers-Kronig relations\textsuperscript{23,27}.
In the case of Pd and Pt in the wavelength range investigated in this work (0.05 – 5 eV) the dielectric function is mainly determined by the response of the free electrons present in the material, although contributions from intraband transitions (transitions between energy levels in the valence or conduction band) are possible. As an example the dielectric function $\varepsilon_2$ of Bulk Pt and a Pt film are shown in Figure 6.

![Figure 6: Dielectric function of an 18 nm thick Pt film (orange) and bulk Pt (black). The maximum in $\varepsilon_2$ at 0 eV is related to the adsorption of free carriers whereas the peak at 0.8 eV is due to an intraband transition. (Bulk values obtained from Zöllner et al.29)](image)

The behavior of the dielectric function observed in Figure 6 can be explained as follows. $\varepsilon_2$ must always be larger than zero meaning that intensity of a wave cannot increase due to the interaction with a material, i.e. the absorption cannot be negative. At very high frequencies electrons are no longer able to respond to the electromagnetic field: $\varepsilon_1(\omega \rightarrow \infty) = 1$ and $\varepsilon_2(\omega \rightarrow \infty) = 0$, indicating that no interaction with the electromagnetic wave occurs. The maximum in $\varepsilon_2$ at 0 eV is related to the absorption of free carriers, and the peak at 0.8 eV is related to an interband transition of Pt30.

The optical properties of an 18 nm thick Pt film are similar to the bulk optical properties of Pt. Below 2.5 eV however deviations from the bulk values occur. This is because the dielectric function of a thin film depends on the thickness, especially below 10 nm23,24. A reason for this is that the thickness of the films becomes in the order of the mean free-path of the electrons, which results in the scattering of the electrons at the surface of the films24. Furthermore the films are often polycrystalline. Scattering then also occurs at the transition regions between different crystallites (grain boundaries)31. Scattering effects lead to a reduced mobility of the free-electrons and thus a lower conductivity. The optical conductivity ($\sigma$) is defined as follows:

$$\sigma(\omega) = \omega \varepsilon_0 \varepsilon_2(\omega)$$

2.2.4
Where $\varepsilon_0$ is the permittivity of free-space. A decrease in the conductivity therefore also explains the lower value of $\varepsilon_2$ for a Pt thin film compared to bulk Pt observed in Figure 6.

In the case of particles additional effects can play a role. Depending on the inter-particle distance the particles also interact with each other similar to interacting dipoles. These phenomena alter the dielectric response of a material during the nucleation phase making it different from the bulk.

### 2.3 Layer parameterization

To determine the dielectric function from the SE and FTIR data two attributes are required: a parameterization that describes the dielectric function of a material and a model that describes the interaction of the electromagnetic wave with the sample using the Fresnel equations. A sample can consist of multiple layers where the properties of each layer are described by its corresponding parameterization. The entire sample is described by a single model containing these parameterizations.

A parameterization describes the dependency of the dielectric function on the frequency of the incident electromagnetic wave. In this work two types of parameterization are used: the Drude-Lorentz parameterization and the B-spline parameterization. Each will be discussed in more detail below.

#### 2.3.1 Drude-Lorentz parameterization

The Drude-Lorentz parameterization is a classical parameterization that describes the interaction between electrons and the nucleus to which they are attached analogous to a damped mass-spring system. Electromagnetic waves incident on this mass spring system apply a force due to the application of an electric field. Because the nucleus has a much larger mass than the electron, it is assumed to be fixed in space. With the use of Newton’s second law the motion of the electron can be summarized in the following equation:

$$m_e \frac{d^2x}{dt^2} = -m_e \Gamma \frac{dx}{dt} - m_e \omega_0 x^2 - e E_0 e^{-i\omega t}$$  \hspace{1cm} \text{(2.3.1)}

Where $m_e$ is the electron mass, $t$ is the time, $x$ is the displacement from the nucleus, $\Gamma$ describes the phenomenological damping constant, $\omega_0$ is the resonance frequency (eigenfrequency) of the spring, $e$ the electron charge, $E_0$ the amplitude of the applied electric field and $\omega$ the frequency of the applied field. The equation represents the forced oscillation of an electron by the application of an electric field varying in time. By assuming a solution of the form $x(t) = a e^{-i\omega t}$, one can solve Equation 2.3.1 for the amplitude $a$. The dielectric function can be calculated by assuming that the dielectric polarization ($P$) of the total amount of electrons, $N_e$, is:

$$P = N_e e x(t) = \varepsilon_0 (\varepsilon(\omega) - 1) \cdot E_0 e^{-i\omega t}$$  \hspace{1cm} \text{(2.3.2)}

The dielectric function can then be written as:

$$\varepsilon(\omega) = \frac{\omega_p}{\omega_0^2 - \omega^2 + i\Gamma_\omega}$$  \hspace{1cm} \text{(2.3.3)}

Where the plasma frequency ($\omega_p$) is:
\[ \omega_p = \frac{e^2 N_e}{\varepsilon_0 m} \]

A combination of multiple oscillators can be used to describe the dielectric function of a material:

\[ \varepsilon(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_{pj}}{(\omega_{pj}^2 - \omega^2) + i\gamma_j \omega} \]

Where \( \varepsilon_\infty > 1 \), is used to take into account any contributions to \( \varepsilon(\omega) \) outside the measured range that are not taken into account by the Lorentz oscillators. A Lorentz oscillator with an eigenfrequency of zero Hz is called a Drude oscillator. A Lorentz oscillator describes the oscillations related to free charge carriers in a material. In the case of Pt, see Figure 6, the maximum at 0 eV related to the oscillations of the free carriers can thus be described using a Drude oscillator. The intraband transition visible at 0.8 eV can be described by several Lorentz oscillators, a deconvolution of the different oscillators that can be used to describe Pt is shown in the inset of Figure 7.

![Figure 7: Deconvolution of the Drude- (dashed line) and Lorentz oscillators (inset) that can be used to parameterize the dielectric function of Pt.](image)

The optical conductivity at \( \omega = 0 \) (Equitation 2.2.4) corresponds to the direct current (dc) conductivity and can be determined using four point probe (FPP). FPP therefore can be used to verify the optical constants obtained by the parameterization.

### 2.3.2 B-spline parameterization

The B-spline parameterization is a relatively new parameterization for the analysis of SE data, introduced by Johs et al.\textsuperscript{33} A B-spline is not based on a physical model; instead a mathematical description is used to parameterize the dielectric function consisting of several spline functions. A spline function is built up out of multiple polynomial segments, which are designed to be continuous up to a
In a certain degree, allowing for a smooth function to describe the optical constants. Basis-splines (B-splines) are a basis set for polynomial splines defined by \(33\):

\[
B^0_i(x) = \begin{cases} 
1 & t_i < x < t_{i+1} \\
0 & \text{otherwise}
\end{cases}
\]

\[
B^k_i(x) = \left( \frac{x-t_i}{t_{i+k}-t_i} \right) B^{k-1}_i(x) + \left( \frac{t_{i+k+1}-x}{t_{i+k+1}-t_{i+1}} \right) B^{k-1}_{i+1}(x)
\]

Where \(k\) is the degree of the B-spline and \(i\) and index for the location of the node points \(t_i\). The nodes or knots are the points in which one polynomial section follows on another. The total spline curve \(S(x)\) is constructed by a linear sum of the individual B-splines and describes the dielectric function:

\[
S(x) = \sum_{i=1}^{n} c_i B^k_i(x) = \varepsilon_2(\omega)
\]

In which \(c_i\) are the spline-coefficients which determine the contribution of each spline to the total spline curve. The total spline curve is constructed to be Kramers-Kronig consistent, giving the B-spline a physical meaning and only requiring the parameterization of \(\varepsilon_2\). In Figure 8 a) the basis splines of 0\(^{th}\), 1\(^{st}\), 2\(^{nd}\) and 3\(^{rd}\) order are shown. How the individual splines are used to construct the total spline curve is shown in Figure 8 b).

---

**Figure 8:** a) basis splines of 0\(^{th}\), 1\(^{st}\), 2\(^{nd}\) and 3\(^{rd}\) order, the dots represent the node points. b) linear sum (red) of the individual splines of 3\(^{rd}\) order (grey) the node points are also indicated the height of the node points represents the magnitude of the spline coefficient for each spline.
2.4 Optical modeling

An optical model is required to extract the physical parameters of a particular layer, such as thickness and dielectric function from the SE and FTIR data. The layer structure used for the different modes is shown in Figure 9. The structure resembles the two different substrates used in the experiments.

![Layer structure of the models used in this work](image)

**Figure 9**: Layer structure of the models used in this work, a) crystalline silicon substrate with an Al₂O₃ layer on which either the Pt or Pd is deposited, b) glass substrate with an Al₂O₃ layer on which either the Pt or Pd is deposited.

The *in situ* measurements are performed on the crystalline silicon substrate, with an Al₂O₃ layer of 500 nm thick. The thickness of 500 nm is required to uniquely determine the dielectric function and thickness of the Pd or Pt layer. This is because of the low optical contrast (difference in Ψ and Δ parameters) of silicon and the noble metals, making it difficult for SE to distinguish between them. The thick Al₂O₃ spacer layer creates interference fringes between the noble-metal layer and the Si substrate. These fringes are visible in the ellipsometric parameters, making them sensitive to thickness variations. This provides sufficient optical contrast to distinguish the noble metal film from the underlying silicon and allows for the determination of both layer thickness and dielectric function.

For the *ex situ* measurements glass is used as a substrate. The reason for this is that backside reflections cannot be eliminated from the FTIR reflection measurements of Si. This results in a distortion of the measured signal due to additional reflections of the backscattered beam inside the FTIR system before detection. Glass cannot be used for the *in situ* measurements; due to its low reflectivity also the metal substrate holder affects the SE signal (when using glass with a rough backside this can be avoided but then transmission measurements are no longer possible). In this case a thickness of 3 nm of Al₂O₃ was chosen to match that of the special TEM substrates used.

For the modeling of the *in situ* and *ex situ* data two different programs are used: CompleteEase™ (J.A. Woollam Inc.) and RefFIT²⁸,3⁵. CompleteEase is required for the *in situ* data as it allows for the real time monitoring and determination of the film properties. RefFIT on the other hand allows for the combination of SE and FTIR data.

Using CompleteEase the different layers of the model in Figure 9 a) are parameterized as follows. The crystalline silicon was parameterized as a semi-infinite (opaque) layer using tabulated values for the optical constants, provided by the CompleteEase program (Si_JAW). For the modeling of the Al₂O₃ a
more elaborate procedure was used. First the $\text{Al}_2\text{O}_3$ layer was parameterized with the Cauchy model\textsuperscript{23}, an empirical dispersion relation for transparent materials:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^3} \quad 2.4.1$$

$$k(\lambda) = 0 \quad 2.4.2$$

Where $A$, $B$ and $C$ are fitting parameters, $n$ the refractive index of the material and $k$ the absorption coefficient. In total four parameters were fitted $A$, $B$ and $C$ and the thickness of the layer $d_{\text{Al}_2\text{O}_3}$. The second step in the parameterization of the $\text{Al}_2\text{O}_3$ involved the use of a numerical inversion, which required the thickness obtained from the Cauchy model as input. Fitting the $\text{Al}_2\text{O}_3$ with a numerical inversion has the advantage that the layer of interest, in this case the Pt or Pd layer, does not include any artifacts of the $\text{Al}_2\text{O}_3$ fit\textsuperscript{28}. The substrate (Si with $\text{Al}_2\text{O}_3$) was characterized prior to a deposition and the fitting parameters were fixed during the noble metal deposition. For the noble metal layer a B-spline parameterization was used. An overview of the parameterizations used by CompleteEase is given in Table 1. How the ‘goodness’ of fit is determined is explained in the next section.

To model the \textit{ex situ} data RefFIT was used, which allows for the simultaneous fitting of both the FTIR transmission and reflection data and the ellipsometric parameters $\Psi$ and $\Delta$. To model the data the layer structure as shown in Figure 9 b) is used, the individual layers are again described using different parameterizations. RefFIT can only use the Drude-Lorentz parameterization or a variational dielectric function (VDF). The VDF is in essence a B-spline; to be precise it is a B-spline of 1\textsuperscript{st} order fitted every 2 data points, i.e. a node is assigned to half of the data points. Since no tabulated values can be used for the optical constants a different approach is used to parameterize the dielectric function of each layer.

First the dielectric function of the glass was determined by measuring the reflectance ($R$), transmittance ($T$), $\Psi$ and $\Delta$ of a bare glass sample. The glass substrate was characterized using a variational dielectric function (VDF) and a Lorentz oscillator. The Lorentz oscillator is used to get a reasonable initial fit. Then the VDF is added to the parameterization. This greatly speeds up the fitting procedure as compared to a VDF alone. From the parameterization the dielectric function of the glass could be determined, shown in Appendix A. Secondly, glass coated with $\text{Al}_2\text{O}_3$ was measured to obtain the dielectric function of the $\text{Al}_2\text{O}_3$ layer, for this the second layer was added to the model, parameterized by a single Lorentz oscillator. During the fitting procedure the optical constants of the glass were kept fixed. The dielectric function obtained can also be found in appendix A. With the substrate parameterized, the dielectric function of the Pd and Pt samples could be determined by adding a third layer to the model, while keeping the fitting parameters related to the glass and $\text{Al}_2\text{O}_3$ layer fixed. An example of such a fit can be found in appendix B. An overview of the parameterizations used by RefFIT can be found in Table 1.
Table 1: Parameterizations of the different layers used in the models of the CompleteEase and RefFIT program, the different measurement range over which the models extend is also indicated. The usage of a Drude-Lorentz oscillator is indicated by OSC

<table>
<thead>
<tr>
<th>Parameterization</th>
<th>Thickness</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CompleteEase</strong></td>
<td></td>
<td>0.75 – 5 eV</td>
</tr>
<tr>
<td>Pt or Pd layer</td>
<td>B-spline</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Point by Point</td>
<td>500 nm</td>
</tr>
<tr>
<td>c-Si</td>
<td>Si_JAW</td>
<td>Semi infinite</td>
</tr>
<tr>
<td><strong>RefFIT</strong></td>
<td></td>
<td>0.05 – 5 eV</td>
</tr>
<tr>
<td>Pt or Pd layer</td>
<td>VDF &amp; OSC</td>
<td>Fitted</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>OSC</td>
<td>3 nm</td>
</tr>
<tr>
<td>Glass</td>
<td>VDF &amp; OSC</td>
<td>0.7 mm</td>
</tr>
</tbody>
</table>

2.5 Assessment of the fit

To determine how well a model describes the experimental data a quantity is needed that describes the ‘goodness of the fit’. For this both CompleaEase and RefFIT use the reduced chi-squared error:

\[ \chi^2 = \sum_{j=1}^{p} \frac{1}{N_{j-M}} \cdot W_j \cdot \left[ \sum_{l=1}^{N} \left( \frac{y_{\text{mod}}^l - y_{\text{exp}}^l}{\sigma_{l}^l} \right)^2 \right] \]

Where \( N \) is the number of points measured, \( M \) the number of fitting parameters, \( p \) the number of data sets, \( Y \) a data set (\( \Psi, \Delta \) etc.) and \( \sigma \) the standard deviation of each data point. In both CompleteEase and RefFIT a weighing coefficient \( w_j \) of 1 is used as a default value. However in the case of RefFIT when fitting multiple data sets different weights are chosen for different data sets to account for the difference in systematic errors between the data sets. In this work the reflectance, transmittance and \( \Psi \) were assigned a weight of 1. \( \Delta \) however was assigned a weight of 0.001 for Pd and Pt films above the percolation threshold. Higher weighting values caused a divergence of the fit most likely caused by a systematic error in \( \Delta \). The CompleteEase software does not use \( \Psi \) and \( \Delta \) for the error calculation, instead the Stokes parameters \( S_1, S_2 \) and \( S_3 \) are used. These are related to \( \Psi \) and \( \Delta \) as following:

\[ S_1 = \cos(2\Psi) \]

\[ S_2 = \sin(2\Psi) \cdot \cos(\Delta) \]
The reason Stokes parameters are used is that their values are bounded between -1 and 1 and their standard deviation is fixed for all measurements, 0.001. This allows for a faster error computation. An overview of the different values used for each program is given in Table 2.

