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Plasma-assisted atomic layer deposition of platinum studied by surface infrared spectroscopy

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Plasma-assisted Atomic Layer Deposition of platinum studied by surface infrared spectroscopy

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August 2014

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Abstract

Atomic Layer Deposition (ALD) has been gaining interest in the last years as deposition technique for its accurate thickness control and high conformality. The three-step plasma-assisted Pt ALD process, noted as the ABC* process, has proven to be able to grow nanoparticles and thin films of Pt at room temperature. The cycle consists sequentially of a Pt precursor (MeCpPtMe3), an O2- and a H2-plasma dosing step. To achieve insight into the surface groups and the associated reaction mechanisms during the process, optimal settings for measuring FT-IR spectra on the platinum surfaces had to be found.

The absorbance spectra show that Pt-H, Pt-OH and CO are found as surface groups at different stages in the process. Their signals increase with the number of ALD cycles, so they are believed to have an important part in the involved reaction mechanisms.

During the H2-plasma step we see that Pt-H is formed, while it is removed during the precursor step. The CO groups are created in the precursor step and removed in the O2-plasma step. Furthermore, Pt-OH is formed during the O2-plasma step and removed in the precursor step. By the assignment of spectral peaks to surface groups a refined view on the reaction mechanisms has been found. Hence, with this FT-IR study more fundamental insights into the Pt ALD process at room temperature has been gained.

Erratum

In the bachelor thesis of J.M.M. Huijs, “Characterising the noble metal ALD process: in situ FT-IR measurements of ALD deposited Pt nanoparticles”, new results from the Pt ALD process have come to light and the view on the associated reaction mechanics is redefined. The assignment of Pt-H in this thesis is found to be incorrect as the results of Huijs indicate that it is associated with Pt-CO.
Contents

Abstract .......................................................................................................................... ii
Erratum ...................................................................................................................... ii

1 Introduction ........................................................................................................... 1
  1.1 Atomic layer deposition .................................................................................. 1
  1.2 Platinum ALD process ..................................................................................... 2
  1.3 Fourier Transform Infrared Transmission Spectroscopy ................................. 3
  1.4 Reaction mechanisms of platinum ALD ........................................................ 5
  1.5 Project goal ....................................................................................................... 6
  1.6 Outline ............................................................................................................. 6

2 Experimental setup ................................................................................................ 7
  2.1 The ALD reactor .............................................................................................. 7
  2.2 FT-IR spectroscopy .......................................................................................... 8
  2.3 Measurement schemes ..................................................................................... 9

3 FT-IR settings ......................................................................................................... 11
  3.1 Resolution ....................................................................................................... 11
  3.2 Averaging ....................................................................................................... 12
  3.3 Signal increase ............................................................................................... 13
  3.4 Stabilization background ............................................................................... 14

4 Room temperature platinum depositions ............................................................ 17
  4.1 Peak assignment ............................................................................................. 17
  4.1.1 Single step measurement at 150 cycles ................................................... 18
  4.1.2 Multiple step measurement at 150 cycles ............................................. 19
  4.2 Development of the absorbance spectra ....................................................... 20
  4.3 Reaction mechanisms ................................................................................... 22

5 Conclusion and outlook ....................................................................................... 23
  5.1 Conclusion ..................................................................................................... 23
  5.1.1 FT-IR settings ........................................................................................... 23
  5.1.2 Reaction mechanisms for plasma-assisted Pt ALD ............................... 24
  5.2 Outlook .......................................................................................................... 24

6 References ............................................................................................................ 27

Appendices ................................................................................................................ I
  Appendix A: Absorbance spectra .......................................................................... I
1 Introduction

1.1 Atomic layer deposition

Atomic layer deposition (ALD) is a thin-film deposition method, in which a sequence of gas phase reactants is used. This sequence consists of separate pulses of the reactants in contrast with the more commonly used chemical vapor deposition (CVD) technique where a continuous flow of substances is present in the reaction chamber. The reactions within each pulse are purely chemical in nature, hence the reactions stop when no more chemical active sites are present at the surface. This self-limiting reaction mechanism results in a sub-nanometer thickness control. Further advantages of ALD are highly uniform films with an excellent conformality. The demand for control of thin-film growth at the atomic level for e.g. the miniaturization in the semiconductor industry has driven the advancement of ALD [1].

In Figure 1.1 a schematic illustration of the principle of the ALD process is shown. A typical ALD cycle consists of two half cycles, respectively the precursor and the reactant half cycle. The precursor is made of molecules containing the element(s) to be deposited with some additional ligands. In the first half cycle the precursor is adsorbed on the substrate which will make bonds with the surface creating a (sub)monolayer of deposited material and also several reaction products in the gas phase. The surface reactions during this half cycle are self-limiting, meaning that a maximum amount of precursor can be adsorbed on the surface due to the finite number of surface sites. In the second half cycle the surface is exposed to the reactant. The reactant removes any remaining precursor ligands from the surface, and reactives the surface for the next precursor cycle, i.e. forming new reactive surface sites. The two half cycles are separated by purge and/or pump steps to remove remaining substances from the reaction chamber. This also ensures that under no circumstances the precursor and reactant are in the reaction chamber simultaneously, to avoid any CVD reactions.

![ALD Cycle Diagram](image)

*Figure 1.1: The principle of the ALD process. A complete ALD cycle consists of the precursor and the reactant half cycles, separated by purges or pump steps.*

There are two different types of ALD processes, namely thermal and plasma-assisted ALD. In a thermal ALD process the reactions are thermally driven, while in a plasma-assisted ALD process the reactions are driven by the radicals in plasmas. These radicals are very reactive, therefore a plasma-assisted process has several potential benefits over a thermal process. It allows for more freedom in processing conditions, e.g. depositions at room temperature and a wider range of material properties.
Additionally it provides an increased growth rate [2][3]. In this study the focus is on the plasma-assisted ALD process of platinum at room temperature.

