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Atomic layer deposition of Ruthenium thin films using oxygen

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Atomic layer deposition of Ruthenium thin films using oxygen

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Abstract

Ruthenium (Ru) is regarded as a potential electrode material on ultra high-k SrTiO₃ dielectric films for future high-density metal-insulator-metal (MIM) capacitors to be used in e.g. next generation DRAM devices. To achieve high quality Ru films with conformal growth and precise thickness control, atomic layer deposition (ALD) of Ru has been investigated. In previously developed ALD processes for Ru the relatively low growth per cycle and the precursors low vapor pressure are an issue. Moreover, thermal ALD of Ru using O₂ gas generally results in a pronounced nucleation delay and high surface roughness. It has been hypothesized that the use of an O₂ plasma could possibly improve the film nucleation by providing oxygen radicals from the gas phase.

The current work aimed at developing thermal and plasma-assisted ALD processes for Ru using the novel CpRu(CO)₂Et precursor and O₂ as reactant on a TiN substrate. The material properties of the obtained Ru films were characterized extensively using several ex situ techniques. A fundamental understanding of the reaction mechanism of both ALD processes was obtained by monitoring reaction by-products in situ.

Thermal and plasma-assisted ALD both resulted in Ru films with similar properties once the film growth started. The obtained polycrystalline Ru films with a low resistivity (20 μΩ·cm) and a high growth per cycle (1 Å/cycle) meet the requirements for the resistivity and thickness set by the industry to follow the roadmap for MIM capacitors. The nucleation behavior of the ALD processes was, however, different. The Ru films nucleated after ~ 40 ALD cycles for the plasma-based process, whereas the thermal process showed a nucleation delay of ~ 80 cycles. Nevertheless, despite the improved nucleation, the plasma-assisted ALD Ru films had a higher surface roughness than the thermal ALD films.

The film composition and surface reactions were examined in order to investigate the differences in nucleation and roughness development. TOF-SIMS measurements showed that more oxygen was present in the plasma-assisted ALD Ru films. In comparison to thermal ALD, also more oxygen was incorporated in the entire TiN substrate for plasma-assisted ALD films. Mass spectrometry provided insight into the reaction products formed (mainly CO, CO₂, and H₂O) and, therefore, into the surface chemistry ruling both ALD processes. It showed that more chemisorbed oxygen is available on the surface for the plasma-assisted ALD process. By combining these results, a reaction mechanism is proposed for these O₂ based ALD processes to understand the differences observed in nucleation and roughness development of the Ru films.
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1. Introduction

Ruthenium (Ru) is a promising candidate as an electrode material for high density metal-insulator-metal (MIM) capacitors. Thermal and plasma-assisted atomic layer deposition (ALD) are considered to be suitable techniques to fulfill the requirements on film properties and growth conformality for the Ru electrodes in these MIM capacitors.

1.1 Application of Ru in metal-insulator-metal capacitors

MIM capacitors (see Figure 1.1) are three dimensional, high aspect ratio ($\geq 10$) trench structures integrated as discrete components in microchips. These capacitors are, among others, used to store charge in dynamic random access memories (DRAM), as RF decoupling capacitors in mobile communication devices, and in high voltage circuits for automotive industry. To follow the MIM capacitors road map, the capacity density of the MIM structures must be increased [1]. The capacitance $C$ of a parallel plate capacitor is given by:

$$C = \varepsilon_0 k \frac{A}{d},$$

(1.1)

where $\varepsilon_0$ is the permittivity of vacuum, $k$ is the relative permittivity of the dielectric (often also indicated by $\varepsilon_r$), $A$ is the surface area, and $d$ is the dielectric thickness.