Table 2: An overview of the different parameters used in the calculation of $\chi^2$ used by RefFIT and CompleteEase. RefFIT can also be used to fit reflectance and transmittance data.

<table>
<thead>
<tr>
<th>Possible data set</th>
<th>RefFIT</th>
<th>CompleteEase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R, T, \Psi, \Delta$</td>
<td>$S_1, S_2, S_3$</td>
<td></td>
</tr>
<tr>
<td>Standard deviation</td>
<td>Raw data</td>
<td>0.001</td>
</tr>
<tr>
<td>Weight</td>
<td>1, except for $\Delta$: 0.001</td>
<td>1</td>
</tr>
</tbody>
</table>

A fit that matches the measured data exactly has a $\chi^2$ of 1. Values lower than 1 are also possible but this indicates that the fit is better than expected from the random measurements error, i.e. measurement noise is included in the fit. Apart from a low value for $\chi^2$ also fit uniqueness is of importance. Fit uniqueness is a measure for the parameter correlations. As an example the uniqueness of the thickness obtained from the fitting of Pd on an Al$_2$O$_3$ (500nm) coated silicon substrate is shown in Figure 10 a). In Figure 10 b) the result of adding an additional fit parameter correlated to the Pd thickness is shown: $\chi^2$ is reduced but the fit is no longer unique.

Figure 10: $\chi^2$ as a function of the Pd Film thickness, each point corresponds to a different fit where the thickness was fixed and all other parameters fitted. a) It can be seen that there is minimum in $\chi^2$ for a thickness of 17.6 nm indicating that a unique value for the thickness is obtained. b) Adding an additional parameter reduces $\chi^2$ but the fit uniqueness is lost as there are multiple thicknesses corresponding to the lowest $\chi^2$ value.
2.6 EMA versus B-spline

In this work a B-spline parameterization is used for the determination of the dielectric function of Pd and Pt. A B-spline can also determine the thickness of the layer measured. However the noble metal layer consists of particles during the nucleation phase. The thickness and dielectric function determined by the B-spline can therefore be interpreted as an effective layer consisting of particles and voids, an effective medium. A schematic representation of this is shown in Figure 11. It should be noted that the effective layer thickness does not necessarily correspond to the maximum particle size, as will be shown in Chapter 4.

**B-spline thickness**

![B-spline parameterization diagram](image)

*Figure 11: A schematic overview of how a B-spline parameterization approximates a particle system. The thickness determined by the B-spline is an effective layer thickness in which both the particles and the voids between them are included.*

The dielectric function obtained from the B-spline is thus a mix of the dielectric function of the particles, that of the space between the particles and the interactions between the particles. In literature such systems are often described by an effective medium approximation (EMA):

\[
\frac{f_a}{\varepsilon_a} + \frac{f_b}{\varepsilon_b} = 0
\]

Where \( f_a \) and \( f_b \) is the volume fraction of each constituent with dielectric function \( \varepsilon_a \) and \( \varepsilon_b \) respectively, in this case Pd or Pt and air. The parameter \( \gamma \) is defined as \((1-q)q\) where \( q \) is a factor related to the shape of the particles (\( q=1/3 \) for spherical particles). \(<\varepsilon>\) is the dielectric function of the mixed material.

There are however problems with the application of EMA approximations that make them not suitable for the modeling the nucleation of Pd and Pd or noble metals in general. This is because an EMA requires an input for the dielectric function of the constituents. For this the values of the bulk material are often chosen. However as stated in Section 2.2 the dielectric function of particles and films is different from those of the bulk material due to scattering effects and interactions between particles. Furthermore EMA theories fail to describe the transition from isolated particles to a closed film. At the transition region a long range order forms between the connected particles, the system becomes conductive. This is not taken into account by EMA models.

For the reasons mentioned above a B-spline parameterization is better suited to model the transition from particles to a closed film than an EMA. Furthermore a B-spline does not require the input of the dielectric functions of the constituents to determine the dielectric function of the effective layer.
Chapter 3  Experimental Details

In this chapter the ALD reactor used to deposit the Al₂O₃, Pt and Pd layers is discussed in Section 3.1. The precursors and reactants used for the depositions together with the other deposition parameters are given in Section 3.2. The material properties of the Pd and Pt deposited by ALD are discussed in Section 3.3. The different diagnostics used in the nucleation study are described in Section 3.4.

3.1 ALD Reactor

The Al₂O₃ layers that are used as a substrate material for the nucleation study as well as the Pd and Pt layers have been deposited by ALD. Al₂O₃ was deposited using the Oxford Instruments FlexAL reactor. For the depositions of Pd and Pt the homebuilt ALD-I reactor has been used. The reactors are similar in design, therefore only the ALD-I reactor is discussed here. A schematic overview of the reactor is given in Figure 12. The main chamber of the reactor consists of a stainless steel vessel to which the other components, a plasma source, pumping system and gas dosing system are connected. All components are isolated from the main chamber with gate valves.

![Figure 12: Schematic overview of the ALD-I reactor used in this work. The main components; the plasma source, turbo pump, and precursor dosing system and in situ SE are indicated in the figure as well.](image)

The inductively coupled plasma (ICP) source consists of a copper coil wrapped around a quartz tube and is connected to a power supply. The power supply generates a radio-frequency plasma with a maximum power of 300W. The ICP source is connected to a gas supply system which allows for the generation of various plasmas. The pumping system consists of a turbo molecular pump backed by a rotary vane pump. It keeps the system under vacuum, at a base pressure of ~1·10⁻⁶ mbar, and removes precursors and reactants form the chamber during deposition. For the dosing of the precursor Ar is used as the
carrier gas. The precursor is heated to achieve reasonable vapor pressure in the bubbler and is transported to the main chamber using an Ar flow. The advantage of using an Ar flow over a vapor drawn based dosing system is that precursors with low vapor pressures can be used. The lines through which the precursor is fed and the reactor walls are heated to prevent precursor condensation. This reduces the amount of precursor used and prevents clogging of the lines.

### 3.2 Deposition Parameters

Table 3 shows an overview of the settings used to deposit Al$_2$O$_3$, Pd and Pt throughout this work. As can be seen in the table both Pd and Al$_2$O$_3$ are deposited using a plasma based ALD process and Pt using regular (thermal) ALD.

Al$_2$O$_3$ is deposited using Tri-Methyl-Aluminum (TMA) as the precursor and oxygen plasma as the reactant. Boron doped Corning 7059 glass and crystalline silicon (100) wafers were used as substrates. The glass substrates were coated with 3 nm of Al$_2$O$_3$ needed to deposit a closed film. On the crystalline silicon substrates a layer of 500 nm of Al$_2$O$_3$ was deposited to provide sufficient optical contrast for the in situ SE measurements.

Pt is deposited using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe$_3$) as the precursor and oxygen as the reactant. This is the most standard ALD process for Pt metal ALD and is therefore chosen here. Pd is deposited using palladium(II)hexafluoroacetylaceonatethe (Pd(hfac)$_2$) and a hydrogen plasma as reactant. The process involving Pd(hfac)$_2$ and formalin is more commonly used but requires a higher substrate temperature compared to the plasma process presented here. The higher substrate temperature is undesirable for many applications and therefore the Pd(hfac)$_2$ and hydrogen plasma process is used.

Before each noble metal deposition the Al$_2$O$_3$ coated substrates were cleaned using 3 min of O$_2$ plasma to remove any surface contaminations, such as adventitious carbon created during the exposure to air.
Table 3: An overview of the ALD processing parameters used for the deposition of Al₂O₃, Pd and Pt. Al₂O₃ and Pd are deposited using PE-ALD and Pt using thermal ALD.

<table>
<thead>
<tr>
<th>ALD Process</th>
<th>Al₂O₃</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD Reactor</td>
<td>FlexAL</td>
<td>ALD-I</td>
<td>ALD-I</td>
</tr>
<tr>
<td>Substrate Temperature (°C)</td>
<td>200</td>
<td>100</td>
<td>300</td>
</tr>
<tr>
<td>Precursor:</td>
<td>TMA</td>
<td>Pd(hfac)₂</td>
<td>MeCpPtMe₃</td>
</tr>
<tr>
<td>Dosing Time (s)</td>
<td>0.025</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Bubbler Temperature (°C)</td>
<td>30</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Line Temperature (°C)</td>
<td>70</td>
<td>70</td>
<td>50</td>
</tr>
<tr>
<td>Reactant:</td>
<td>O₂</td>
<td>H₂</td>
<td>O₂</td>
</tr>
<tr>
<td>Plasma Power (W)</td>
<td>200</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Pressure (mbar)</td>
<td>0.033</td>
<td>0.01</td>
<td>1</td>
</tr>
<tr>
<td>Exposure Time (s)</td>
<td>2</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

3.3 Material properties
In this section the material properties of Pd and Pt deposited by the ALD processes described in the previous section are discussed. The properties were determined in earlier work and serve as a reference of the work done here⁴. An overview of the material properties is given in Table 4, were also the different measurement techniques used are indicated.

In the case of Pt films the films are atomically very pure, i.e. the contamination levels lie below the detection limit (<5%) of the Rutherford backscattering spectroscopy (RBS) technique used to determine their composition. Furthermore the value of the mass density is in good agreement with the values of bulk platinum (20.45 g·cm⁻³). The resistivity of Pt is slightly higher than the bulk value (10.5 μΩ·cm) and comparable to those reported in literature¹⁶.

In the case of Pd however a large amount of carbon impurities is present in the film (11 ± 5%) this results in a higher resistivity as compared to the bulk (10.8 μΩ·cm). The presence of carbon in the Pd films is related due to the incomplete removal of carbon during the hydrogen plasma step of the ALD process. This is because the hydrocarbons created on the surface are strongly bonded to the substrate and therefore cannot be completely removed by the hydrogen plasma process in which an
oxygen plasma is added to remove the remaining hydrocarbons from the surface is still under development. Initial results on this process suggest that in this case a pure Pd metal can be deposited.

The roughness measured by atomic force microscopy (AFM) was 1.0 ± 0.3 nm for a 16 nm thick Pd film and 0.7 ± 0.3 nm for a 27 nm thick Pt film. This is comparable to the values found in literature (0.75-4nm)\textsuperscript{16}.

\textit{Table 4: Material properties of Pd and Pt films used in this work. The properties were determined by in situ SE, X-ray reflectometry (XRR), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS), and four-point probe (FPP)}

<table>
<thead>
<tr>
<th>Properties</th>
<th>Measurement Method</th>
<th>Pd</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>SE</td>
<td>16.0 ± 0.5</td>
<td>27.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>XRR</td>
<td>16.5 ± 0.3</td>
<td>26.6 ± 0.3</td>
</tr>
<tr>
<td>Roughness (nm)</td>
<td>AFM</td>
<td>1.0 ± 0.3</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>GPC (Å)</td>
<td>SE</td>
<td>0.16 ± 0.03</td>
<td>0.45 ± 0.03</td>
</tr>
<tr>
<td>Mass Density (g·cm\textsuperscript{-3})</td>
<td>RBS</td>
<td>10.3 ± 0.5</td>
<td>20.1 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>XRR</td>
<td>11 ± 1</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>Resistivity (μΩ·cm)</td>
<td>FPP</td>
<td>48 ± 3</td>
<td>13 ± 1</td>
</tr>
<tr>
<td>Metal (%)</td>
<td>RBS</td>
<td>89 ± 5</td>
<td>100</td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>RBS</td>
<td>11 ± 5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>RBS</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Grazing incidence X-ray diffraction (XRD) measurements (not shown here) indicated that both the Pd and Pt films are crystalline. In the case of Pt a (220) preferential growth orientation was observed, contrary to the Pd films which have a random orientation.
3.4 Diagnostics for the particle growth study

3.4.1 Transmission electron microscopy

Transmission electron microscopy (TEM) is an imaging technique where a beam of electrons is transmitted through a thin sample. The amount of material present, the crystallinity and atomic mass of the material determine how many electrons are transmitted. The transmitted electrons thus contain information of the sample properties. The electrons are focused using electrostatic and magnetic lenses and imaged using a CCD detector. The entire system is kept under high vacuum (typically $10^{-6}$ mbar). This allows for the usage of a high voltage required to transmit the electrons through the sample without creating an arc and prevents the collision of electrons with neutral atoms in the chamber. Due to the small de Broglie wavelength of electrons imaging resolutions up to the atomic scale can be achieved. A schematic of a TEM is shown in Figure 13.

![Figure 13: Schematic overview of a TEM system showing the electron gun that is focused on the specimen using several lenses. The beam is focused on a screen where a CCD detector converts it to an image. The entire system is kept under high vacuum (typically $10^{-6}$ mbar) to prevent the collision of the electrons with background species present in chamber.]
A TEM can be operated in two different modes:

**Bright-Field TEM (BFTEM):** in this case the primary electron beam is used for the transmission measurement. Regions where more material is deposited or material with a high atomic number is present will appear dark, while the regions without deposition, the field, appear bright.

**High Angle Annular Dark-Field (HAADF):** here the primary electron beam is excluded from the measurement and only scattered electrons are detected. The scattering depends on the presence of free electrons and the atomic mass of a species, therefore this imaging mode is also known as Z-contrast imaging. A region where no scattering occurs appears dark on the image, while scattering centers appear bright.

TEM requires the use of a very thin sample, to allow the electrons to pass through the material, for this a special substrate needs to be used. This can either be a lamellae or TEM window. In this work a TEM window is used schematically shown in Figure 14. The substrate consists of a 17 nm thick Si₃N₄ layer deposited on a silicon wafer. Parts of the silicon have been etched creating a free standing membrane of only 17 nm thick and 100 by 100 μm in size. Since the nucleation of Pt and Pd is investigated on Al₂O₃ the TEM substrate has been coated with 3 nm of Al₂O₃ using the process described in Section 3.2. The TEM window is placed horizontally in the ALD reactor. Due to the roughness of the substrate heater it can occur that it lies not perfectly flat on the heater and some deposition can also take place on the opposite side of the window. For this reason the Al₂O₃ coating is applied on both sides.

![Figure 14: Schematic cross-section of the samples used for TEM analysis. The sample consists of a crystalline silicon substrate coated with a 17 nm Si₃N₄ layer. 3nm Al₂O₃ is deposited on both sides of the sample.](image)

The TEM used in this work is a FEI Tecnai F30ST transmission electron microscope operated at 300 kV. The obtained images where analyzed using the iTEM software to determine the surface coverage and get an estimation of the island density. The particle size and size distribution were determined by manual counting of the particles. Manual counting is necessary to include the smallest particles (<1 nm) which are not detected by the software.

### 3.4.2 SE & FTIR

The spectrometer used in this work is a J.A. Woolam, Inc. M2000U Rotating Compensator Ellipsometer (RCE) with a measurement range of 0.75-5.0eV. An RCE has the advantage that the Δ values contain less noise compared to other SE configurations and allows for the determination of Δ over the full parameter range (0-360°)⁷."
For *in situ* measurements the ellipsometer is mounted on the ALD-1 Setup under an angle of 68°. The data were obtained every 10 cycles, by temporarily interrupting the ALD process. For the *ex situ* measurements the SE was mounted on a variable angle stage. In this case the spectroscopic parameters are measured at the Brewster angle, the angle of highest sensitivity, 75° for silicon and 57° for glass\textsuperscript{23,27}.

The FTIR transmission and reflection measurements were performed using a Brucker Tensor 27. The spectra were acquired in the range of 0.05-0.87 eV with a resolution of 5·10\textsuperscript{-4} eV. The reflection spectra were acquired at an angle of 12°.