### 1.2 Platinum ALD process

In this study a three-step plasma-assisted ALD process is used to deposit platinum on the substrate. Platinum, as a noble metal, is chemically stable against oxidation, even at high temperatures. It also has great catalytic and electrical properties, plus a high work function (5.6 eV) [4]. The platinum is provided by the precursor trimethyl(methylcyclopentadienyl)platinum(IV) (MeCpPtMe3) and is shown in Figure 1.2.

![Figure 1.2: Structural formula of the precursor MeCpPtMe3. The ring structure is a cyclopentadienyl, which is attached to the platinum atom, as well as a methyl group. Additionally three other methyl groups are attached to the platinum atom.](image)

The used scheme for the plasma-assisted Pt ALD cycle is shown in Figure 1.3. This scheme was optimized for depositions at room temperature in previous studies [5] and is referred to as an ABC* scheme. In step A the precursor MeCpPtMe3 is dosed via bubbling with argon as carrier gas. The first oxidant, an O2-plasma, and the second oxidant, a H2-plasma are dosed in step B and C* respectively. Because the O2-plasma oxidizes the Pt, resulting in deposition of PtOx, the H2-plasma step is required to reduce the PtOx layer back into Pt. All three dosages are separated by pump steps to remove the remaining precursor/oxidant and reaction products.

### Details of the RT Pt ALD cycle

<table>
<thead>
<tr>
<th>Step</th>
<th>Ar (s)</th>
<th>O2-plasma (s)</th>
<th>H2-plasma (s)</th>
<th>Cycle length</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>42 seconds</td>
</tr>
<tr>
<td>B</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>C*</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.3: The plasma-assisted Pt ALD cycle, noted as ABC*. One complete cycle takes approximately 42 seconds to complete. All numbers indicate the time in seconds. The three numbers at each plasma step represent the time that the gasses are dosed, the time the plasma source is turned on and the time the plasma is purged from the plasma source respectively.

The initial growth of platinum is an evolving process that changes as a function of the number of ALD cycles. There are four distinct stages in the ALD process that describe the growth of the deposited material [6]: Island formation, island growth, island
coalescence and finally layer-by-layer growth. In Figure 1.4 a schematic overview of these stages is given. The growth begins with the formation of individual islands, also known as nucleation. These islands will grow in size and number as the ALD process proceeds. Eventually the islands start to grow onto other islands and form clusters, so-called island coalescence. Finally, after multiple ALD cycles, the growing clusters form a closed film and from that moment growth continues layer-by-layer.

![Figure 1.4: A schematic overview of Pt ALD growth stages on an Al2O3 substrate](image)

### 1.3 Fourier Transform Infrared Transmission Spectroscopy

The main diagnostic used in this study is Fourier Transform Infrared Transmission Spectroscopy (FT-IR). With this technique the absorption by the substrate as a function of the frequency can be measured. Molecular bonds in the sample vibrate at a specific frequency based on their composition and absorb the incident IR light with the same frequency to varying degrees. Based on this absorbance spectrum the chemical composition of the substrate can be determined. In this thesis particular the absorbance spectrum will be used to identify the materials deposited on the substrate.

The most important part of a Fourier Transform spectrometer is a Michelson interferometer, of which a schematic diagram is shown in Figure 1.5. In this diagram the waves represent the electric field of the light beams. The infrared beam is directed to a beam splitter, where the beam is split into two different beams with different pathways. One beam is reflected by the beam splitter and travels to a fixed mirror, the other is transmitted and travels to a moveable mirror. Both beams are reflected back to the beam splitter where interference occurs. The detector measures the intensity of the incident beam as a function of the position of the moveable mirror, $I(x)$, known as the interferogram. The spectral intensity distribution function $I(\nu)$ is calculated by Fourier transforming the interferogram as in equation (1.1).

$$I(\nu) = \int_{-\infty}^{\infty} I(x) \exp(-2i\nu x) dx \quad (1.1)$$

The absorbance $A$ can be measured by simply placing a sample between the interferometer and the detector, and calculating by means of equation (1.2).
$A = -\log_{10} \frac{I}{I_0}$  \hspace{1cm} (1.2)

In this equation $I$ is the measurement with a sample between the interferometer and the detector, and $I_0$ is a background measurement without sample.

![Diagram of a Michelson interferometer](image)

*Figure 1.5: Schematic diagram of a Michelson interferometer, which consists of a beam splitter, a fixed and movable mirror, and a detector.*

To examine the change in the chemical composition of the substrate the difference spectrum $A_{diff}$ is used. This is calculated by equation (1.3).

$$A_{diff} = -\log_{10} \frac{I_1}{I_2}$$  \hspace{1cm} (1.3)

With this equation the difference spectrum of a sample undergoing a treatment can be calculated where $I_1$ and $I_2$ are respectively the measurement of the sample after and before applying the treatment.