To meet the specifications for the next generation MIM capacitors (Table 1.1 [2]), the capacitance density has already been increased in various ways. First, the surface area of the capacitor was increased by using high aspect ratio trench structures. Second, the capacitance was increased by decreasing the thickness of the dielectric. However the decrease in dielectric thickness results also in an increased leakage current that can deteriorate the capacitor performance. To circumvent this effect, ultra high-$k$ dielectrics, such as SrTiO$_3$ (STO, $k > 300$ [3]), are currently researched to further increase the capacitance density while maintaining acceptable low leakage currents.

![Fig. 1.1: Schematic picture of the 3D trenches of a MIM capacitor with a Ru film serving as a top and bottom electrode material and STO as a dielectric.](image)

The use of ultra high-$k$ dielectrics in a MIM capacitor sets demanding constraints on the metal electrode of choice. The metal electrode should have a low resistivity to obtain a good conductivity, and preferentially only a few nanometers thick. It should have a high work function to hinder injection of electrons from the metal to the dielectric in order to minimize the leakage current. Also, the interface between the metal and dielectric should be chemically stable to prevent interdiffusion of the materials. Due to its low resistivity (7.1 $\mu\Omega\cdot$cm [3]), high work function (4.7 eV [3]), and a chemically stable interface, Ru is researched as a metal electrode in combination with an STO dielectric layer (Fig. 1.1) [4,5]. The bulk material properties of Ru are summarized in Table 1.2.
Table 1.1: Physical requirements of next generation MIM capacitors [2].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Requirements for MIMcaps</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance density</td>
<td>&gt; 500 nF/mm²</td>
</tr>
<tr>
<td>k-value dielectric</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>Electrode thickness</td>
<td>5 – 30 nm</td>
</tr>
<tr>
<td>Resistivity</td>
<td>≤ 300 μΩ cm</td>
</tr>
<tr>
<td>Leakage current</td>
<td>≤ 10⁻⁸ A/cm²</td>
</tr>
</tbody>
</table>

Often oxidation of an electrode (e.g. during the deposition of the oxide insulator material) results in the formation of an insulating metal oxide. For Ru, however, the oxidation likely results in the formation of a RuO₂ film that also has conducting properties (a resistivity of 46 μΩ cm [3]). The conducting RuO₂ is even considered as a possible electrode material for MIM capacitors due to its high work function of ~ 5 eV, and the ability to form a stable interface with dielectric oxides. A thin RuO₂ layer can also improve the crystallization of the STO dielectric layer and reduces the formation of interfacial layers with a low k-value [4,5].

For the application of Ru nanometer thick films in high aspect ratio trench structures, high quality films have to be deposited with excellent conformality and precise thickness control. Especially the requirement on the growth conformality is difficult to achieve by means of conventional techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Therefore, atomic layer deposition (ALD) is the most suitable technique to deposit Ru (and STO) for MIM capacitors due to its self-limited surface chemistry.

Table 1.2: Physical properties of Ruthenium [3].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight</td>
<td>101.07 u⁸</td>
</tr>
<tr>
<td>Bulk resistivity</td>
<td>7.1 μΩ cm</td>
</tr>
<tr>
<td>Mass density</td>
<td>12.4 g/cm³</td>
</tr>
<tr>
<td>Work function</td>
<td>4.7 eV</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Hexagonal-closed-packing</td>
</tr>
<tr>
<td>Oxide formation</td>
<td>RuO₂ (s), RuO₃ (g), RuO₄ (g)</td>
</tr>
</tbody>
</table>

a: u = Atomic mass unit
1.2 Atomic layer deposition of Ru thin films

Atomic layer deposition (ALD) is a CVD-like technique suitable for the deposition of metals, metal oxides, and metal nitrides with thicknesses in the nanometer range. ALD has the ability to deposit high quality layers with low impurity content in high aspect ratio trench structures with precise thickness control and excellent conformality [6-8].