### 3.4.3 Four Point probe

Four point probe (FPP) is an electric resistance measurement technique. FPP uses 4 wires (probes) for the determination of the sheet resistance of a material. A schematic representation of the technique is given in Figure 15. A current is applied over the outer two wires, while the voltage is measured over the inner two wires. All wires are separated by a distance $L$. Since the impedance of the voltage meter is very high almost no measurable current flows through the voltage meter. The voltage drop measured is then only dependent on the resistance of the sample, allowing for an accurate determination of the sheet resistance as the contact resistance is excluded from the measurement.

![Figure 15: Graphical representation of a FPP measurement. A current is applied by the outer two wires while the voltage drop is measured over the inner two wires.](image)

For the determination of the sheet resistance a Singatone four-point-probe system with a Keithly 2400 Source Measurement Unit was used, $L = 0.3$ cm.
Chapter 4  Initial growth study of Pt and Pd

In this chapter the results of the growth study of Pd and Pt on Al₂O₃ using ALD is presented. In Section 4.1 an overview of the terminology used to describe the growth of Pd and Pt is given and the TEM results are presented. A comparison is made between the nucleation of Pd and Pt during ALD and the similarities and differences are highlighted. In Section 4.2 the results of the SE analysis (both in and ex situ) are presented and a comparison with the TEM data is made.

4.1 TEM analysis

4.1.1 Terminology

The terminology used in this work used to describe the evolution from particles to thin films will be clarified using Figure 16, in which a schematic overview of the ALD process for Pd and Pt is given:

- **Coalescence**: The formation of clusters of particles (Figure 16 C).
- **Layer-by-layer growth**: The deposition of a (sub-)monolayer of material each ALD cycle over the whole substrate.
- **Nucleation**: The formation of island during the first few ALD cycles (Figure 16 A).
- **Nucleation phase**: The overall process of particle growth which ends with the formation of a closed film (Figure 16 A-C).

*Figure 16: Schematic overview of the ALD growth of Pd and Pt on Al₂O₃. The growth starts with the formation of islands a) which increase in size with the number of ALD cycles performed b). Eventually the islands start to touch each other until a closed film is formed c) and growth continues in a layer-by-layer manner.*
• **Percolation threshold:** The insulator to metal transition, i.e. the formation of a conductive medium of particles. Below the percolation threshold the particles or clusters of particles are isolated and unable to conduct current. Above the percolation threshold the system behaves as a metal where the conduction of electrons over a long range is possible \( (L = 0.3 \text{ cm}) \) (the distance over which FPP measures the conductivity is used in this work).\(^{32}\)

• **Ripening:** The merging of one or more particles or the diffusion of Pd atoms from smaller to larger particles (Ostwald Ripening)\(^ {22}\).

### 4.1.2 TEM of Pd and Pt

TEM was used to examine the nucleation of Pd and Pt as a function of the number of ALD cycles; the images are shown in Figure 17 and Figure 18 for Pd and Pt respectively. Both the deposition of Pd and Pt starts with the formation of isolated islands, which is in agreement with observations reported in literature\(^ {11,13,40,42}\). As the number of ALD cycles is increased, the islands grow until they merge and a continuous film is formed. In the case of Pd the particles are spherical throughout the deposition. The density of particles decreases after 200 cycles indicating the occurrence of ripening. Coalesced islands of several particles become visible after 500 cycles (I. Figure 17). This is also visible in Figure 19 a) where the Pd island density is depicted as a function of the number of ALD cycles. The island density increases during the initial stages of the ALD process and reaches a maximum of \( (1.3 \pm 0.1) \cdot 10^{12} \text{ islands/cm}^2 \). Then it decreases due to the ripening and coalescence of the particles\(^ {43,44}\). The Pd particles are crystalline indicated by the difference in contrast between particles corresponding to different crystallite orientations (II. Figure 17). After 1000 cycles the Pd layer is almost fully coalesced and only small voids (<2nm) are still visible between the particles.

Compared to Pd the nucleation of Pt occurs much faster, a closed film without voids is formed after 300 cycles. The isolated Pt particles formed during the nucleation are spherical. Agglomerates of Pt particles are however without a distinctive shape, this in contrast to Pd where the particles are spherical throughout the nucleation phase. This can be caused by a difference in the wetability (the ability to form a continuous film) between Pd and Pt on \( \text{Al}_2\text{O}_3 \). A lower wetability results in a higher contact angle of the particle and thus a more spherical shape. The Pt Island density shows a similar trend to compared that of Pd and reaches a maximum island density of \( (1.7 \pm 0.2) \cdot 10^{12} \text{ islands/cm}^2 \), shown in Figure 19 b). The density of the islands decreases for Pt after 100 cycles due to ripening and coalescence. However, small Pt particles are visible throughout the nucleation phase, either because new particles keep being formed, due to Ostwald ripening where the large particles grow and the smaller ones decrease in size until they disappear or the deposition of particles on both sides of the TEM window (I. Figure 18).

In the case of Pd the difficulty of removing the hfac ligands from the surface is believed to be main cause of the long nucleation phase\(^ {45,46}\). Goldstein et al. showed that the during initial Pd(hfac)\(_2\) exposure both Pd(hfac) and Al(hfac) surface species are formed. The Al(hfac) species are not removed during the reactant exposure and remain on the \( \text{Al}_2\text{O}_3 \) surface poisoning it, i.e. preventing the adsorption of new precursor molecules on these sites. Although Goldstein et al. used formalin as the reactant it is believed that a hydrogen plasma is also unable to remove these strongly bonded ligands. The high carbon content of as deposited Pd films \((11\pm5 \%)\) supports this hypothesis. In the case of Pt the ligands are
believed to be removed from the surface completely due to the higher reactivity of oxygen and the high purity of the films obtained (~100%). Pt atoms are therefore continually deposited on the Al₂O₃ surface which could be a reason why small particles are visible throughout the nucleation phase of Pt.

Figure 17: TEM images of Pd as a function of the number of ALD cycles. The scale bar has a size of 50 nm. The formation of interconnected particles (I.), the presence of different crystal orientations (II.) and voids (III.) is also indicated.
Figure 18: Pt TEM images as a function of the number of ALD cycles. The scale bar indicates a size of 50 nm. The presence of particles on both sides of the TEM window can be observed (I.).

Figure 19: a) Pd and b) Pt island density as a function of the number of ALD cycles obtained from the TEM images.

In Figure 20 a) and Figure 20 b) the development of the surface coverage as a function of the number of ALD cycles is displayed for Pd and Pt respectively. The data were obtained by analyzing several TEM images of each sample taken at different spots of the sample. The error bars are indicated and are less than 4%. Both for the Pd and Pt an s-shaped behavior for the increase of the surface coverage is
observed. The s-shape of the coverage development is typical for the nucleation of a system that starts with the formation of particles\textsuperscript{43,47–49}.

Yim et al. observed the same trend for the nucleation of Ru deposited by ALD on SiO\textsubscript{2}\textsuperscript{44,50}. They explained the observed trend as follows. During the early stages of the ALD process the adsorption of precursor on the substrate surface is dominant and adsorption on the noble metal particles can be neglected. As the amount of ALD cycles is increased the particles grow and precursor adsorption on particles occurs as well. The adsorption of precursor on Ru is more efficient than on the oxide surface, which results in an increase of the amount of material deposited per cycle as the number of cycles progresses due to the increasing Ru surface area. Yim et al. attribute the difference in adsorption efficiency to a difference in the density of adsorption sites. As shown in Chapter 1 however, also the catalytic activity of the noble metal plays an important role in the ALD process. Furthermore a less effective adsorption (lower sticking probability) of the precursor molecules on the oxide surface can play a role. The amount of material deposited per cycle eventually saturates; due to particle coalescence and agglomeration the surface area of the noble metal decreases.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure20.png}
\caption{a) Pd surface coverage and b) Pt surface coverage as a function of the number of ALD cycles, calculated from the TEM images.}
\end{figure}

In Figure 21 a) the development of the Pd particle size distribution as a function of the number of ALD cycles is shown. The data was obtained by manually analyzing the TEM images, creating a histogram with an interval size of 0.5 nm and dividing by the total number of particles analyzed. It can be seen that the maximum peak intensity shifts towards larger particle sizes as the number of ALD cycles is increased indicating the growth of the particles. Initially the size distribution is narrow but broadens as the particles get bigger. The broadening of the distribution is observed in literature as well and is caused by the ripening of the particles\textsuperscript{47}. Catalytic applications require a narrow as possible particle size distribution, therefore using ALD to synthesize Pd particles with a diameter > 5 nm might not be the best option. Below 5 nm the size distribution is very narrow.
Figure 21: a) Size distribution of the Pd particles as a function of the number of ALD cycles, b) the average particle diameter as a function of the number of ALD cycles, for comparison a previous series is added which shows excellent agreement with the data obtained in this work.

The increase in the average of the average Pd particle size is shown in Figure 21 b). To indicate the reproducibility of the experiments also the data from an earlier series using the same deposition conditions was added. The data, obtained one year ago, shows excellent agreement with the results obtained in this work. The samples of 100 cycles have an average particle size of 1.6 ± 0.5 nm and 1.8 ±0.5 nm the other samples follow the same growth development indicating the reproducibility of the used process. The particle size as a function of ALD cycles has been fitted with a straight line. The first three data points are excluded, because the smallest particles cannot be seen with TEM. Therefore the average particle size is overestimated for these points. From the fit a horizontal GPC of 0.14 ± 0.01 Å in diameter is obtained, i.e. 0.070 ± 0.005 Å in radius. How this relates to the GPC obtained from SE and literature is discussed in Section 4.2. The extrapolated x-axis intercept lies at 12 cycles indicating a short nucleation delay.

Figure 22 shows the development of the particle size distribution of Pt as a function of the number of ALD cycles. During the nucleation of Pt small particles keep being formed, which results in a significant broadening of the size distribution. After 100 cycles the average particle diameter is 5.2 nm with a standard deviation of 5 nm. This makes the Pt ALD process less attractive for the synthesis of particles for catalytic applications; to confirm this however also a deposition with less than 60 cycles should be investigated.
4.1.3 Conclusion

From the TEM analysis of the nucleation phase of Pt and Pd it was confirmed that both Pd and Pt nucleate in the form of particles on Al₂O₃. As the number of ALD cycles is increased the particles grow due to the deposition of material, coalescence of particles and ripening. Pt nucleates much faster, a closed film is formed after 300 cycles compared to 1000 for Pd. The Pt and Pd process show similar behavior for the development of coverage and island density. A maximum island density of $1.3 \times 10^{12}$ islands/cm$^2$ and $1.7 \times 10^{12}$ islands/cm$^2$ is obtained for Pd and Pt respectively which decreases rapidly due to the coalescence and ripening of the particles. In the case of Pd the particles are circular throughout the nucleation phase. For Pt the initial particles are circular but agglomerates and coalesced particles are without a distinctive shape. A difference in wetability of the noble metal on the Al₂O₃ surface is believed to be the cause of this although surface poisoning with precursor ligands can also be of influence.

The size distribution of the Pd particles is suitable for catalytic applications when their average size is < 5 nm. The Pd data obtained here agree well with results obtained previously and illustrates the reproducibility of the process. Pt has a broad size distribution; the standard deviation is similar to the average particle size, making this process less attractive for catalytic applications.
4.2 SE analysis

In this section the results of the *in* and *ex situ* SE analysis are presented, obtained from fitting the SE data using the models discussed in Section 2.3 and 2.4. The (effective layer) thickness obtained from the B-spline parameterization of the *in situ* SE data is shown in Figure 23 a) and b) for Pd and Pt respectively. From the thickness development as a function of the number of ALD cycles a transition in the growth behavior is visible for both Pd and Pt. During the initial stages of the ALD process (up to 150 cycles for Pd and 70 for Pt) the growth observed is low. Then the growth per cycle suddenly increases considerably. A constant thickness increase is obtained after 380 cycles for Pd and 125 cycles for Pt. The region up to 380 and 125 cycles is indentified as the nucleation phase (I. in Figure 23).

![Figure 23: a) Pd and b) Pt film thickness as a function of the number of ALD cycles, determined from the B-spline parameterization. The in situ SE data was measured every 10 cycles. The transition from nucleation to a constant linear growth and GPC are indicated. In the case of Pd also the average particle size as determined from TEM is added. The $\chi^2$ of the fits is indicated in c) and d) for Pd and Pt respectively.](image)

In the case of Pd also the average particle size as determined from TEM is added. The $\chi^2$ of the fits is indicated in c) and d) for Pd and Pt respectively.
The sudden increase in the GPC is also observed by Knaut et al. for the ALD of Ru on SiO$_2$ but they were unable to determine the cause of this sudden increase$^{51}$. The sudden increase could be related to the occurrence of particle-particle interactions, resulting in a higher effective thickness of the B-spline layer$^{24}$. After the nucleation phase a stable GPC is obtained of 0.17 ± 0.03 Å for Pd and 0.45 ± 0.03 Å for Pt. This is in agreement with values obtained in literature in the layer-by-layer growth regime$^{16,40,52}$.

The $\chi^2$ corresponding to the fits is indicated in Figure 23 c) and d) for Pd and Pt. The $\chi^2$ of Pd is always below 10 which is considered to be acceptable for metal films$^{53}$. In the case of Pt the $\chi^2$ is higher than 10 between 150 and 300 cycles but the fit obtained is unique. A maximum in the $\chi^2$ is visible for both Pd and Pt after a linear growth is obtained indicating the reduced ‘goodness’ of fit in this region. Possibly because approximating the particles as an effective layer is no longer possible due to the broad size distribution of the particles as determined from the TEM data (Figure 21 and Figure 22) because the optical properties of the particles are size dependent$^{24}$.

In Figure 23 a) also the average particle size as obtained from the TEM analysis is added, where the assumption has been made that the Pd particles are spherical. Whether this is indeed the case depends on the wetability of the particles on the substrate. The thickness as determined from the B-spline shows very good agreement up to 250 cycles with the average particle size. Above 250 cycles however the average particle size is lower than the thickness obtained from the B-spline parameterization and the maximum particle size appears to correspond to the B-spline thickness (indicated by the error bar). At the transition region 150-380 cycles the thickness of the effective layer changes from the average particle size to the maximum particle size. Since the B-spline determines an effective the film thickness that contains both the particles and voids between them, it is likely that larger particles have bigger influence on this effective layer thickness resulting in the transition observed. The difference in GPC observed between TEM and SE (0.070 ± 0.005 Å compared to 0.17 ± 0.03 Å) and the difference in nucleation delay might also be caused by this.

Because of the assumptions the information obtained from comparing the SE and TEM data is limited. However SE and FTIR data can be linked indirectly to the TEM data by establishing a library. For future depositions SE or FTIR can then be used to obtain an estimate of the particle size and distribution without the need of TEM. Such a library is shown in Figure 24 for Pd (the procedure followed can also be applied to Pt and possibly other materials). In Figure 24 the FTIR transmittance and ex situ SE data of 300, 500 and 1000 cycles is compared to the TEM images, as a reference the Al$_2$O$_3$ substrate is also added. The FTIR transmission decreases as the number of ALD cycles is increased due to the increase in absorption of the Pd. Changes are however only visible for 500 cycles and up. This is related to the percolation threshold (discussed further below). For the SE data it can be seen that $\Psi$ increases as a function of the ALD cycles. On the other hand the transition visible in $\Delta$ (at 2.55 eV for Al$_2$O$_3$) shifts towards lower energy as the number of ALD cycles is increased. Both the increase in $\Psi$ and the shift in $\Delta$ are caused by changes in the dielectric function and thickness of the deposited material. SE (<500 cycles) and FTIR (> 500 cycles) can therefore be used to get an indication of the particles properties by consulting the library.
Figure 24: Transmittance spectra measured by FTIR, TEM images and the ellipsometric parameters, \( \Psi \) and \( \Delta \) of Pd for 0, 300, 500 and 1000 cycles.
From the modeling of the SE data also information on the optical properties of the effective medium layer is obtained. In Figure 25 the dielectric function of Pd and Pt obtained from the B-spline parameterization of the in situ SE data is shown. The dashed arrow indicates the trend observed as the number of ALD cycles is increased. The imaginary part of the dielectric function, Figure 25 c) and d), increases with the number of ALD cycles due to the increased absorption of the Pd and Pt. If the increase in absorption is only related to the free-electrons present in the material, the corresponding real part $\varepsilon_2$ should be negative (visible also in Figure 6)\textsuperscript{32}. However, first an increase in $\varepsilon_1$ is observed indicating that other material-light-interactions also play a role.