Peaks in the difference spectrum indicate a change in absorbance in respect to the reference measurement at that specific frequency. An example of a typical difference spectrum can be seen in Figure 1.6. The blue positive peak in the spectrum signifies a higher absorbance in respect to the reference measurement. This means that the number of molecules that vibrate at this specific wavelength is increased. On the other hand the red negative peak means less molecules vibrating at that frequency.
1.4 Reaction mechanisms of platinum ALD

In this section the reaction mechanisms of Pt ALD are discussed by considering the previously ALD reaction mechanisms studies and the Pt surface science results proposed by Mackus *et al.* [8] and Kessels *et al.* [9]. These studies use an ALD process different from the ABC* process described in section 1.2: The cycle consists of MeCpPtMe$_3$ and O$_2$-gas half reactions. In Figure 1.7 the proposed reaction mechanisms of the MeCpPtMe$_3$ and O$_2$ gas half reactions are schematically shown. At the start of the MeCpPtMe$_3$ half reaction (a) the surface is covered in O atoms. When the MeCpPtMe$_3$ is adsorbed on the surface, it undergoes combustion and dehydrogenation reactions, resulting in CO$_2$ and H$_2$O reaction products. When the O atoms become depleted the reactions continue with dehydrogenation and incomplete oxidation, which releases H$_2$, CO and CH$_4$ and other hydrogenation products. During the O$_2$ half reaction (b) the carbonaceous layer formed in the previous half reaction is combusted and O$_2$ is dissociatively chemisorbed at the surface providing surface-bound O atoms similar to the start of this cycle.

These results can be used to search for similarities and differences in the reaction mechanisms between the two different Pt ALD processes. It is expected that during the extra H$_2$-plasma step in the ABC* process the Pt-O bonds are removed and replaced by Pt-H.
Figure 1.7: Schematic representation of the reaction mechanisms during ALD of Pt [8]: (a) MeCpPtMe3 and (b) O₂ gas half reactions. The blue and orange orbs are Pt and O atoms respectively.

1.5 Project goal

There is much to learn about the reaction mechanisms involved in the recently developed three-step Pt ALD process (ABC*) as well as the surface chemistry at each individual step of the process. Therefore, the main goal of this thesis is to study the surface reactions during the ALD process with FT-IR spectroscopy and gain fundamental insight into the reactions mechanism involved. To achieve this it is important to find optimal settings for measuring FT-IR spectra on the platinum surfaces.

1.6 Outline

In Chapter 2 of this thesis the experimental setup is discussed. Here the reactor and the schemes used for measuring the difference spectra are described. In Chapter 3 the explanation of the FT-IR settings are given and in Chapter 4 the results of identification of specific peaks in the difference spectra are presented. The conclusions that are drawn from the results are discussed in Chapter 5. Additionally an outlook and further improvements will be given.
2 Experimental setup

In this chapter the ALD technique and the FT-IR setup will be described. First the ALD reactor is described in section 2.1. In section 2.2 the Fourier transform infrared spectroscopy setup will be explained. The measurement schemes used in this study will be discussed in section 2.3.

2.1 The ALD reactor

The experiments were done in a home-build ALD reactor [10]. A schematic overview of the setup can be seen in Figure 2.1.

![Schematic overview of the ALD-I setup.](image)

The reaction chamber is connected with a RF inductively coupled plasma (ICP) source. The ICP is created by a copper coil winding around the quartz tube, generating 100 W plasma power. Both a turbomolecular and a rotary van pump are used to pump the chamber to a base pressure of \( \sim 10^{-6} \) mbar.

The chamber is also connected to supply lines for various precursors and gasses. The precursor bubbler was heated to 30 °C and dosed via bubbling using Argon as carrier gas. The carrier gas was added to facilitate the transport and to guarantee no remaining precursor in the supply lines. This led to a more reproducible dosing of the precursor. Each plasma pulse was preceded by a 3 s gas exposure to obtain a stabilized gas flow and followed with 1 s gas exposure after switching off the plasma. All the gasses were set to a pressure of 7.5 mTorr [5]. For the delivery of the precursor and reactants into the reactor fast ALD valves are used (\( \sim 20 \) ms switching time) to ensure accurate dosing.
The deposition takes place on a Si(100) wafer placed inside the chamber. KBr windows in the reactor walls are used for in situ probing of the deposition process by FT-IR spectroscopy. The protective valves in front of the KBr windows were only opened during the FT-IR measurements, to avoid undesired deposition on the windows. The wall and substrate heating were turned off, so the whole reactor was at room temperature.

2.2 FT-IR spectroscopy

For the FT-IR measurements a Vector 22 from Bruker Optics (resolution > 1 cm⁻¹) was used which has a mid-infrared light (MIR) source that produces a broad spectrum of infrared light (~7000 – 350 cm⁻¹ range). Within this study a range of 4000 - 600 cm⁻¹ was used. A schematic overview of the FT-IR setup can be seen in Figure 2.2. With this setup both in situ and ex situ measurements are possible. However, the setup was only used in the in situ mode.

During in situ measurements the IR beam will be generated by the MIR source, travel through the interferometer before passing through the reaction chamber. The amplitude of the beam can be reduced by decreasing an aperture. The beam passes in and out of the chamber through two KBr windows, which are well-known for the high transmittance of IR light in a broad wavelength range. After passing through the reaction chamber the beam will be reflected by an off-axis parabolic gold coated mirror towards a liquid N₂ cooled Mercury Cadmium Telluride (MCT) detector (Bruker D316, range: 10.000 – 750 cm⁻¹). To minimize the signal from H₂O and CO₂, which are present as products from reactions, the chamber is pumped down. The rest of the setup is continuously purged with dry nitrogen gas to remove the IR active gas species present in the ambient air.

The resolution originates from the displacement step size of the movable mirror in the interferometer (Figure 1.5). A smaller step size equals a higher resolution (lower cm⁻¹) and will result in a more detailed spectrum. The scan time can be set in time length or in number of scans, where the mirror passes through the entire range and back in a single scan. These settings are discussed in more detail in sections 3.1 and 3.2.
The output signal of the MCT detector is redirected to the Vector 22, where this signal is Fourier transformed into an IR spectrum, which can be analysed by the FTI-IR software from Bruker (OPUS 5.5).