To illustrate this point more clearly the evolution of $\varepsilon_1$ and $\varepsilon_2$ at 0.75 eV is shown for both Pd (Figure 26 a) and c) ) and Pt (Figure 26 b) and d)). Both Pd and Pt show the same behavior: in region I. $\varepsilon_1$ is positive and the absorption $\varepsilon_2$ is zero. In region II. $\varepsilon_1$ starts to increase while $\varepsilon_2$ remains zero. Eventually (region III.) $\varepsilon_2$ starts to increase as well, while $\varepsilon_1$ goes through a maximum. In region IV. $\varepsilon_1$ becomes negative and $\varepsilon_2$ keeps increasing.

Figure 25: Dielectric function as determined from the B-spline parameterization, the real part $\varepsilon_1$ is shown in a) Pd and b) Pt whereas the imaginary part $\varepsilon_2$ is shown in c) Pd and d) Pt. The dashed arrow indicates the trend observed as the number of cycles is increased.
A similar behavior has been observed for the nucleation of Au deposited by sputtering by Hövel et al. and is explained as follows\textsuperscript{32}. During the initial stages of growth the particles are isolated and do not interact (region I.). Resulting in a dielectric function similar to that of a dielectric medium, i.e. a positive $\varepsilon_1$ and $\varepsilon_2 = 0$. However as the particles grow and come closer to each other the particles start to interact capacitively, leading to an increased optical conductivity $\sigma$ and a positive $\varepsilon_1$ (region II.). As the particles start to coalesce the percolation threshold is reached resulting in free carrier absorption. The free carrier absorption leads to a decrease of $\varepsilon_1$ and increase of $\varepsilon_2$. $\varepsilon_1$ therefore goes through a maximum until it becomes negative as observed in regions III. and IV.

To get a more detailed view of the percolation the FPP data is shown in Figure 27 for both Pd and Pt. Only points that resulted in a measurable sheet resistance are indicated. The transition from insulator to metal is best visible in the FPP data of Pd, Figure 27 a), where a decrease in the sheet resistance over more than five orders of magnitude is observed. The reason the transition is better observed for Pd is probably related to the longer nucleation phase compared to Pt. In the case of Pt the sample of 100 cycles has an immeasurable resistance whereas the sample after 150 cycles is only 20 times higher than the thin-film value obtained after 500 cycles. The faster nucleation also means that Pt is more sensitive
to changes in the nucleation delay, apparent from the samples of 150 and 200 cycles which have a similar sheet resistance.

Figure 27: a) Pd and b) Pt sheet resistance as a function of the number of ALD cycles, the percolation threshold can be observed by a decrease in the sheet resistance over more than five orders of magnitude in the case of Pd.

The behavior observed can be explained as following: below the percolation threshold no transport of the electrons is possible resulting in an immeasurable sheet resistance. At the percolation threshold the conduction of electrons is possible, but the conductivity remains high due to the surface scattering. The surface scattering decreases as the particles coalesce resulting in a decrease of the sheet resistance. The final resistance of the film is determined by scattering at the grain boundaries and impurities present in the film, such as carbon in the case of Pd.

The sheet resistance can be linked to $\varepsilon_2$ by Equation 2.2.4. However due to the intraband absorption of Pt at 0.8 eV (Figure 6) no distinction can be made between this peak and the peak related to the absorption of the free carriers situated at 0 eV. This is because the intraband absorption peak lies at the edge of the measured spectrum of SE (0.75-5eV). The combination of FTIR and ex situ SE is used to discriminate between the two peaks, FTIR extends the measurement range from 0.05 to 5 eV. The result of the combination of FTIR and SE is shown in Figure 28, where it is now possible to compare the conductivity, obtained by the optical analysis, with the FPP data.

In the case of Pd the dc conductivity (0 eV) agrees well with the conductivity obtained from Drude – Lorentz parameterization for the samples of 700 and 1000 cycles. For 500 cycles however, a strong deviation is observed. This is because 500 cycles is close to the percolation threshold of Pd. Below the percolation threshold the DC conductivity is zero, whereas the optical conductivity depends on the capacitive coupling between the islands. Extrapolating the DC conductivity from the optical conductivity therefore results in an overestimation.
Figure 28: Pd a) and Pt b) conductivity as a function of the photon energy for several cycle numbers. The values of the dc conductivity are also included, solid squares at 0 eV. The measurement range of the FTIR (0.05-0.87 eV) and SE (0.075-5 eV) is also indicated.

When looking at Figure 25 b) and Figure 28 b) it can be seen that the intraband absorption of Pt that saturates at 0.8 eV starts out at higher energy (> 2eV) and slowly shifts towards its final position. The behavior is the result of the interactions between the metal particles and results in the shift of this peak to lower energies as the interaction between particles becomes stronger. An interband absorption peak is also present for Pd around 1.0-1.1 eV. It shows the same behavior as the one for Pt but the peak is less pronounced.

4.2.1 Conclusion

Using in situ SE it is possible to make a distinction between a nucleation phase and a linear growth phase when investigating the effective layer thickness determined by the B-spline parameterization. The thickness obtained from SE corresponds to the average TEM particles size during the initial stages of ALD growth, under the assumption that the deposited particles are spherical. As the number of ALD cycles is increased a transition occurs and the maximum particle size corresponds to the layer thickness obtained from SE. The SE and FTIR data can be linked establishing a library, which can be used to quickly get an indication of the particle properties without the need of TEM. The SE parameter Δ showed to be sensitive to changes in the particle size below the percolation threshold and the FTIR transmission above the percolation threshold. From the dielectric function information on the percolation threshold and particle-particle interactions is obtained. The conductivity obtained from FPP measurements agrees well with the optical data for films that have coalesced. However, deviations occur around the percolation due to the capacitive coupling of the particles, which lead to an overestimation of the DC conductivity extrapolated from the SE and FTIR data.
Chapter 5  Conclusions and Outlook

In this work the nucleation of Pd and Pt on Al₂O₃ has been investigated as well as the viability of SE is as a technique for monitoring the nucleation of noble metals on oxide supports during ALD. In comparison to TEM, which is often used for the characterization of the nucleation phase, SE is a cheap and fast analysis technique. Furthermore it can be implemented in situ in the ALD process with relative ease due to the cyclic nature of the deposition process.

First the nucleation was characterized using TEM. This provided information about particle coverage, size and morphology as a function of the number of ALD cycles. During the initial stages of the nucleation process both Pd and Pt form particles and similar behavior for the increase in surface coverage and island density is observed for both materials. However Pd has a longer nucleation phase, 1000 cycles compared to Pt, 300 cycles. The differences are related to the different surface chemistry of both processes, such as the stability of the hfac ligand on Al₂O₃ in the case of Pd, the sticking probability of the precursor and the catalytic activity of the noble metal in its own growth process. This also resulted in a different particle shape for Pd and Pt. Pd has circular particles throughout the nucleation phase. In the case of Pt the initial particles are circular but coalesced particles are without a distinctive shape.

For the analysis of the in situ SE data a B-spline parameterization was used. Two growth phases could be distinguished when investigating the layer thickness development, a nucleation phase and linear growth phase. The layer thickness obtained during the early stages of Pd ALD corresponded to the average particle size obtained from TEM (<250 cycles). After 380 cycles the maximum particle size corresponded to the B-spline thickness. Qualitative information about the percolation threshold and particle coalescence could be obtained from the dielectric function determined by the B-spline. To extract quantitative information about the percolation threshold such as dc conductivity a combination of ex situ SE and FTIR was required, because of the intraband absorption present in the case of Pd (1.1 eV) and Pt (0.8 eV) at the edge of the SE measurement range (0.75 eV) making it impossible to extrapolate the dc conductivity. The conductivity obtained from SE and FTIR agreed well with the FPP data in the case of thin films, but deviations occurred around the percolation threshold. This was caused due to capacitive coupling of the particles which led to an overestimation of the extrapolated DC conductivity.

Combining the TEM, SE and FTIR data it was possible to establish a library that provided a link between the data, allowing for an indication of the particle properties without the need of TEM. Below the percolation threshold the ellipsometric parameter Δ was shown to be sensitive to changes in the particle size. Above the percolation threshold the FTIR transmission is the most sensitive to changes in the film properties and can be used as reference.
5.1 Outlook
To further identify the processes that play a role during the nucleation of Pd and Pt further research is required. One option would be to use in situ FTIR to investigate the precursor adsorption and reaction steps. Using FTIR species that adsorb on a surface can be identified as well as the relative change in these species between precursor and reactant step. This can be used to investigate the difference in chemistry (adsorption sites and catalytic activity) on the oxide surface compared to that of the noble metal, needed to gain a better understanding of nucleation process.

In the case of Pd, surface poisoning by hfac ligands plays an important role in the nucleation process. This poisoning that blocks the adsorption of Pd(hfac)$_2$ on the oxide surface could possibly be used to affect the island density of Pd particles. Using a longer H$_2$ plasma exposure during the first few ALD cycles possibly more hfac ligand is removed, increasing the amount of adsorption sites. Whereas decreasing the hydrogen plasma exposure the number of adsorption sites can be reduced, providing control over the particle density.

For Pt the nucleation is fast and the particle distributions are broad. Mackus et al. have shown that the oxygen pressure plays an important role in the speed of the nucleation process, possibly because oxygen induces Ostwald ripening or the more efficient removal of ligands from the surface at higher pressure$^{54}$, here a relatively large oxygen pressure of 1 mbar was used. Reducing the oxygen pressure during depositions therefore might provide a better control of the particle properties and size distribution.

For the optical characterization of Pt and Pd only a B-spline parameterization is used in this work. In literature there are however many more parameterizations available. Apart from determining the dielectric function some parameterizations also give information on the particle size. It would be interesting to see if such parameterizations can also be used for the data obtained in this work and what additional information they provide.
PART II:

Temperature Programmed Desorption
Chapter 6  Introduction

Temperature programmed desorption (TPD) is a method in which a sample is exposed to a gaseous adsorbent and the sample is heated linearly in time afterwards. The species leaving the surface are identified and monitored using a mass spectrometer. TPD is used in surface science to examine the desorption of gases from the surface of single crystalline or poly crystalline materials\(^{55-57}\), however also some examples are available where thin films or even nanoparticles are investigated using TPD\(^ {58}\). On crystals the adsorption sites are much better defined and there are less different sites available compared to polycrystalline thin-films or particles. The data analysis for single crystals is therefore less ambiguous and is performed first before thin films or particles are studied.

During heating also species present in the bulk of a material can diffuse towards the surface and desorb. In this case the term temperature programmed effusion (TPE) is used, although it is not uncommon to refer to it as TPD. TPE is used to study changes in the material under investigation such as crystallization or the out-gassing of particular species\(^ {37}\).

From the obtained TPD and TPE spectra the species present on the surface or in the bulk of the material can be identified, as well as the desorption energy, the kinetics of its release and the surface coverage of the species. Information on these parameters gives insight into how the material performs in a catalytic reaction, its thermal stability or the concentration of a specific species when a calibration point is available\(^ {37,59}\).

6.1 Motivation and Outline

The interaction of adsorbents with a surface is of great importance for the field of catalysis. Gaining more knowledge about how species adsorb on the surface and how strongly they are bound to it is necessary to develop new and further improve existent catalysts, such as the nanoparticles discussed in the previous part of this thesis. In addition the adsorption of precursor on a surface plays an important role in ALD processes. TPD could therefore provide additional information on the chemical reactions involved in ALD.

TPE can be used to provide information on the composition, stability and crystallization of a material. Therefore TPE can provide additional information on the structural properties of the materials created within the Plasma & Materials Processing (PMP) group.

This part of the thesis describes the work carried out on the Hiden Analytical TPD Workstation, recently acquired by PMP. The goal is to investigate whether comparable results can be obtained using this TPD and literature, and perform a basic analysis of several materials synthesized at PMP. In order to achieve this, the work has been divided into several sub goals:
• Provide an overview of the different TPD & TPE analysis methods available and a detailed description of the TPD Workstation. TPD is new to the PMP group and the work presented here should serve as a reference for future work.

• Basic TPE experiments of several materials synthesized at PMP to show the possibilities of the technique.

• Upgrading the TPD Workstation with a gas injection system and the combination of TPD and SE. Currently the TPD workstation is not equipped with a gas injection system needed for desorption experiments.

• Analysis of oxygen ad- and desorption of Pd and Pt single crystals which can be compared to results obtained in the literature and serve as a basis of the analysis of Pd and Pt films synthesized at PMP.

6.1.1 Outline Part II
In Chapter 7 the theory related to TPD is discussed and an overview of the different analysis techniques is given. Also several different TPE experiments are discussed in this chapter. Chapter 8 contains a detailed description of the TPD workstation as well as an overview of the different problems encountered during its operation and the possible solutions. The initial experiments where performed at Hiden Analytical, to which the TPD has been returned to solve several issues, and are presented in Chapter 9. Chapter 10 contains the conclusion and outlook.
Chapter 7  Theory

In this chapter the theory related to TPD is discussed. First the basics of adsorption are given in Section 7.1. The TPD technique is discussed in Section 7.2. An overview of the most common analysis methods is presented in Section 7.3. In Section 7.4 several TPE methods will be discussed.

7.1 Adsorption

At the basis of temperature programmed desorption lies the adsorption of species on the surface. How species adsorb on a surface depends on the species themselves and the surface with which they interact. Two end states are possible on the surface; a physisorbed state or a chemisorbed state, where chemisorption is almost always preceded by physisorption. Both processes will be discussed in more details below.

Physisorption is the result of the Van-Der-Waals interaction between an adsorbate and a surface and/or the interaction between adsorbates themselves. Almost all species can physisorb on a surface under the right conditions, indicating that it is a non-specific process\(^60\). During physisorption, the structure and electrical properties of adsorbate and surface remain unchanged. Since the Van-Der-Waals interaction does not involve a chemical interaction, the energies involved are low, typically below 50 kJ/mol\(^{61}\).

In the case of chemisorption, the overlap between the molecular orbitals of adsorbate and the surface allow for the formation of a chemical bond. In this case the energies involved are well above 50 kJ/mol, usually around 200 kJ/mol\(^60\). During chemisorption the adsorbate often dissociates, due to the weakening of the intra molecular bonds. This dissociation is important in catalysis since it reduces the energy barrier of a given reaction\(^{59,60}\).

The combined process of physisorption and chemisorption is displayed in Figure 29. In this figure the potential energy diagram for the adsorption of a molecule is shown as a function of the distance to the surface with \(E_{\text{chem}}\), the chemisorption energy, \(E_{\text{phys}}\), the physisorption energy and \(E_{\text{act}}\) the activation energy. In the case that \(E_{\text{act}} > 0\) the chemisorption process is described as activated chemisorption, since an additional energy \(E_{\text{act}}\) has to be supplied to the adsorbate to achieve chemisorption on the surface. This is for example the case for the dissociative adsorption of oxygen on most metal surfaces. At room temperature the oxygen dissociatively adsorbs but around 100K only physisorption occurs, because there is not enough thermal energy available to overcome the activation barrier.

If enough energy is supplied to adsorbed species, they can leave the surface and desorb. Depending on whether the chemisorption is an activated process or not, the desorption energy is different. In the case of activated chemisorption the adsorbed species needs to overcome both the chemisorption potential and the activation barrier, \(E_{\text{des}} = E_{\text{chem}} + E_{\text{act}}\). If the adsorption is not activated the desorption energy is equal to the chemisorption energy, \(E_{\text{des}} = E_{\text{chem}}\). The way a species desorbs depends on the configuration of the adsorbed molecules on the surface and the type of desorption, for example whether it is an associative process or not. This is discussed in the next section.
Figure 29: The potential energy diagram for adsorption of a molecule that approaches a surface, depending on the energy barrier the chemisorption can be with our without activation.
7.2 Kinetics of Desorption

In this section the kinetics of TPD are discussed. The TPD process is driven by the thermal energy delivered to the adsorbed species on the surface, which leads to desorption from the surface due to thermal vibrations. During a TPD measurement the temperature, \( T \), of the sample is increased linearly in time i.e.:

\[
T(t) = T_0 + \beta t
\]

Where \( t \) is the time, \( T_0 \) the starting temperature and \( \beta \) the heating rate, which is typically between 20 and 30 K/min. The adsorbates desorbing from the surface are detected using a mass spectrometer during the TPD measurement.

The desorption rate, \( r_{\text{des}} \) defined as the relative change in surface coverage with time, is given by the following equation\(^{59,62} \):

\[
r_{\text{des}} = -\frac{d\theta}{dt} = k_{\text{des}} \theta^n = \nu(\theta) \theta^n \exp\left(\frac{-E_{\text{des}}(\theta)}{RT}\right)
\]

This formula is also known as the rate-equation for desorption or Polanyi-Wigner equation, where:

- \( \theta \) the surface coverage of the adsorption sites in monolayers
- \( t \) time
- \( k_{\text{des}} \) the reaction constant for desorption
- \( n \) order of the reaction
- \( \nu \) pre-exponential factor of desorption
- \( E_{\text{des}} \) activation energy of desorption
- \( R \) gas constant
- \( T \) temperature

Where the Arrhenius equation is used to describe \( k_{\text{des}} \), and both \( \nu \) and \( E_{\text{des}} \) depend on the surface coverage due to attractive or repulsive interactions between the adsorbates or between adsorbates and the surface. In Equation 7.2.2 it is assumed that readsorption on the surface or chamber walls can be neglected\(^{57,59} \).

TPD data is usually presented as a mass signal (as recorded by a mass spectrometer) plotted as a function of the surface temperature of the substrate. The temperature is time dependent as shown in Equation 7.2.1. As an example, three different TPD spectra are shown in Figure 30. The experiments shown in Figure 30 were conducted on single crystals of Ru(0001) (a), Rh(111) (b) and Rh(100) (c). The surface of these crystals was exposed to a gaseous species which adsorbed on the surface. The figure shows the desorption rate of these species (Ag (a), CO (b) and N\(_2\) (c)) for different initial coverages \( \theta \) as a function of the temperature. As the temperature is increased so does the desorption rate (Equation 7.2.2). However due to the removal of material \( \theta \) decreases during the measurement resulting in maximum in the desorption rate. The presence of multiple peaks indicates that adsorption sites with different activation energies are being occupied. Figure 30 a, b, c correspond to a zero-, first- and second-order desorption reaction respectively and will be discussed in more detail below.
Figure 30: TPD spectra for a) zero-, b) first- and c) second-order desorption kinetics (adapted from Niemantsverdriet et al. 57,63,64)

In the case of first-order desorption as displayed in Figure 30 b), the desorption rate is proportional to the adsorbate surface coverage. This is the simplest case where the adsorbate directly leaves the surface independent from the site on which it was adsorbed. Since the carbon monoxide molecules on the Rhodium (111) surface do not interact for coverages below 0.5 mono layer (ML), the desorption peaks maxima stay at the same positions. This is typical for a first order reaction. For higher coverages a second peak starts to appear in the spectrum, indicating that also other sites start to be occupied. The occupied states cannot be determined from TPD data alone and additional information (for example from low energy electron diffraction measurements) is needed to determine the adsorbate structure on the surface 60.

Concerning second-order desorption processes, such as nitrogen adsorbed on a Rhodium (100) surface, shown in Figure 30 c), the desorption rate is proportional to the surface coverage squared. This corresponds to associative desorption where first the adsorbate needs to recombine before desorption can take place. The characteristics of this desorption process are a symmetrical shape of the desorption peak and the shifting of the desorption maximum to lower temperatures, when the amount of adsorbate on the surface is increased.

Zero-order reaction kinetics exhibits a less intuitive behavior. The desorption rate is coverage independent and only depends on the substrate temperature. An example is given in Figure 30 a), where the desorption of silver from ruthenium (0001) is shown. The silver adsorbs as 2D islands on the ruthenium surface. During heating, the silver only desorbs from the edges of these 2D Islands creating a zero-order behavior. This type of behavior has also been observed for desorption of adsorbents from homogeneous multi-layer systems where the material is removed from the surface in a layer-by-layer fashion. Peaks due to zero-order desorption kinetics show a common leading edge and an increasing maximum desorption rate. The maximum also shifts towards higher temperature as the adsorbate surface coverage increases, followed by a sharp drop after the maximum has been reached.
7.3 Analysis Methods

Although the acquisition of TPD spectra is quite straightforward, their analysis can be complicated. Four analysis methods will be discussed in this section: the Redhead method, the Heating rate variation method, the leading edge analysis and the complete analysis.

7.3.1 Redhead Method

The Redhead method for TPD analysis was developed by Redhead in 1962. Redhead derived an equation for the activation energy of desorption known today as the Redhead equation. This equation, can be derived by combining equation 7.2.1 and 7.2.2. Under the assumption that both the pre-exponential factor and the desorption energy are independent of the surface coverage and that the desorption rate follows first order kinetics. Then taking advantage of the fact that the derivative is zero at the maximum desorption rate, at a temperature $T_{\text{max}}$, results in equation 7.3.1:

$$E_{\text{des}} = RT_{\text{max}} \left( \ln \frac{v_{\text{t}}T_{\text{max}}}{\beta} - \ln \frac{E_{\text{des}}}{RT_{\text{max}}} \right)$$  \hspace{1cm} 7.3.1

To determine the activation energy of desorption, the term in $\ln \frac{E_{\text{des}}}{RT_{\text{max}}}$ is often estimated to 3.64. This can be done as this term is relatively small as compared to $\ln \frac{v_{\text{t}}T_{\text{max}}}{\beta}$. This assumption introduces an error of less than 1.5% for values of $v/\beta$ between $10^8$ and $10^{13}$ K$^{-1}$. The usefulness of the Redhead equation lies in the fact that only a single TPD spectra is needed to determine the activation energy of desorption. However, to calculate $E_{\text{des}}$, a good estimate for the pre-exponential factor $v_{\text{t}}$, is needed. In the case of first-order desorption kinetics, this factor has the units of frequency s$^{-1}$ and is called the attempt frequency. It can be interpreted as the number of attempts the adsorbate makes per second to leave the surface. The most common value used for this frequency is $10^{13}$ Hz, which is roughly the order of magnitude at which the atoms vibrate in the lattice. This assumption is only correct if the adsorbate is immobile on the surface.

7.3.2 Heating rate variation method

The heating rate variation method (or Falconer-Madix method) is similar to the Redhead method as presented in the previous section. The main difference is that this method requires multiple spectra of a sample, with the same adsorbate coverage but taken at different heating rates ($\beta$). Furthermore no assumption is made on the coverage dependence of the desorption energy and the pre exponential factor. Following the same procedure as used for determining the Redhead equation yields the following formula for both first- and second-order desorption kinetics:

$$\ln \frac{T_{\text{max}}^2}{\beta} = \frac{E_{\text{des}}}{RT_{\text{max}}} + \ln \frac{E_{\text{des}}}{v_{\text{t}}R}$$  \hspace{1cm} \text{(1$^{\text{st}}$ order)}  \hspace{1cm} 7.3.2

And:

$$\ln \frac{T_{\text{max}}^2}{\beta} = \frac{E_{\text{des}}}{RT_{\text{max}}} + \ln \frac{E_{\text{des}}}{v_{\text{t}}R\theta_0}$$  \hspace{1cm} \text{(2$^{\text{nd}}$ order)}  \hspace{1cm} 7.3.3
Where each logarithmic parameter has been divided by its own unit, i.e. \( \tilde{R}, \tilde{E} \), etc are dimensionless. The desorption energy can then be determined from the slope of a plot of \( \ln \frac{\tilde{R}_{\text{max}}}{\tilde{P}} \) versus \( 1/ RT_{\text{max}} \), provided several different heating rates are measured. The pre-exponential factor of desorption can be determined from the intercept with the y-axis. In the case of first-order reaction kinetics, detailed knowledge on the surface coverage is not needed as long as it is similar for all the samples tested. For second-order reaction kinetics knowledge of the initial coverage, \( \theta_0 \), is needed to determine the frequency factor.\textsuperscript{61}

### 7.3.3 Leading edge analysis

The leading edge analysis as introduced by Habenschaden and Küpers et al. makes use of the low temperature, high coverage part of a TPD spectrum\textsuperscript{66}. In this case only the leading edge of the spectrum is used. Selection of only a small part of the spectrum ensures that both variations in the temperature (\( T \)) and surface coverage (\( \theta \)) over this selection are insignificantly small. Both the coverage dependency and temperature dependency of the kinetic parameters \( E_{\text{des}} \) and \( \nu \) are taken into account.

The kinetic parameters can then be determined by creating an Arrhenius plot of the selected part of the spectrum which involves plotting \( \ln \tilde{r}_{\text{des}} \) versus \( 1/T \) for the selected section.

\[
\ln \tilde{r}_{\text{des}} = -\frac{E_{\text{des}}}{RT} + \ln \tilde{v}_n + n \cdot \ln \tilde{\theta}
\]  \(7.3.4\)

In Equation 7.3.4 is the logarithmic version of Equation 7.2.2. The desorption energy can be determined from the slope of this plot and the pre-exponential factor from the y-axis intercept if the coverage and order of the reaction are known.

The advantage of this method is that almost no assumptions are made and that even for high adsorbate coverages reliable results on the activation energies are obtained. However, because only the leading edge of the spectrum is used, data with a very high signal to noise ratio are required.

### 7.3.4 Complete Analysis

The complete analysis as first used by King et al. is the repetitive application of the Polanyi-Wigner equation to the measured TPD spectra\textsuperscript{67}. Since both \( E_{\text{des}} \) and \( \nu \) depend on the adsorbate surface coverage, they need to be determined for each coverage separately.

This is done by acquiring different TPD spectra of the same sample at the same heating rate but using different initial adsorbate coverages. In each of the spectra, the points corresponding to one coverage, for example 0.8 ML, are determined and an Arrhenius plot of the acquired data points is made. Similar to the leading edge analysis, the kinetic parameters can be determined from the slope of the Arrhenius plot and the y-axis intercept. This procedure is repeated for all the different coverages of interest. In the determination of the pre-exponential factor, knowledge about the order of the reaction is needed to evaluate the term \( n \cdot \ln \tilde{\theta} \). However, for coverages above 0.1 ML, this term can often be neglected as it is much smaller than \( \ln \tilde{v}_n \).
The determination of which analysis technique is the best to be used is difficult. Also, estimating the order of the reaction (and in case of the Redhead-equation also the pre-exponential factor) is not straightforward. Therefore, literature can be helpful and should always be consulted to make a good choice. As an example on how the different methods perform, an overview is given in Figure 31. Figure 31 a) shows simulated TPD data for which the kinetic parameters are known as a function of coverage. Figure 31 b) shows a plot of the desorption energy versus the coverage as determined by the different analysis methods. Both the leading edge and complete analysis give a good match to the data. However, the approximate methods such as the Redhead method and the Falconer-Madix (FM) method, fail to provide a good fit to the data.

Obtaining the kinetic parameters of desorption at different coverages gives information on the adsorbate-surface interactions but also on the adsorbate-adsorbate interactions. Rapid changes in $E_{des}$ with coverage can indicate either that the clustering of adsorbents on the surface (if the interaction is attractive) or the weakening of adsorbate-surface bonds (if the interaction is repulsive). Both interaction energies can be estimated using TPD.

\[ E_{des} \]

**Figure 31:** a) simulated TPD data for an adsorbate-surface system, b) a comparison of the different analysis methods. The term FM refers to the Falconer-Madix method which is a heating rate variation method (adapted from Niemantsverdriet et al\textsuperscript{59}).
7.4 Temperature Programmed Effusion

In the previous section the desorption of species from the surface of a material has been discussed. However, also species present in the bulk of the material can diffuse towards the surface and desorb. This can be investigated using TPE.

In TPD measurements one wants to limit these background species. If single-crystalline materials are used this is done by repetitive heating cycles or ion bombardment. However the properties of materials synthesized in the laboratory often change during heating, for example the transition from amorphous material to crystalline material can occur but also out-gassing is possible. Although these phenomena make these materials unsuitable for TPD since identical samples are required, for most analysis methods, they provide the opportunity to study crystallization and effusion.

For the study of these phenomena the same analysis methods can be used as described for TPD, if the rate limiting step of the effusion process is the desorption of a species from the surface. Otherwise, diffusion and readsorption of the effusing species have to be taken into account.

In the case of TPE measurements readsorption of species during the diffusion to the surface can occur, but taking readsorption processes into account in an analysis is often complicated. For this reason an in-depth analysis, as presented in Section 7.3, is not always possible. Effusion measurements can however provide useful insight on the composition of materials, their crystallization temperature, the way they crystallize, and where the diffusing species are located; in the bulk, in voids or the surface of the material. Three different types of TPE measurements will be discussed next.

7.4.1 Crystallization & Thermal Stability

If the heating initiates a crystallization process, this can often be detected by effusion of species from the surface, caused by a densification of the material during crystallization. Due to this densification, voids are annihilated and the gasses trapped in these voids can escape. The material composition can change during crystallization as well, for example during the crystallization of amorphous silicon hydrogen is released.

The temperature stability of materials can be investigated during a TPE experiment. The decomposition temperature of the material can be detected by monitoring the effused gasses. This gives information on the temperature stability of samples or the temperature at which unwanted compounds are removed from the sample.

7.4.2 Thickness Variation

In the case of thickness variation TPE measurements, identical samples with different thicknesses are tested. In these measurements effusion peak positions and peak shape give information about where species are present in the material and the rate-limiting step of their release. This is because the thickness of the samples varies but the surface is the same. Desorption peaks related to the surface, should therefore occur at the same temperature, whereas the peaks related to the bulk should shift towards higher temperatures as the sample thickness is increased. If the rate-limiting step of a species
coming from the bulk is desorption from the surface, the species can still be identified as coming from the bulk. This is because as the thickness is increased more material is available to effuse, resulting in a broader peak with an increased maximum effusion rate. For these reasons varying the thickness is a straightforward way to determine the rate limiting process of desorption and the location of the species, surface or bulk. (With de rate-limiting process known the appropriate analysis method can be de determined.)

### 7.4.3 Ion Implantation

The implantation of noble gas ions is a way to gain more insight on the relationship between the effusion of a species and the microstructure of a material. Because noble gas atoms are unable to form chemical bonds, only information on the structural properties of the host material is obtained. Implantation of Helium, Neon or Argon ions in the material can be done during the synthesis of the material or afterwards using ion implantation, in which an implantation depth at half the film thickness is often chosen.