2.3 Measurement schemes

In this section the different measurement schemes will be described. By measuring between each step (A, B or C*) a series of difference spectra can be calculated with equation (1.3) by using a different measurement as reference.

In Figure 2.3 the measurement scheme is given to calculate the difference spectra between individual steps in the ALD cycle. After a fixed number \( n \) of ALD cycles and purge time the first FT-IR measurement is done. After each step of the ALD process this FT-IR measurement is repeated. The difference spectra are then calculated with equation (1.3) by using two consecutive measurements. In this way the absorbance is determined for each step of the ALD cycle.

![Figure 2.3: Measurement scheme for difference spectra between individual steps.](image)

To determine the absorbance for multiple consecutive steps in the ALD cycle a different measurement scheme is needed. This scheme is shown in Figure 2.4. In this scheme the reference measurement stays the same, namely in this example the first measurement after the fixed number of ALD cycles and purge time (i.e. before the precursor dose). Other difference spectra can be calculated by changing the reference measurement from before step A to after step A, B or C*.

![Figure 2.4: Measurement scheme for difference spectra with same base measurement.](image)
To determine the difference spectra between $n$ ALD cycles the measurement scheme from Figure 2.5 has been used. This provides information about the development of the surface over multiple complete cycles. The measurements after each step, similar to those of the previous schemes, are compared to those same measurements that are done after $n$ ALD cycles. For instance, a measurement before step A is compared to the measurement after $n$ cycles and again before step A. This is the same for the other measurements (after A, B and C*).

Figure 2.5: Measurement scheme for difference spectra between $n$ ALD cycles.
3 FT-IR settings

In this section the optimized FT-IR settings will be shown and explained. These settings were optimized for this setup and this particular ALD process; however they can be easily adjusted for other setups or ALD processes.

3.1 Resolution

To determine the effect the resolution has on the signal and difference spectra, measurements have been performed on a test wafer with thickness of around 280 µm. Before any FTIR measurement 10 cycles of Pt ALD, as described in section 1.2, were deposited on this wafer to produce some surface groups from the ABC* process. The intensity was then measured with different resolutions (2, 4, 6, 8 and 16 cm⁻¹), and measured again after an additional ALD cycle of Pt ALD. The difference spectra of those measurements can be seen in Figure 3.1. The resolution 2 cm⁻¹ is omitted from this graph so the small differences between the spectra are more easily seen.

![Absorbance spectra](image)

*Figure 3.1: Plasma-assisted absorbance spectra (300 scans) with variable resolution between one full ALD cycle. The range of the peak of CO₂ (2450, 2250 cm⁻¹) is magnified for more clarity.*

The differences between the spectra are not easily observable, but when looking closer to the absorbance peak of CO₂ (2360 cm⁻¹) they become more notable, as can be seen in the inset in Figure 3.1. As predicted in section 2.2 the two peaks of CO₂ become less distinguishable as the resolution decreases. It is difficult to see two separate peaks at a resolution of 16 cm⁻¹, and as the resolution increases more details in the signal become visible.

There are however two drawbacks to further increasing the resolution. Firstly, the time for a measurement is dependent on the resolution. Measurements with higher resolutions increase the measuring time considerably. For dynamic experiments,
where the composition of the sample changes during measurements, this could be a problem. Luckily, in this study the final composition of the surface is much more important than the changes that may or may not occur. For future experiments one may incorporate multiple short measurements after each step of the process to study this effect. More information about this will be given in the outlook in Chapter 5.

Another drawback is seen in Figure 3.2, where the difference spectrum with a resolution of 2 cm\(^{-1}\) is shown. At a high enough resolution interference fringes arise which can obscure small spectral features [11]. These fringes originate from the small difference in pathlength as a result of internal reflection in the wafer, as can be seen in Figure 3.3. When two times the thickness of the wafer is equal to a multitude of the half-wavelength of the IR light beam, in turn constructive or destructive interference takes place. This gives rise to an oscillation in the baseline of the absorbance spectrum.

![Figure 3.2: Plasma-assisted absorbance spectra (300 scans) where the 2 cm\(^{-1}\) resolution with interference fringes is shown in black.](image)

![Figure 3.3: Interference in reflected and transmitted light.](image)

On account of these previously explained effects the optimal resolution is a middle ground between a high resolution for more detail in the spectral features, but low enough to prevent fringes that obscure these. One should also keep in mind that the measurement times increase with a better resolution. This is especially important for dynamic processes. For the main part of this study (Chapter 4) the resolution of the interferometer was set to 6 cm\(^{-1}\).

### 3.2 Averaging

Similar to the resolution, the scan time also has an effect to the signal and difference spectra. These measurements were done at the same moment as the previous section, so the same measurement scheme was used. In this case, the resolution was set to a fixed value of 8 cm\(^{-1}\) and the scan time was varied. The scan time is measured in number of consecutive scans and the values that were used are 10, 50, 100, 200, 300, 400, 500, 800 and 1000 scans. The resulting difference spectra can be seen in Figure 3.4.
Figure 3.4: Infrared absorbance spectra with variable scan time between one full ALD cycle. The range of the peak of CO$_2$ (2500, 2200 cm$^{-1}$) is magnified for more clarity.

Again the differences are best observed at the extremities. The spectrum with a very short scan time of just 10 scans has a low signal/noise ratio, which conceals small spectral features. Longer scan times equal less influence of background noise on the signal. Similar to higher resolutions which led to longer scan times, also an increasing scan time masks the dynamic properties of the surface. This is only a problem when the surface changes during the measurement. As discussed in section 3.1, during this study the final composition of the surface is the most important part of the measurements, so this effect has been ignored for the moment. Figure 3.4 also shows that there is an upper limit at which point further increasing the scan time does not significantly improve the signal/noise ratio.

Additionally, the required scan time depends on the amount of vibrational states available that can be excited by the IR beam. If the measurement is during the nucleation stage of the ALD process and deposited nanoparticles are still very small, the absorbance spectrum has only small spectral features related to the Pt nanoparticles. Further in the process, during the coalescence or layer-by-layer growth, these spectral features are increased and are easier to differentiate from the background noise. During nucleation the required scan time is therefore higher than during layer-by-layer growth to achieve the same signal/noise ratio.

### 3.3 Signal increase

An important aspect of this experiment is to acquire a good signal/noise ratio so even the smallest changes in the absorbance spectra are visible. Besides lowering the background noise by increasing the scan time, one can also achieve a better signal/noise ratio by increasing the amplitude of the signal. One way to do this is to expose a larger surface area to the IR beam, e.g. by putting multiple wafers in a row.
For this reason a different setup was used to study the benefits and drawbacks of this method.

The setup is unaltered in every way but one: the sample in the reaction chamber. In the previous setup the sample was a single wafer where the IR beam could go through. In the new setup three wafers are placed consecutively longitudinal to the IR beam, tripling the surface area of the film excited by the beam as shown in Figure 3.5. A maximum of three wafers after each other could be used before the signal was too low to measure. The result of this experiment is given in Figure 3.6.

![Figure 3.5: Sample setup with multiple consecutive wafers.](image)

![Figure 3.6: Difference spectrum (8 cm⁻¹, 1500 scans) for a 6 seconds precursor pulse with three consecutively placed wafers.](image)

It is clear to see a sinusoidal signal in the baseline of the difference spectrum. This particular signal is only visible in measurements with multiple samples and when a step in the ALD process has been performed (A, B or C*). The origin of these oscillations can be found in the differences in path lengths of the IR beam as a result of reflection between the wafers, which causes the interference seen in the figure. This effect is absent when two sequentially measurements are done, without any precursor or gas exposure in between. It is most likely that this is because of the spatial and angular shifts of the wafers that occur due to pressure differences during the ALD process, causing the wafers to slightly alter their position with respect to each other.

### 3.4 Stabilization background

To interpret the data correctly it is important that the spectral features in the absorbance difference spectra originate only from changes in the vibrational states at the surface of the sample. It is therefore necessary to examine what the influence of parts of the experiment is on the background. The main parts we investigated are the (re)cooling of the detector and running the several ALD cycles in a row.

In Figure 3.7 the influence of cooling the detector is depicted. Three consecutive absorbance spectra were made at each step of the experiment, i.e. before, directly after and 30 minutes after adding liquid nitrogen to the detector. The difference spectra visualize the stability of background signal in between two sequentially measurements. The difference spectra show the removal of CO₂ (2360 cm⁻¹) and H₂O (regions 3900-3500 cm⁻¹ and 1800-1400 cm⁻¹) during the cooling of the detector. They are negative because the concentration is decreasing in time due to the purging...
of the detector box. After 30 minutes the difference spectra are similar to the spectra before the cooling, which means that change in background is negligible. In other words, the background is stable again.

![Absorbance spectra](image)

*Figure 3.7: Absorbance spectra (resolution 6 cm⁻¹, 1000 scans, aperture 3 mm) to examine the influence of cooling the detector on the background. From up to down: just before cooling the detector, the next two right after finishing cooling and the last 30 minutes after cooling. The scale for each graph is the same. The peaks correspond with CO₂ (2360 cm⁻¹) and H₂O (3900-3500 cm⁻¹, 1800-1400 cm⁻¹).*

A similar experiment was performed to determine the influence of running multiple ALD cycles to the background signal. Again three consecutive measurements were made directly after and 30 minutes after running 19 ALD cycles. Difference spectra were made from two consecutive measurements to visualize the stability of the background signal. The results can be seen in Figure 3.8. The spectra show the formation of CO₂ and H₂O, just like after cooling the detector, after running the ALD cycles. After 30 minutes the peaks were substantially reduced, so that the change in background is yet again negligible.

As seen in Figure 3.7 and Figure 3.8, adding liquid nitrogen to the detector and running multiple ALD cycles have a significant effect on the background as both things change the amount of CO₂ and H₂O present in the purge box or the reaction chamber, respectively. These molecules can mask the signal of the surface, in which we are interested. Thus, it is of vital importance to wait until the background is stabilized again. During the measurements it took approximately 30 minutes for the background to stabilize. However, this depends on the number of ALD cycles, the size of the reaction chamber, the pump capacity and perhaps much more aspects of the setup and ALD process. So, this has consequences if these FT-IR measurements are performed with a different setup or ALD process.
Figure 3.8: Absorbance spectra (resolution 6 cm\(^{-1}\), 1000 scans, aperture 3 mm) to examine the influence of reaction products of the ALD process on the background. From up to down: the first two spectra are made just after running 19 ALD cycles and the last 30 minutes after these cycles. The scale for each graph is the same. The peaks correspond with CO\(_2\) (2360 cm\(^{-1}\)), H\(_2\)O (3900-3500 cm\(^{-1}\), 1800-1400 cm\(^{-1}\)).
4 Room temperature platinum depositions

In this chapter FT-IR measurements will be used to determine the chemical composition of the surface and the reaction mechanisms during the ABC* platinum ALD process. The difference spectra shown in the graphs will use different reference measurements as discussed in section 2.3 and are calculated with equation (1.3). In Table 4.1 the symbols used to represent the different spectra in graphs are denominated and explained.

Table 4.1: Denomination and description of elements occurring in graphs.