The diffusion of these noble gasses has been described as a type of doorway diffusion in which the implanted atoms are trapped in voids. They can only escape if the thermal motion of the host atoms is large enough so they can pass through. The activation energy $E_d$ for doorway diffusion can be described using the following formula\(^\text{68}\):

$$E_d = 4\pi G r_d (r - r_d)^2$$ \hspace{1cm} 7.4.1

Where $G$ is the shear modulus of the material $r$ the radius of the inert gas atom and $r_d$ the size of the doorway opening. The diffusion coefficient $D$ related to this thermally driven process is given by:

$$D(T) = D_0 \exp\left(-\frac{E_d}{k_B T}\right)$$ \hspace{1cm} 7.4.2

With $D_0$ diffusion prefactor, $k_B$ the Boltzmann factor and $T$ the temperature of the material in which the ions are implanted. Performing TPE measurements on samples implanted with inert gas ions thus gives information about the structural properties because the density of the material and the size of the diffusing noble gas atoms used, determine the diffusion properties. Also information about the homogeneity of the material is obtained, since sharper peaks correspond to a smaller size distribution of the voids in which the noble gas atoms were trapped\(^\text{37}\).
Chapter 8  TPD Workstation

In this chapter the TPD setup is described in Section 8.1. An overview of the problems that surfaced during the setup of the system, how they have been fixed and what remains to be done to ensure the system is functioning properly is given in Section 8.2.

8.1 Setup description

Figure 32: The TPD Workstation obtained from Hiden Analytical. The main components are indicated.

In Figure 32 a picture of the Hiden Analytical TPD Workstation is shown. The four main components of the setup are; an analysis chamber, a sample transfer system consisting of a load lock and transfer arm, a quadrupole mass spectrometer and the heater assembly. In the next section the analysis chamber and the sample transfer system will be discussed in more detail. The quadrupole mass spectrometer (QMS) and heater assembly will are described in Sections 8.1.2 and 8.1.3 respectively. The setup of a basic TPD measurement is discussed in Section 8.1.4
8.1.1 The Analysis Chamber & Sample Transfer System

The analysis chamber is a spherical stainless steel vessel with a viewport upfront and several flanges on which additional equipment can be installed, for example a gas injection system or a SE. At the moment no additional equipment is installed and only effusion measurements are possible. A schematic view of the main chamber as seen through the main viewport is shown in Figure 33 where the configuration of the main parts in the machine is visible. The orifice of the mass spectrometer is located directly above the heater on which sample is placed. This allows for line of sight detection of the effused species. This ensures that species are detected as they come off the surface with a high detection accuracy.

![Schematic cross-section of the main chamber of the TPD setup. The heater is directly under the orifice of the mass spectrometer to allow for line of sight detection of the effusing species.](image)

In order to minimize the contributions of the background to the detected mass spectrometer signals, the main chamber is constantly held under ultra high vacuum. A background pressure of \(\sim 10^{-9}\) mbar can be reached, measured by a total pressure penning gauge. To achieve this pressure the chamber is evacuated using a turbo molecular pump with a pumping speed of 240 Liters per second backed up by an oil-free rough vacuum pump. For a fast sample transfer and to keep the main chamber under continuous vacuum a load lock is used, separated from the main chamber by a manual valve (see Figure 32).
The sample is transferred to the main chamber using a transfer-arm and placed on the heater by pushing it off the transfer arm. For this a metal rod with a ceramic tip is used. The heater can be moved in the z-direction, i.e. towards and away from the mass spectrometer, to position it in such a way that transferring the sample to and from the heater is possible. This system is fragile and this is one of the problems discussed in Section 8.2.

### 8.1.2 Quadrupole Mass Spectrometer

The mass spectrometer used for the detection of the effused gasses is a Hiden HAL 3F/301 PIC analyzer, a three filter quadrupole mass spectrometer (QMS) with a 300 amu. mass range. The mass spectrometer consists of three main components; an electron impact ionizer for the ionization of the effused gasses, the quadrupole analyzer for ion selection and the ion detector (an electron multiplier). A schematic overview of a QMS is given in Figure 34.

![Schematic overview of the Quadrupole Mass Spectrometer.](image)

**Figure 34: Schematic overview of the Quadrupole Mass Spectrometer.**

The ionization of the effused gasses is achieved using electron impact ionization. The electrons are emitted from an oxide coated Iridium filament. These electrons are accelerated over a tunable potential difference between 0 and 150 V (70V is typically used). The ionized species then travel to the quadrupole where the mass selection takes place. The quadrupole consists of four cylindrical rods arranged around the central axis of QMS. Opposite rods are placed in electrical contact with each other and a voltage is applied to the two pairs:

$$V_1 = U + V \cos(\omega t)$$

$$V_2 = -U - V \cos(\omega t)$$

Were $V_1$ is the voltage applied to the first pair and $V_2$ the voltage applied to the second pair, $U$ the DC component of the applied voltage and $V \cos(\omega t)$ the AC component with an amplitude $V$, radial frequency $\omega$ at a time $t$. The applied field causes the ions to undergo complex motions resulting in a 3D-wave.
An ion with a specific mass charge (m/z) ratio can be filtered using a specific value of DC and AC component: Ions with a smaller m/z ratio than the m/z ratio selected accelerate more quickly in the electric field and thus have a larger oscillation amplitude. If this amplitude is large enough the ions recombine via collisions with the quadrupole rods and do not reach the detector. Ions with a larger m/z ratio are unable to respond to the AC component of the electrical field and slowly drift away from the center of the quadrupole due to the DC field. Once they reach the quadrupole they are too far away from the center of the axis and unable to strike the detector. By adjusting the DC and AC components of the electric field different m/z ratios can be measured. The stable ions are detected using a pulsed ion counter (PIC) and converted to a number of counts per second. The QMS has a maximum of $10^7$ counts per second with a minimum acquisition time of 2 milliseconds.

It should be noted that with a QMS only m/z ratios can be measured and that doubly charged ions thus appear at half their mass, triply charged ions at one third and so on. This should always be taken into account when analyzing QMS data, but can also be used to detect masses outside of the 300 amu detection range.

### 8.1.3 Heater Assembly

The heater assembly is schematically depicted in Figure 35. The heated part is shown as number 14 in the figure. It consists of a molybdenum disk to which power cables are connected. For cooling purposes a stainless steel shroud (number 12) is placed around the heater which is cooled by a water flow, set at a temperature of 20°C. Two thermocouples are used for the detection of the heater temperature and are spring-loaded, number 9 and 16, against the back of the heater to ensure a firm contact with the heater.

![Figure 35: A schematic of the heater assembly used in the TPD Workstation.](image)

The temperatures detected by the thermocouples are used as input for the temperature controller (a Eurotherm 3000 proportional-integral-differential (PID) controller). One of the thermocouples serves as a backup and is used to confirm if the heater is working properly (large differences between the readout...
of these two thermocouples can indicate a problem with the heater assembly). The PID controller ensures the temperature is increased at the desired heating rate, with a maximum of 30K/min and a maximum temperature of 1100°C. At this time, it is only possible to measure the control temperature of the heater assembly. This is because there are some issues with the detection of the sample temperature, discussed in Section 8.2.

During a measurement the sample is placed directly on the heater and pressure is applied on the sample using molybdenum pins (suspended in the main chamber). This ensures a good contact between sample and heater. It is actually the heater that is being pushed on the molybdenum pins as it is movable in the z-direction.

8.1.4 TPD measurement
A computer is used for the control of the effusion experiment to which both the heater assembly and the QMS are connected. To execute a measurement the TPDSof software developed by Hiden Analytical, is used. In this software the desired heating rate and end temperature of the experiment are programmed. Multiple heating and controlled cool down steps can be programmed at once, but since the properties of the materials used in this work change during an effusion experiment only one heating step is used.

With the temperature profile programmed in the software a QMS scan configuration can be chosen, to be executed during the experiment. In general two types of mass scans are possible; a BAR (Broad Acquisition Range) scan in which a mass range is scanned. Up to 300 m/z ratios can be scanned in succession; a tradeoff has to be made between the amount of m/z ratios scanned, the resolution in temperature and the acquisition time of a m/z ratio. Scanning a large amount of masses or using a long acquisition time adversely affects the temperature resolution, whereas a high temperature resolution results in an increased measurement noise. For higher temperature accuracy a MID (Multiple Ion Detection) scan can be used in which up to 16 different m/z ratios can be selected to be measured.

Using the TPDSof software it is only possible to measure one point per m/z peak. To ensure the maximum of each peak is measured the system must be calibrated. This is done using the software for the QMS, MassSoft 7. The software package allows for the calibration of the QMS parameters: multiplier voltage, peak alignment and electron energy. All these parameters should be checked at least once every two weeks of operation to ensure a proper functioning of the QMS.

8.2 Setup Problems
In this section the different problems that appeared during the installation of the TPD and the possible solutions are discussed. The issues encountered were communicated to Hiden Analytical, the manufacturer of the TPD workstation. A visit to Hiden Analytical was arranged to oversee the redesign of the system. During this visit the first experiments were performed which will be discussed in the next Chapter. Due to the problems encountered it was not possible to upgrade the TPD workstation during this work with a gas injection system.
During operation of the TPD several issues of the heater assembly became apparent. These problems were caused by the fact that the heater assembly is only attached to the TPD Workstation using the bottom flange, shown as number 4 in Figure 35. This causes the heater to move inside the chamber when transferring a sample to or from the heater, which can lead to damage of the heater parts within the cooling shroud. The parts within the cooling shroud are the power connectors and the thermocouples used for the temperature control, as shown in the bottom drawing of Figure 35. The power cables are connected to the heater using two barrel connectors, inside the cooling shroud, with two screws sticking out, number 23 and 24. If these come in contact with the shroud a short circuit occurs between the heater and the vessel causing the heater to malfunction. This was communicated with Hiden Analytical and the following solution was implemented: the placement of a ceramic tube inside the cooling shroud that isolates the barrel connector from the shroud preventing a short circuit.

During the first experiments also a deviation in the temperature (of several hundred degrees) between the two thermocouples located on the back of the heater, number 9 and 16 in Figure 35, was observed. This was caused by the detachment of either one of the thermocouples from the heater head and led to excessively high amount of power to be supplied to the heater. This resulted in the melting of a silicon sample to the heater, shown in Figure 36. Silicon has a melting point of 1414°C. This indicates that the heater reached a higher temperature than what according to the specifications would be possible (1100°C). To solve this problem a spring was attached to the thermocouples that presses them against the heater, ensuring a good thermal contact.

Figure 36: Photograph of the heater head with a melted silicon wafer piece.
Initially the sample temperature was measured by pressing a thermocouple against the sample. The pressure applied to the sample was rather arbitrary and only the thermocouple was used to press in one corner of the sample, which resulted in a temperature gradient over the sample during heating. This is also visible from Figure 36 where only the corner of the sample, on which the thermocouple was pressed, is melted to the heater. To solve this problem 3 molybdenum pins where installed by Hiden Analytical, in addition to the thermocouple, to be pressed on the other 3 corners of the sample.

However, the usage of a thermocouple to register the sample temperature is not the best option, because when a sample starts effusing the thermal conduction between the sample and thermocouple increases and the temperature registered by the thermocouple rises suddenly. Therefore, several alternative temperature measurement methods have been tested. Hiden Analytical suggested the measurement of the sample temperature using a pyrometer, attached to one of the viewports of the chamber. The pyrometer detects the thermal radiation of the sample and thus is insensitive to the effusion of a species from a sample. However, a pyrometer only functions properly from 300 °C and up. Another issue with measuring the temperature with a pyrometer is that silicon is partly transparent for the wavelength used (1.65 μm). Therefore the temperature measured by the pyrometer is a combination of the sample temperature and the heater temperature. For this reason, a pyrometer is not suited for the detection of the temperature of silicon substrates (used in this work).

When looking in literature it has been found that temperature measurements in high vacuum are challenging. In TPD machines where single crystalline samples are measured, the thermocouple is usually soldered onto the sample. This ensures a good thermal contact between the thermocouple and the sample. The main issue with this technique is that the soldering needs to be done outside of the chamber and the entire chamber needs to be opened when installing the sample with its soldered thermocouple. Using single crystalline samples, this is not a problem as usually complete studies are done on one sample (the chamber only needs to be opened once every few months). If one wants a higher throughput or if the samples studied undergo changes during heating this is not an option.

To determine the temperature of a silicon substrate Hirashita et al. introduced a standard temperature calibration method. The calibration method consists of measuring several samples which start to effuse at a known temperature. By measuring these samples a linear relationship can be established between the measured temperature and the actual sample temperature. This relationship can then be used to determine the effusion temperature of an unknown sample. An overview of the different samples used by Hirashita et al. is given in Table 5. The ramp rate is also indicated since the effusion maximum is ramp rate dependent. For the samples that are implanted with ions the implantation energy and dosage is indicated in the table as well.
Table 5: Overview of the materials used by Hirashita et al. to calibrate the silicon substrate temperature. The desorption temperature obtained at a ramp rate of 30°C/min is also indicated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample specification</th>
<th>Desorption (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H⁺ implanted Si (with 40 kV /1·10⁷ cm⁻²)</td>
<td>H₂ (411)</td>
</tr>
<tr>
<td>2</td>
<td>CaC₂O₄·H₂O pellet on Si</td>
<td>Ca (533) CO₂ (593)</td>
</tr>
<tr>
<td>3</td>
<td>Ar⁺ implanted Si (with 60 kV /2·10¹⁵ cm⁻²)</td>
<td>Ar (705 and 992)</td>
</tr>
<tr>
<td>4</td>
<td>BF₂⁺ implanted Si (with 60 kV /5·10¹⁵ cm⁻²)</td>
<td>SiF₄ (671)</td>
</tr>
<tr>
<td>5</td>
<td>H-terminated Si(100) surface</td>
<td>H₂ (408 and 530)</td>
</tr>
</tbody>
</table>

Using this calibration method Hirashita et al. obtained a temperature precision between different types of TPD instruments of 5.7°C. This option is now also investigated by Hiden Analytical. At the moment only silicon implanted with argon ions are used, but as shown by Hirashita et al. multiple samples are preferred to provide a good temperature calibration. A disadvantage of this method is that a temperature calibration needs to be carried out for each different substrate and heating rate to be used.

Using calibration samples for the determination of the sample temperature is still underway and was not possible for the experiments performed in this work. Instead the control temperature is used as an indication for the sample temperature. The sample temperature is estimated about 20% lower than the control temperature, determined by a pyrometer.
Chapter 9  TPD Results

In this chapter the results of TPD measurements obtained during a one week visit to Hiden Analytical in England will be discussed. Care should be taken with the interpretation of the data because the sample temperature could not be measured accurately. The data presented serves to give an indication of the possibilities of the TPD Workstation. Three types of samples were tested using silicon substrates:

- The effusion of poly-methyl methacrylate (PMMA) from graphene. This serves as an example of a thermal stability experiment
- The effusion of hydrogen and water from ALD- aluminium oxide (Al₂O₃) thin films. This experiment serves to identify the origin of hydrogen and water effusion peaks and provides an example of the thickness variation method described in Section 7.4
- The crystallization of Strontium Titanate (STO, SrTiO₃) as an example of a crystallization study.

All of the materials described above were synthesized in the PMP group and the results contribute to the ongoing research of the group. In the next section each of the three experiments will be described in detail together with a short introduction on the material and how TPD experiments could contribute to the ongoing research on these materials.

9.1 PMMA Evaporation from Graphene

One of the materials created within the PMP group is graphene, a monolayer of carbon atoms in a hexagonal two-dimensional arrangement. It has gained a lot of interest lately due to its distinctive properties, such as mechanical strength, high thermal conductivity and extremely high mobility of electrons. For applications such as field-effect transistors it is desirable to use graphene on a silicon substrate such that it can be implemented in silicon based device technology. As of yet it is not possible to synthesize graphene directly on silicon. Graphene can be grown on single crystal silicon carbide by vacuum annealing, on transition metals by chemical vapor deposition (CVD) or by the deposition of graphene oxide from a liquid suspension followed by a chemical reduction. The graphene used in this work is grown on copper foils by CVD as introduced by Li et al\textsuperscript{71}.