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt, O₂ or H₂</td>
<td>Difference spectrum of a single ALD step (resp. the precursor, O₂⁻ or H₂-plasma step). The spectrum is calculated with measurements before and after this step.</td>
</tr>
<tr>
<td>Pt + O₂ (+ H₂)</td>
<td>Difference spectrum of multiple consecutive ALD steps. The spectrum is calculated with a reference measurement before the precursor step and a measurement after resp. the O₂⁻ or H₂-plasma step.</td>
</tr>
<tr>
<td>O₂ + H₂</td>
<td>Difference spectrum of both the reactant steps. The spectrum is calculated with a reference measurement before the O₂-plasma step and a measurement after the H₂-plasma step.</td>
</tr>
<tr>
<td>n + (Pt/O₂/H₂)</td>
<td>Difference spectrum of a number (n) of full ALD cycles and part of another cycle (up to resp. the precursor, O₂⁻ or H₂-plasma step). The spectrum is calculated with a measurement after resp. the precursor, O₂⁻ or H₂-plasma step and n cycles (counting from clean wafer) and the reference measurement will be specified at the graph.</td>
</tr>
</tbody>
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4.1 Peak assignment

To determine the reaction mechanisms of the plasma-assisted ALD process ABC*, the assignment of the peaks found in the difference spectra to chemical surface groups is essential. The determined surface groups at the sample after 150 full cycles are discussed within this section. These specific spectra are chosen because at this moment the sample contains a fair amount of deposited platinum, and the signal from the surface bonds is easier to observe. The other spectra are shown in Appendix A.
4.1.1 Single step measurement at 150 cycles

In Figure 4.1 the absorbance spectra for the individual steps of the ALD process can be seen. The spectrum during the precursor pulse displays the Pt-H peak at 2063 cm\(^{-1}\) [12][13]. This peak is formed in the H\(_2\)-plasma step and removed during the precursor dose. At 1996 cm\(^{-1}\) and 1803 cm\(^{-1}\) the linear and bridged modes of the CO groups are visible [14]. The peaks for both modes are formed in the precursor step and removed in the O\(_2\)-plasma step. In addition, the spectrum during the O\(_2\)-plasma step shows the bend and stretch modes of Pt-OH bonds at respectively 1012 cm\(^{-1}\) [14] and the region \(\sim 3600-3000\) cm\(^{-1}\) [15], and OCO symmetric stretch bonds at 1333 cm\(^{-1}\) [16]. All those bonds are formed in the O\(_2\)-plasma step and removed during the H\(_2\)-plasma step.

The spectra for all steps show the signal of H\(_2\)O (bands in the regions around 1500 cm\(^{-1}\) and 3800 cm\(^{-1}\)) [9], but most notable during the precursor and H\(_2\)-plasma doses. The formation of H\(_2\)O during the H\(_2\)-plasma step implies the reduction of a PtO\(_x\) surface formed in the O\(_2\)-plasma step to Pt, in a reaction with H\(_2\) that releases H\(_2\)O as the reaction product. Also two small peaks related to CO\(_2\) at 2360 cm\(^{-1}\) can be seen in all steps [9]. These bonds are formed during the oxidation doses and removed in the precursor step. However, because of the small size of the peaks this is most likely caused by a small perturbation in the background.

It is important to note that the peak positions of the measurements can differ slightly from the literature values. This is partly caused by the resolution of the interferometer, so that the difference between the measured and the actual value can be as large as the resolution. However, the environment of the surface groups has also a significant effect on the vibrational mode, making it rather difficult to compare results from different processes.

![Figure 4.1: Surface absorbance spectra of the sample after 150 ALD cycles for the MeCpPtMe\(_3\), O\(_2\)- and H\(_2\)-plasma steps. The peak positions of Pt-H (2063 cm\(^{-1}\)), Pt-OH (bend 1012 cm\(^{-1}\); stretch \(\sim 3600-3000\) cm\(^{-1}\)), CO (linear 1996 cm\(^{-1}\); bridged 1803 cm\(^{-1}\)) and OCO (1333 cm\(^{-1}\)) are indicated, as well as the range for H\(_2\)O.](image)
When combining the individual reactant steps, i.e. the O₂- and H₂-plasma steps, into a single reactant step, the absorbance spectra in Figure 4.2 become apparent. The two spectra are almost their perfect inverse of each other, meaning most of the bonds created in the precursor step are removed in the subsequent oxidations step and vice versa. The spectra show that the Pt-H bonds are created in the reactant step and removed during the precursor step, while this is reversed with the linear and bridged CO bonds.

![Absorbance spectra](image)

*Figure 4.2: Surface absorbance spectra of the sample after 150 ALD cycles for the MeCpPtMe₃ and the oxidations steps. The peak positions of Pt-H (2063 cm⁻¹), CO (linear 1996 cm⁻¹; bridged 1803 cm⁻¹) and CO₂ (2360 cm⁻¹) are indicated, as well as the range for H₂O.*

### 4.1.2 Multiple step measurement at 150 cycles

In Figure 4.3 the absorbance spectra of multiple ALD steps can be seen instead of the individual steps in Figure 4.1. The scheme of this measurement can be seen in Figure 2.4. This way the net change of the surface chemistry in respect to the start of the cycle can be observed. The peaks are found at the same wavenumbers as in Figure 4.1 and Figure 4.2, albeit with different magnitudes and signs. The absorbance spectrum of the full ALD cycle (Pt+O₂+H₂ in Figure 4.3) is equal to both the sum of the spectra in Figure 4.1 as well as the sum of the spectra in Figure 4.2.

The peaks associated with Pt-H at 2063 cm⁻¹ are in all steps negative. The negative peak for a full cycle (Pt+O₂+H₂) shows that there are more Pt-H bonds broken than there were created during the cycle. This does not however concur with our assumption that during the process more Pt is deposited on the layer and therefore more Pt sites are created on which hydrogen can bind. If this is the case and during an ALD cycle more Pt sites are created, more Pt-H bonds would be created than removed and the peak of Pt-H for a full cycle would be positive. It is therefore necessary to check if this peak is indeed correctly assigned to Pt-H bonds. More information about possible experiments is given in the outlook in section 5.2. For now the peak will still be associated with Pt-H.
In contrast with the negative Pt-H peak, the peaks of Pt-OH bending (1012 cm\(^{-1}\)) en stretching (around 3200 cm\(^{-1}\)) are positive after a complete cycle. This does agree with the assumption that more Pt sites are created in the process, so that more Pt-OH bonds can be formed in the H\(_2\)-plasma step than are removed in the previous steps.

![Absorbance spectra](image)

**Figure 4.3:** Surface absorbance spectra of the sample after 150 ALD cycles for multiple ALD steps (i.e. A, AB and ABC*). The peak positions of Pt-H (2063 cm\(^{-1}\)), Pt-OH (bend 1012 cm\(^{-1}\); stretch 3200 cm\(^{-1}\)), CO (linear 1996 cm\(^{-1}\); bridged 1803 cm\(^{-1}\)), CO\(_2\) (2360 cm\(^{-1}\)) and OCO (1333 cm\(^{-1}\)) are indicated, as well as the range for H\(_2\)O.

### 4.2 Development of the absorbance spectra

To determine if the surface chemistry changes during the ALD process, i.e. after a different number of cycles, the development of the absorbance spectra has to be examined. It can also be used to see which peaks are essential for this ALD process, as these should grow significantly as a function of the amount of deposited platinum (i.e. the number of cycles). The absorbance spectra of each step up to cycle 150 is therefore displayed in Figure 4.4. The absorbance spectra after cycle 150 are omitted from the graph for clarity, because these do not have flat baselines and are difficult to compare with (as can be seen in Appendix A). The results are split into three graphs with each displaying only one step of the process (precursor, O\(_2\)−, or H\(_2\)-plasma).

It is evident from the graphs that the peaks associated with Pt-H (2063 cm\(^{-1}\)), linear CO (1996 cm\(^{-1}\)) and Pt-OH bend (1012 cm\(^{-1}\)) become larger with increasing number of ALD cycles. It is therefore safe to assume that these bonds have an important role in the surface chemistry during the ABC* process. In addition, the peaks of bridged CO (1803 cm\(^{-1}\)), Pt-OH stretch (around 3300 cm\(^{-1}\)) and OCO symmetric stretch (1333 cm\(^{-1}\)) are only observable after many cycles. This might indicate that these
bonds occur after the initial nucleation growth when the platinum islands start to grow and coalesce.

Noteworthy is the fact that the peaks of CO$_2$ and H$_2$O are relatively larger early in the process. This is caused by the lack of sufficient purge time between measurements. After the problem was recognized and longer purge times were used, the signal of these products decreased.

![Figure 4.4: Surface absorbance spectra of each individual step in the ALD process. From left to right the steps from respectively the precursor, O$_2$- and H$_2$-plasma doses are displayed. The numbers indicate the number of cycles associated with the measurements.](image)

In Figure 4.5 the absorbance spectra from all steps in the ALD process are displayed in a single graph. Again for clarity purposes, only the steps till 150 cycles are shown. This time however, the reference measurement is held constant for each spectrum to show the development of the surface over multiple cycles. All measurements are compared with the reference after 43 full cycles. This results in a repetitive set of
three different spectra, i.e. after precursor, O₂- and H₂-plasma dose, which change in the course of the ALD process. Again it is easily seen that the peaks of Pt-H and linear CO increase significantly in size after more cycles. Also another peak becomes very noticeable, at ~1079 cm⁻¹. Nevertheless this peak is not surface related, but is the effect from the ever-growing deposited layer. In the region 3600-3000 cm⁻¹ a wide peak is visible, which could be the stretching mode of Pt-OH. It is however not clear, because the results don’t explain the varying shape of the peak.

4.3 Reaction mechanisms

Due to the peak assignments of the previous sections it is now possible to evaluate our current view on the reactions taken place during the ABC* process. In Figure 4.6 the presumed surface groups after each step in the process can be seen.

At the start of the cycle the platinum particles are covered in hydrogen atoms. During the precursor step (A) the hydrogen atoms are removed and platinum atoms are deposited. Additionally, some CₓHₓ that originates from the precursor ligands bind to the surface. These bonds are removed in the O₂-plasma step (B) and replaced with O and OH. After the last step of the cycle, the H₂-plasma step (C*), the surface is yet again covered in hydrogen, like at the start of the cycle. This process is repeated each cycle with a slightly altered surface as platinum atoms are deposited.

Due to the change in reactant steps, this view differs from the proposed reaction mechanisms by Mackus et al. [8] and Kessels et al. [9], described in section 1.4. The extra H₂-plasma step causes the surface to be covered in hydrogen instead of oxygen. In addition, after the O₂-plasma step of the ABC* process the surface groups consists of O and OH, while after the O₂ gas step only O groups are found. This might be caused by the increased reactivity from the plasma. Additionally, CO bonds are found on the surface after the precursor step.

*Figure 4.6: Schematic representation of the surface groups during ABC* process, where platinum atoms are represented by the blue orbs.*
5 Conclusion and outlook

In this chapter all important conclusions of this thesis are summarized. These will be split into two parts: the findings of the FT-IR settings and of the measurements from the ABC* process. There will also be given an outlook on how to improve these measurements as well as future experiments to further increase the insight gained in this thesis.