Independent of how the graphene is grown, lift-off techniques are required to transfer the graphene from the material on which it synthesized to the desired substrate. The transfer process investigated in this work consists of several steps. The first step involves the spin coating of PMMA, with a thickness of approximately 90nm, on the graphene coated copper substrate. PMMA supports the graphene during the second step: the removal of the copper substrate in an iron nitrate solution. This creates a free-floating graphene layer supported by the PMMA. The third step involves the transfer of the graphene-PMMA membrane to the desired substrate, by placing the substrate under the free floating graphene/PMMA stack. The substrate is then carefully removed from the solution with the graphene-PMMA membrane on top. In this work a silicon substrate coated with 90nm of SiO₂ was used as the
target substrate. This allows for the optical characterization of the graphene\textsuperscript{72,73}. The final step consists of the removal of PMMA from the graphene using hot acetone rinsing for 1 hour at 80°C.

Optical measurements using spectroscopic ellipsometry, as discussed in the first part of this thesis, showed that approximately 3nm of PMMA remained on the surface after the final step of the transfer process. In literature this residue is usually removed by an additional annealing step. This can be done both under a gas atmosphere such as hydrogen or under vacuum. For vacuum conditions temperatures ranging between 300°C and 500°C with an annealing time of two hours are typically used\textsuperscript{74–76}. TPD measurements can provide more insight in the temperature and rate at which PMMA is removed under vacuum conditions.

The monomer methyl methacrylate, C\textsubscript{5}H\textsubscript{8}O\textsubscript{2} has a molecular weight of 100 amu. Because PMMA might decompose as it comes off the surface, a QMS MID scan, where only the masses related to cracking pattern of PMMA are scanned, might provide an incorrect view of the effusion process. For this reason a BAR scan is chosen from m/z ratio 1 to 100. The heater was set to a temperature of 1000°C to be reached at a ramp rate of 30°C per minute. To make sure all the PMMA was removed the sample was kept at 1000°C for two hours.

The results of the TPD experiment are shown in Figure 37, for clarity not all the m/z ratios are plotted. In Figure 37 a) the control temperature as measured by the thermocouple in the heater is displayed as a function of the elapsed time together with several m/z ratios. As seen in the Figure 37 a) a linear temperature ramp is achieved as a function of time. At a certain point the temperature is high enough for species to desorb from the surface of the sample and they are detected by the QMS. To get a better indication of the temperature at which this occurs, the different m/z ratios are plotted as a function of the control temperature in Figure 37 b).

Figure 37: TPD of a graphene sample with ~3 nm of PMMA; a) the control temperature as registered by the heater thermocouple and the counts per second of several m/z ratios displayed as a function of time, b) the m/z ratios signals as a function of the control temperature.
In Figure 37 b) three peaks can be observed in m/z ratio 28 at 660, 720 and 816°C respectively. The peak at 720 °C is also present in the other m/z ratios displayed, although a difference of about 6°C in peak position between m/z 1 and 100 is observed. This is caused by the time required to scan 100 m/z ratios (11 sec) and the continuous increase in temperature (30°/min) during the data acquisition.

The mass spectrum acquired at 660°C, corresponding to the first peak, is shown in Figure 38. A baseline has been subtracted to allow for a comparison between literature and the data obtained here. The baseline takes into account species present in the background such as H₂ (m/z 1 and 2), H₂O (m/z 17 and 18), etc. The mass spectrum obtained at 425°C during the measurement has been used as a baseline. Preferably a background signal at 660°C should be measured and used as a baseline (since the background is temperature dependent). However since the system was not baked properly, i.e the background changed over time due to outgassing of species from the chamber walls, this was not possible.

As a reference for mass spectrum at 660 °C the cracking pattern of CO and CO₂ from the National Institute of Standards and Technology (NIST) database are added. The reference spectra show good agreement with the measured spectra indicating that both CO and CO₂ are released. Several additional m/z ratios are visible in the spectra; these are related to the species that reach a maximum at 720°C. Because the C⁺ and O⁺ signals are lower than what would be expected from NIST database probably also some N₂⁺ contributes to the m/z 28 signal, believed to be present in voids of the PMMA.

The presence of N₂⁺ in the PMMA could be confirmed by the m/z 14 signal. However in this signal no distinct peaks can be discriminated due to the high level of noise. A measurement in which only the m/z 12, 14 and m/z 28 peaks are measured should provide more insight due to the higher measurement accuracy (to be done in the future).

![Graph](https://via.placeholder.com/150)

**Figure 38:** Mass spectrum measured at 660°C (same sample as displayed in Figure 37). A background correction was made using the spectrum taken at 425°C before the onset of the first peak in the m/z 28 signal.

The mass spectrum of the peak at 720 °C is displayed in Figure 39. As a reference the cracking pattern of PMMA from the NIST database is added. Figure 39 shows that indeed PMMA is evaporating from the surface, since good agreement is obtained between the measured spectrum and the reference spectrum.
of PMMA. However some m/z signals are much higher in intensity than expected; m/z 2, 12, 14, 26, 27, 28, 29, 31, 32 and 44 differ the most. This indicates that also other species are desorbing from the surface. The m/z signals most likely correspond to \( \text{H}_2, \text{CO}_2, \text{CO}, \text{N}_2 \) and hydrocarbon fragments such as \( \text{C}_2\text{H}_6 \). These species are related to the decomposition of the PMMA on the surface during heating, as well as nitrogen trapped in voids of the material and the remnants of solvents used in the deposition process of PMMA.

From Figure 37 it appears that, once desorption starts, after 400-550 seconds all the PMMA has desorbed. This in contrast to literature where often annealing is done for several hours\(^{74,75} \). However in these cases the temperature used is much lower (300- 500 °C) resulting in a slower desorption rate, also visible in Figure 37. SE measurements of the graphene sample showed that not all the PMMA had been removed from the surface after the TPD measurement. In fact according to SE a layer of 1.6nm was still remaining. Since this layer is not removed during the TPD measurement it indicates that this layer is strongly bonded to the graphene and cannot be removed by a thermal treatment under vacuum conditions.

The desorption observed in Figure 37 appears to follow 0\(^{\text{th}}\) order kinetics when comparing Figure 30 and Figure 37 b). To confirm this more measurements with different PMMA thicknesses should be carried out. Unfortunately this was not possible due to the lack of time during the visit at Hiden.
Figure 39: Full mass spectrum measured at 720°C (same sample as displayed in Figure 37b), for all the m/z ratios measured. A background correction was made using spectrum taken at 425°C before the onset of the first peak in the m/z 28 signal. The species corresponding to CO$_2$, N$_2$ and fragments from PMMA are linked to their respective m/z ratios.
9.2 Aluminium Oxide Thickness variation

ALD- Aluminium oxide is used extensively in the PMP group, because it has interesting properties for application in silicon solar cells, in which it acts as a surface passivation layer. Al₂O₃ reduces the defect density at the Al₂O₃ / Si interface leading to a lower surface recombination velocity of charge carriers in the Si. The Al₂O₃ also has a built-in negative charge that reduces the electron density at the Si surface, leading to field-effect passivation. Both processes can lead to the enhancement of the efficiencies in solar cells⁸,⁷⁸. ALD-Al₂O₃ is also used as a substrate for the deposition of other materials such as Platinum, Palladium and Ruthenium for applications in catalysis¹²,⁵².

The reduction in the defect density at the Al₂O₃ / Si interface is achieved after annealing the Al₂O₃ at ~400°C. During annealing hydrogen present in the Al₂O₃, diffuses to the interface and passivates the dangling bonds of the silicon. The Al₂O₃ is deposited using ALD of tri-methyl-aluminium and an oxygen plasma on a silicon substrate (the same process was used to create the glass coated Al₂O₃ described in Section 3.2 of this thesis). The hydrogen content of the Al₂O₃ is 3%, as measured by Rutherford Back Scattering⁶⁸. The hydrogen incorporated in the film originates from the TMA precursor. Because the annealing process involves hydrogen diffusion through the material, TPD measurements might provide more insight on how the hydrogen diffuses and where it is located, at the surface or in the bulk. Although the annealing temperatures required for activating the surface passivation are only around 400°C, during the manufacturing of solar cells temperatures up to 800°C are required to create metal contacts. The temperature stability of the Al₂O₃ at high temperatures is therefore also of importance. Insight into the temperature behavior of Al₂O₃ is also useful to get insight into whether or not ALD-Al₂O₃ films can be used as a substrate for TPD measurements of other materials.

Previous TPD experiments on ALD-Al₂O₃ films performed by Dingemans et al., showed that H₂O, H₂, CO and CO₂ are released from the ALD-Al₂O₃⁶⁸. For this reason only the m/z ratios 1, 2, 17, 18, 28 and 44 were scanned. This allows for a much better time and temperature resolution as compared to the PMMA experiments where 100 individual m/z ratios were scanned. An overview of the measurements preformed is given in Table 6.

### Table 6: Overview of the experiments performed on the Al₂O₃. ALD films. Al₂O₃ films of different thickness were measured at a ramp rate of 25°C/min. Measurements on several samples where repeated, to check the reproducibility. For the 500nm Al₂O₃ film also different heating rates were applied.

<table>
<thead>
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<th>Al₂O₃ Thickness</th>
<th>20°C/min</th>
<th>25°C/min</th>
<th>30°C/min</th>
<th>Repeated</th>
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<td>250 nm</td>
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<td>X</td>
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</tr>
<tr>
<td>500 nm</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
A thickness series consisting of Al₂O₃ films of 10, 50, 100, 250 and 500 nm was analyzed. Dingemans et al. used a ramp rate of 20°C/min up to a maximum temperature of 1100 °C. Since the control temperature measured here is around 20% lower than the actual sample temperature, the ramp rate is also approximately 20% lower. For this reason a ramp rate of 25°C/min with a maximum control temperature of 1100°C was used in this work. The offset of 20% however, is a rough estimate. A calibration of the sample and heater temperature, or a temperature measurement of the sample surface is needed for a higher accuracy. Some of the measurements were repeated to check the reproducibility. For the 500nm Al₂O₃ film also different heating rates were applied (the 500nm thickness was used because of the higher signal to noise ratio for these samples). Unfortunately the uncertainty in the sample temperature is too large and makes the results obtained for the different heating rates not trustworthy; therefore they are not included in this work.

In Figure 40 two measurements performed on a 50 nm Al₂O₃ piece of the same sample are shown. The same settings were used for the two experiments. There are several differences apparent from Figure 40: a difference in peak position of about 30°C, as well as difference in peak shape and artifacts in the measurement displayed in Figure 40 b). The increase in effusion rate visible in all m/z ratios above 1000°C is due to the radiative heating of other parts of the TPD workstation and subsequent effusion from these parts. A proper system bake-out should reduce this effect.

Figure 40: The measured data as determined by measuring an Al₂O₃ sample of 50nm thick. Differences in peak shape, position and artifacts are visible despite the use of a piece of the same sample for both the experiments.

The difference in peak position of 30°C was observed also for the other repeated measurements and is related to the unknown sample temperature. Even if the control temperature is the same, the sample temperature can be slightly different for each measurement. This is caused by the variation in the pressure applied by the molybdenum pins, used to ensure a firm contact between heater and sample. This gives rise to variation in heat transfer between the heater and the sample. For this reason no reliable results could be obtained from varying the heating rates, as changes in peak position where within the 30°C margin.

The difference in peak shapes is most likely caused by in-homogeneities of the sample or small differences in the concentrations of the effusing species from sample to sample. The artifacts as
displayed in Figure 40 b) at 350 and 400°C could be the result of the ablation of dust or other contaminants present on the sample surface. The spikes in the m/z signals are caused by the QMS itself where degradation of the filaments leads to a sudden increase in the emission current.

The results of the measurements carried out on samples with different thicknesses of Al₂O₃ are given in Figure 41. The m/z signals measured correspond to CO⁺, CO₂⁺ H₂⁺ and H₂O⁺ shown in Figure 41 a, b, c and d respectively. The peaks related to CO⁺ and CO₂⁺ stay within 30°C of each other from sample to sample and their intensity is similar. Taking the measurement error of approximately 30°C into account, this indicates that these peaks are most likely related to the surface of the Al₂O₃. The CO⁺ and CO₂⁺ containing species are most likely created on the surface due to the exposure to air.

The peak in the hydrogen signal at low temperatures, around 300°C, also stays within 30°C for the different samples. As the peak position is independent of the thickness this suggests that the hydrogen is coming from the surface layers of the Al₂O₃. Interestingly the experiments done by Dingemans et al. did not reveal this peak. In their work, the QMS is located at the turbo pump and no line of sight detection was possible. This reduces the detection sensitivity for hydrogen because of the low pumping capacity of the turbo pump for hydrogen, resulting in a lower measurement sensitivity. The detection of this peak indicates that hydrogen can already effuse at temperatures below 300°C. This is consistent with the observation that annealing temperatures of ~320°C already lead to passivation of defects at the silicon interface.

Considering the H₂O signal (Figure 41 d), the development of a peak with increasing thickness is visible (between 800-1100°C, depending on the sample thickness). It shifts to higher temperatures and broadens as the Al₂O₃ thickness increases. The area under the peak also increases indicating that it is related to the bulk of the film as discussed in Section 7.4.2.

This H₂O peak, also observed by Dingemans et al., is caused by the reaction of two OH groups present in the film forming Al-O-Al bonds and H₂O:

\[ 2\cdot\text{Al-OH} \rightarrow \text{Al-O-Al} + \text{H}_2\text{O} \]  \( \text{9.2.1} \)

This reaction is suggested to be very efficient as the Al-O bonds are very stable. In Figure 41 d), for a film of 100nm the peak is visible at 880°C. Dingemans et al. reported this peak at 680°C, measured on an identical sample, indicating that the sample temperature is indeed around 20% lower than the control temperature.
During the formation of Al-O bonds, hydrogen can also be created:

\[
\text{Al-OH} \rightarrow \text{Al-O} + \text{H}
\]

Several peaks are visible in the Hydrogen signal for 700°C and up (Figure 41 c). The behavior is very different for thin films as compared to thicker films. This is due to the fact that hydrogen cannot diffuse through thick layers of Al$_2$O$_3$, which leads to an accumulation of hydrogen at the Si/Al$_2$O$_3$ interface\textsuperscript{68}. The creation of blisters on the film surface follows when the hydrogen pressure at the interface becomes too high. The blisters are visible using an optical microscope. In Figure 42 blisters formed on a 500nm and 250nm Al$_2$O$_3$ film after a TPD measurement are shown. The formation of blisters can also be observed indirectly through the formation of a noisy hydrogen peak at 950 and 1100°C for the samples of 250 and 500nm respectively. Because not all blisters break at the same time the pressure in the TPD chamber fluctuates between $1 \cdot 10^{-8}$ and $5 \cdot 10^{-8}$ mbar.

For Al$_2$O$_3$ films with a thickness above 100nm the hydrogen thus accumulates at the substrate interface and leads to the destruction of the film under the formation of blisters, at a control temperature

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**Figure 41:** The effusion spectra for different thicknesses of Al$_2$O$_3$ for a) CO, b) CO$_2$, c) H$_2$ and d) H$_2$O as a function of the control temperature.
between 950 and 1100°C. Considering the 20% lower sample temperature, these peaks occur between 760-880°C. This may cause problems if such films are to be used in the fabrication process of solar cells where temperatures up to 800°C are required. How this blistering can be prevented is still under investigation. Preliminary results show that a long annealing step at 600°C allows for a slow effusion of hydrogen from the films, without the formation of blisters. The reader is referred to the master project of Luuk Hennen for more details. The use of Al₂O₃ as a substrate is possible if films of 10nm or lower are deposited, since only surface contributions are observed in this case.

Figure 42: The presence of blisters on the Al₂O₃ film as seen through an optical microscope after a TPD measurement for samples of a) 500nm and b) 250nm.

9.3 Crystallization of Strontium Titanate

To meet the increasing demand for the downscaling of metal-insulator-metal (MIM) capacitors, materials with low leakage currents and a linear voltage characteristic are required. Next generation dynamic random access memory (DRAM) devices require an equivalent oxide thickness (EOT) below 0.5 nm. Traditionally silicon dioxide is used as dielectric material. To meet the requirements of downscaling, a thickness of 0.5 nm would be required to reach a capacitance > 500nF/mm² needed to meet the demands of device fabrication. At this thickness however, the leakage currents are too high to ensure proper device operation. Instead of decreasing the thickness another option is to use a material with a higher $k$ value than silicon dioxide ($k = 3.90$). One of these materials is strontium titanate (STO) with a theoretical $k$-value of ~300.

The STO created within the PMP group is deposited using ALD of (pentamethylcyclopentadienyl) trimethoxy-titanium, [[(Cp*)Ti(OMe)₃] and bis(trisopropylcyclopentadienyl)-strontium with 1,2-dimethoxyethane adduct, [Sr(Pr₃Cp)₂DME] for the precursor step and an oxygen plasma during the reactant step. The composition of the films can be adjusted by changing the Sr and Ti precursor cycle ratio. However, the deposited films are amorphous and need to be crystallized to reach the desired $k$ values. To crystallize the films annealing is performed at temperatures between 500°C and 600°C, depending on the stoichiometry of the STO. To get more insight on what happens during the annealing
and to get a better understanding of the influence of the stoichiometry on the annealing process, TPD measurements have been done.

TPD was performed on two STO samples of different stoichiometry (0.65 Sr / 0.35 Ti and Sr 0.5 / 0.5 Ti) but with the same thickness of 30nm. The samples where heated at a ramp rate of 30°C/min to a temperature of 1100°C. For the measurement of the different m/z ratios a BAR scan was used, scanning m/z 1 to 50. The results of the TPD on the sample with a stoichiometry of 0.65 Sr to 0.35 Ti are shown in Figure 43. From Figure 43 a) several effusion maxima are visible in the different m/z ratios at 450, 620, 832 and 884 °C.

\[\text{Figure 43: a) m/z signals as a function of the control temperature for STO with a stoichiometry of 0.65 Sr / 0.35 Ti, not all m/z signals are plotted for clarity. b) Cracking pattern of the m/z peak at 832°C displayed in Figure 43 a). As a reference the cracking pattern at 300°C was used.}\]

The cracking pattern of the peak visible at 832°C is shown in Figure 43 b). Reference spectra for CO\(_2\) from the NIST database and the database of Hiden Analytical are added\(^{17}\). The difference between the two is that in the Hiden database also the C\(^{13}\) isotope is taken into account. The cracking pattern measured matches to that of CO\(_2\) indicating that this peak is created due to the effusion of CO\(_2\) alone.

The peak at 450 °C is visible in m/z ratio 44 and 30 only. Due to low signal to noise ratio in the other m/z signals, no clear distinction between the counts/s at 450°C and the background signal (taken at 300°C) could be made. It is therefore unclear what the cause of this effusion maximum is. When looking at the mass spectrum of the peak present at 620°C shown in Figure 44 it can be seen that the effusion of CO\(_2\) fails to describe the different m/z ratios observed. The mass spectrum is most likely a combination of several hydrocarbons effusing from the material. For example the m/z ratios of 30,31,32,43 and 44 indicate the presence of methoxy-groups. This is supported by the fact that a dimethoxycarbethane adduct is present in the Sr precursor. The incomplete removal of the Sr and Ti precursor ligands during the deposition process leads to the incorporation of these groups is the synthesized STO film. The peak present at 450°C is probably also related to remnants of the precursors used.
The presence of methoxy-goups is further supported by a comparison of films of different stoichiometry, shown in Figure 45. The STO with a Sr content of 0.65 shows a higher intensity of effusion peaks furthermore an additional peak at high temperature is visible in m/z 28 compared to the film with a Sr content of 0.5. An increase in CO\textsubscript{x} related species for a higher Sr content is also reported by Langereis et al., and is related to the strong bonding of carbonates to Sr as compared to Ti\textsuperscript{81}. Apart from the extra peak for a higher Sr content the peak maxima are shifted to a lower temperature as the Sr content is increased. The global effusion maximum occurs at a control temperature of 832°C for a Sr content of 0.65 as compared to 888°C for a Sr content of 0.5. The difference in crystallization temperature is observed in literature also and is directly related to the difference in stoichiometry\textsuperscript{82}. A higher Sr content results in a higher nucleation density and thus faster film crystallization. During the annealing crystallization and film densification occurs, a thickness reduction of ~15% has been observed in earlier work\textsuperscript{81}. The densification of the film and a wider inter-atomic spacing due to heating (doorway diffusion principle) is the onset at which species trapped in voids can escape.
Chapter 10  Conclusion & Outlook

An introduction to TPD has been given together with a description of several TPD data analysis methods. The TPD workstation used in this work has been described in detail and several issues have been discussed. It was found that the heater assembly easily creates a short circuit, which could be prevented by the installment of a ceramic tube. The determination of the sample temperature using a thermocouple proved to be unsuccessful, because of variations in the thermal contact between the heater and sample during a measurement due to the effusion of material. To solve this problem a calibration method has been suggested, using ion implanted samples that start to effuse material at a known temperature.

TPE measurements have been performed on several materials created within the PMP group:

- It has been shown that PMMA effuses from graphene at a control temperature of 720°C in about 7-9 min. During the evaporation of PMMA air trapped in voids of the PMMA and remnants of solvents used in the spin coating process are also removed. SE measurements showed that not all PMMA is removed, since a layer of 1.6 nm remained on the graphene.

- For Al₂O₃ hydrogen and water present in the bulk and the surface of the material have been identified. Similar to the work of Dingemans et al. the formation of blisters on the surface was observed, for temperatures above 700°C. The blisters were confirmed to contain hydrogen, which was unable to diffuse through the Al₂O₃ and escaped when the pressure inside the blisters became too high.

- During the crystallization of STO, it has been found that hydrocarbons and CO₂ were released from the material. This is related to ligands of the Sr and Ti precursors used in the deposition process. Films with a higher Sr content showed more effusion caused by the strong binding of carbonates to Sr resulting in a higher content of COₓ related species in these films.

The measurements performed at Hiden Analytical give a good indication of what measurements will be possible once the TPD workstation will be reinstalled at the TU/e.

To further increase the measurement possibilities of the TPD workstation several upgrades are recommended. For example, TPD experiments in which adsorbates are introduced on the surface by gas-dosing are not possible at the moment. For this a gas-injection system needs to be designed and installed. There are two options available to implement this: dosing the gas via the background in the chamber or directly on the sample surface using a dosing needle. The second option has the advantage that lower amounts of gas are needed to be dosed in the chamber. The amount of molecules that hit the sample by directed dosing with a needle is much higher. This reduces the unwanted adsorption on other parts of the machine and thus reduces the background signal during a measurement. Dosing with a needle can be done without a significant increase of the background pressure (that is below 5·10⁻⁶ mbar) allowing for the use of the QMS during dosing. The flux of gas hitting the sample should be known so
that a calculation of the dosage as received by the sample is possible. The parts needed to make this possible have been ordered or are already available, except for the dosing needle.

The installation of a dosing system will also allow for the calibration of the QMS in such a way that counts/second of m/z ratios can be related to an amount of molecules effusing per second. This would enable the calculation of the total amount of desorbed molecules from TPD spectra. This is very useful when information about adsorbate coverage or the composition of a material is required. For initial analysis crystals of Pd (111), Pt (111) and Ru (0001) have been ordered. Adsorption on single crystals is more straightforward to analyze as contributions from effusing species can be eliminated.

The combination of TPD and in situ SE is another interesting option. The optical properties of a material may change due to the effusion of species or crystallization. This could be monitored by using SE in addition to QMS during a TPD experiment. SE gives a better understanding of crystallization events as the dielectric function of the material can change drastically. This is also the case for STO where crystallization is used to obtain the desired high-k values needed for applications. It is also possible to measure the temperature with SE, an accuracy of ~5°C can be obtained. This could provide a means of measuring the sample temperature easily without worrying about the effects of pushing a thermocouple on the sample surface.
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54. Mackus, A.J.M., Verheijen, M.A., Leick, N. & Kessels, W.M.M. Atomic layer deposition of metallic ultra-thin films, nanoparticles, and nanopatterns through oxygen-induced particle ripening. *To be published*


64. Dolle, P. *et al*. Mechanism of twoRdimensional AgAu alloy formation on Ru(001. 5, 2849-2853 (1987).


77. NIST Chemistry WebBook. at <http://webbook.nist.gov/chemistry/>


Appendix A

In this appendix the fits of the glass substrate and the Al₂O₃ layer are shown, together with the optical constants obtained from these fits.

**Figure A.1:** Measured values of a) reflectance, b) transmittance, c) Ψ and d) Δ together with the fit generated by the model for a bare glass substrate. The Ψ and Δ values were obtained at an angle of 57° and the reflectance at 12°.

The results of fitting the glass are given in Figure A.1. It shows the measured and modeled values of the reflectance, transmittance, Δ and Ψ, of a bare glass substrate of 0.7mm thick. Visually the fit shows good agreement to the measured data. The model consisted of two Lorentz oscillators and a Variational Dielectric Function (VDF). The oscillators are necessary to prevent that the VDF goes out of bounds at the edges of the spectrum. The value of ε_∞ was fixed at 1, see Equation 2.1.9. The obtained values of the two oscillators are given in Table A.1. The weights used for the fitting procedure and the chi-squared error of the individual fits are given in Table A.2. In case of the glass substrate all four data sets are weighted equally. The total number of data points was 8200 and 2056 fitting parameters were used. Of
the fitting parameters correspond to the VFD spaced two data points apart and 6 to the two oscillators used.

Table A.1: resonance frequency, plasma frequency and the scattering rate of the two Lorentz oscillators used in the fitting procedure.

<table>
<thead>
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<th>Oscillator</th>
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<th>$\Gamma$</th>
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</tr>
</tbody>
</table>

Table A.2: chi-squared error of the fits of the different data sets, together with the weights used in the fitting procedure and the number of data points fitted.

<table>
<thead>
<tr>
<th>Data Set</th>
<th>$\chi^2$</th>
<th>Weight</th>
<th>Number of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectance</td>
<td>0.03</td>
<td>1</td>
<td>3438</td>
</tr>
<tr>
<td>Transmittance</td>
<td>0.04</td>
<td>1</td>
<td>3438</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>3.54</td>
<td>1</td>
<td>662</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>4.82</td>
<td>1</td>
<td>662</td>
</tr>
<tr>
<td>Total</td>
<td>8.43</td>
<td></td>
<td>8200</td>
</tr>
</tbody>
</table>

The optical constants obtained for the glass are shown in Figure A.2 and Figure A.3. In the measurement range of the SE (0.75-5eV) the optical constants are smooth and are taken into account by the Lorentz oscillator with the highest plasma frequency, i.e. the VDF does not improve the fit in this range and fitting without it is possible. In the range measured by FTIR several peaks appear which cannot be modeled accurately by a Lorentz oscillator and a VDF is required. The peaks visible in the spectra up to 0.2eV are obtained from the reflectance data. Since the transmittance is zero in this range no information can be acquired, from a transmission measurement. The inset in Figure A.3 shows the additional information obtained from the transmittance measurement. Though the absorption peaks are small they absorb up to 90% of the incoming light in the transmittance measurement, due to the thickness of the glass sample. This illustrates nicely the benefit of combining different measurement types and techniques to gain a full picture of the optical properties of a material.
Figure A.2: $\varepsilon_1$ for the glass substrate used as a function of the energy, obtained from the fit shown in Figure A.1. The peaks visible up to 0.25eV are related to the ones measured in the reflectance spectra.

Figure A.3: $\varepsilon_2$ of glass as a function of the energy, obtained from the fit shown in Figure A.1.Apart from the peaks related to the reflectance spectra, the inset shows how the features in the transmittance are caused by small absorption peaks present in $\varepsilon_2$. 
Figure A.4: The optical constants a) $\varepsilon_1$ and b) $\varepsilon_2$ of Al$_2$O$_3$ obtained from the Lorentz oscillator used for the modeling.

For the determination of the optical constant of the Al$_2$O$_3$ the optical constants obtained from the glass were kept fixed and a layer describing the Al$_2$O$_3$ was added. For this a single Lorenz oscillator lying far outside the measured range could be used with $\varepsilon_\infty = 1$ (fixed) or only fitting $\varepsilon_\infty$. The optical constants are shown in Figure A.4. Since the Al$_2$O$_3$ has a bandgap of 7eV, the adsorption is zero and therefore also $\varepsilon_2$. The adsorption lying far outside the measured range does have an influence on $\varepsilon_1$, which increases as a function of the energy. This shows that $\varepsilon_1$ is much more sensitive for oscillations outside the measured range compared to $\varepsilon_2$.

During the fitting of the Pd and Pt films the optical constants of the glass and Al$_2$O$_3$ shown in this appendix were used and kept fixed during the fitting procedure.
In this appendix an example of a fit used to determine the optical constants of Pd and Pt from the \textit{ex situ} FTIR and SE measurements is given. A similar fitting procedure was used for all samples.

![Figure B.1](image-url)\textit{Figure B.1: Measured values of a) reflectance, b) transmittance, c) $\Psi$ and d) $\Delta$ together with the fit generated by the model, for a Pd film after 1000 ALD cycles. The $\Psi$ and $\Delta$ values were obtained at an angle of 57° and the reflectance at 12°.}

Figure B.1 shows the result of the modeling of a Pd layer after 1000 ALD cycles. Visually the fit is in good agreement with the obtained data. For the fitting two Lorentz oscillators and one Drude oscillator are used a VDF is applied in the range measured by SE. Extending the VDF over the FTIR range does not reduce the chi-squared error and is therefore omitted. This greatly reduces the amount of fitting parameters which speeds up the fitting procedure. A total of 340 fitting parameters was used, 331 for the VDF the others corresponding to the oscillators and $\varepsilon_{\infty}$. The values obtained for the oscillators are shown in Table B.1. The value obtained for $\varepsilon_{\infty}$ was 1.54. The resonance frequency of the Drude oscillator was kept fixed at 0. Table B.2 shows the corresponding chi-squared error and weights used. The error in $\Delta$ is large compared to the other ones, and is set to a weight of 0.001. Using a higher weight was not
possible, i.e. the other data sets could not be fitted in this case. The optical constants obtained from this fit are visible in Figure 28.

Table B.1: resonance frequency, plasma frequency and the scattering rate of the two Lorentz oscillators and Drude oscillator used in the fitting procedure.

<table>
<thead>
<tr>
<th>Oscillator</th>
<th>$\omega_0$</th>
<th>$\omega_p$</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lorentz 1</td>
<td>28359</td>
<td>201773</td>
<td>240379</td>
</tr>
<tr>
<td>Lorentz 2</td>
<td>8964.1</td>
<td>23725</td>
<td>5569.3</td>
</tr>
<tr>
<td>Drude</td>
<td>0</td>
<td>39475</td>
<td>1688</td>
</tr>
</tbody>
</table>

Table B.2: chi-squared error of the fits of the different data sets, together with the weights used in the fitting procedure and the number of data points fitted. In the calculation of the total chi-squared error the weights have been taken into account.

<table>
<thead>
<tr>
<th>Data Set</th>
<th>$\chi^2$</th>
<th>Weight</th>
<th>Number of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectance</td>
<td>0.08</td>
<td>1</td>
<td>3438</td>
</tr>
<tr>
<td>Transmittance</td>
<td>0.04</td>
<td>1</td>
<td>3438</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>2.30</td>
<td>1</td>
<td>662</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>0.23</td>
<td>0.001</td>
<td>662</td>
</tr>
<tr>
<td>Total</td>
<td>2.65</td>
<td></td>
<td>8200</td>
</tr>
</tbody>
</table>

For the fitting of Pt an extra Lorentz oscillator was required to take into account the peak at 0.8 eV visible in Figure 6.