5.1 Conclusion

5.1.1 FT-IR settings

The settings for the FT-IR measurements are crucial to be able to draw any conclusions from the spectra. Therefore, a lot of time has put into finding optimal settings for the setup.

The resolution of the interferometer affects the detail of the spectra greatly. It has to be high enough for sufficient detail in the spectral features. If multiple peaks close to each other need to be individually assigned, the resolution should obviously be higher. However, if the resolution is too high, fringes appear in the spectra, making it impossible to observe any features at all. Additionally, the error in the measurements increases proportionally with the resolution. These are all things to be taken into account when choosing the correct resolution for the process.

To improve the signal/noise ratio of the measurements more averaging can be used, which leads to more spectral detail. There is a limit on the effect of averaging, where further increasing the scan time does not significantly improve the signal/noise ratio. The required amount of averaging also depends on the (expected) signal of the vibrational states. If the sought after signal is low (relative to the noise), the necessary amount of averaging is higher than for high signals.

Worth mentioning is that increasing the resolution or the amount of averaging also increases the measurement time. While this is not always a problem, it is when studying dynamic processes where the chemical compositions change quickly. In this thesis the emphasis is on the final composition of the surface and not on the possible intermediate steps. However, it might be useful to decrease the measurement times for future experiments, as is discussed in the outlook in section 5.2.

In many absorbance spectra it was found that the signal for the reaction products H₂O and CO₂ is quite substantial. It is essential to this study that the peaks of the absorbance spectra belong only to the surface groups and not to any residual material in the reactor. Consequently, the purge time between measurements must be adequate to remove these residual materials. It is found that H₂O and CO₂ are produced during steps in the ALD process and during the cooling of the detector with liquid nitrogen. A purge time of 30 minutes was sufficient to stabilize the background, reducing the effect from the background on the measurements.
5.1.2 Reaction mechanisms for plasma-assisted Pt ALD

With the FT-IR measurements a big step is made in the understanding of the three-step plasma-assisted Pt ALD process. From peaks in the absorbance spectra and several literature references a refined view on the surface groups in each step of the process and the reaction mechanisms involved is proposed.

The absorbance spectra showed the linear and bridged modes of CO, Pt-OH bending and stretching, and Pt-H as surface groups. The signal of each of these groups increased as the deposition of platinum continued. It is therefore safe to assume that these bonds have an important role in the surface chemistry during the ABC* process.

The current view of the ABC* process is displayed in Figure 5.1. At the start of the cycle the platinum film is covered in hydrogen atoms. During the precursor step (A) the hydrogen atoms are removed and platinum atoms are deposited. Additionally, CO and some C,H, that originate from the precursor ligands bind to the surface. These bonds are removed in the O₂-plasma step (B) and replaced with O and OH. After the last step of the cycle, the H₂-plasma step (C*), the surface is yet again covered in hydrogen, like at the start of the cycle. This process is repeated each cycle with a slightly altered Pt-film as platinum atoms are deposited.

![Figure 5.1: Schematic representation of the surface groups during ABC* process, where platinum atoms are represented by the blue orbs.](image)

There is a fair amount of uncertainty about the assignment of Pt-H. In the absorbance spectrum of a full cycle the peak associated with Pt-H was negative, meaning more Pt-H bonds were broken than created during the cycle. Assuming that during a complete cycle, platinum is deposited on the surface, more platinum sites are created where hydrogen can bind unto. If this is the case and more platinum sites are created during a full cycle, more Pt-H groups should have been created than removed and the peak of Pt-H of a full cycle should be positive. It is therefore necessary to check if this peak is indeed correctly assigned to Pt-H.

5.2 Outlook

To study possible dynamic processes, shorter measurements could be made each step of the ALD process. To prevent a decrease in the signal/noise ratio, the short measurement should be repeated multiple times in quick succession. This way more information about the dynamic properties of the process can be extracted, and further improve our understanding of the ABC* process.

Due to the uncertainty of Pt-H, it is important to check if this assignment is correct. By using deuterium plasma instead of hydrogen plasma, the peaks associated with Pt-H (as well as Pt-OH) should shift if correctly assigned. If incorrectly assigned however, the peaks will remain at the same wavenumbers.
During the process many carbonaceous compounds are formed, while only CO is attached to the surface in significant amounts. To investigate how easily CO is attached to the Pt surface, CO gas could be dosed during different steps of the process.

These surface FT-IR measurements could also be complemented with gas-phase FT-IR measurements of the same ABC* process. By comparing the spectra more information about the surface groups as well as the reaction products can be obtained. Additionally, the thermal process of Pt ALD could be used to acquire more insight of the reaction mechanisms involved.
6 References


Appendices

Appendix A: Absorbance spectra

In this appendix the absorbance spectra of each measurement will be shown, except for 150 cycles which can be seen in section 4.1. The symbols used in the graphs are explained in Table 4.1.

![Graph showing absorbance spectra](image)

Figure A.1: Surface absorbance spectra of the sample after 10 ALD cycles.
Figure A. 2: Surface absorbance spectra of the sample after 43 ALD cycles.
Figure A. 3: Surface absorbance spectra of the sample after 60 ALD cycles.
Figure A. 4: Surface absorbance spectra of the sample after 80 ALD cycles.
Figure A. 5: Surface absorbance spectra of the sample after 100 ALD cycles.
Figure A.6: Surface absorbance spectra of the sample after 125 ALD cycles.
Figure A.7: Surface absorbance spectra of the sample after 175 ALD cycles.
Figure A.8: Surface absorbance spectra of the sample after 200 ALD cycles.
Figure A.9: Surface absorbance spectra of the sample after 225 ALD cycles.
Figure A.10: Surface absorbance spectra of the sample after 250 ALD cycles.