The technique is based on two alternated dosing steps with self-limiting surface reactions; one in which the substrate is exposed to a volatile precursor molecule and a second in which the substrate is exposed to reactant species. The two half reactions are separated by purge steps to remove the excess of precursor or reactant and reaction by-products. In Figure 1.2 a schematic overview of an ALD cycle for thermal ALD of Ru is displayed. After one ALD cycle (a fraction of) a monolayer of the Ru metal is deposited and the cycle can be repeated until the desired thickness is reached. More reactivity can be supplied to the ALD process by activating the reactant by a plasma in so-called plasma-assisted ALD (see Figure 1.2). This ALD technique is very useful to enhance the film nucleation on substrates and to tune the material properties as recently demonstrated for ALD of Pt [9].

Aaltonen et al. reported thermal ALD of Ru using several precursors such as RuCp₂ and Ru(thd)₃, and O₂ as a reactant [11,12]. For both processes she reported a nucleation delay and a relatively low growth per cycle of 0.45 and 0.36 Å/cycle using RuCp₂ and Ru(thd)₃, respectively [11,12]. Besides the growth characteristics and material properties, she also investigated the reaction mechanism of these processes to obtain a fundamental understanding of the surface reactions taking place during the ALD cycle.

![Fig 1.2: Schematic illustration of one ALD cycle for the deposition of the Ru metal. An ALD cycle consists of the alternate exposure of precursor and reactant gas to the substrate separated by purge steps. Both surface reactions rely on the presence of chemisorbed oxygen at the surface provided by the O₂ reactant in the second half cycle.](image)

---
The ALD processes of Ru rely on the presence of chemisorbed oxygen on the surface, which will lead to combustion of the precursor ligands in both ALD half reactions. During the precursor adsorption step, precursor will react with chemisorbed oxygen from the previous O₂ reactant exposure. This chemisorbed oxygen on the surface oxidatively decomposes the ligands (i.e. in this case the carbon-containing groups bonded to the metal) of the precursor forming the reaction by-products. The amount of chemisorbed oxygen at the surface is limited; therefore the ligands are only partially oxidized and the precursor adsorption is terminated when no chemisorbed oxygen is available anymore. In the second half cycle, the catalytically active Ru surface dissociates the molecular oxygen from the gas phase to form atomic oxygen chemisorbed at the surface. The adsorbed oxygen then reacts with the remaining ligands of the adsorbed precursor forming again reaction by-products. After complete removal of the ligands, a certain amount of chemisorbed oxygen stays at the surface and will be used for the combustion reaction during the precursor adsorption in the next ALD cycle [10].

Thermal ALD of Ru relies on the dissociative chemisorption of oxygen on the catalytically active Ru surface. In plasma-assisted ALD oxygen radicals are directly provided by the plasma and, therefore, the growth does not rely strictly on the catalytic activity of the surface [9]. This can cause differences in the nucleation properties of the Ru film, compared to thermal ALD. In other reports several thermal ALD processes for different Ru precursors using O₂ as a reactant were investigated and showed a nucleation delay, which is related to the absence of a catalytic-active Ru surface at the beginning of the deposition. Besides the nucleation delay also the low growth per cycle and the relatively low vapor pressures of the precursors were indicated as points for improvement [11-17]. In the literature also several reports on plasma-assisted ALD of Ru using an NH₃ plasma can be found [13,18,19]. In general, the Ru films obtained by plasma-assisted ALD using an NH₃ plasma showed a lower roughness and almost no nucleation delay with respect to thermal ALD using O₂ gas. An overview of the available ALD processes for thermal and plasma-assisted ALD is given in Appendix A.1.

For MIM capacitors, the use of an NH₃ plasma for the Ru deposition of the top electrode can cause nitridation and/or reduction the underlying STO layer, which might degrade the dielectric properties of the material. To prevent this, it is of interest to investigate whether the whole MIM stack can be deposited with O₂ as a reactant. Therefore the development of an oxygen based ALD process for Ru is desired. Smooth films are required to obtain a sharp interface between the Ru and STO layers. Based on the results of thermal and plasma-assisted ALD of Pt using O₂ [9], it can be anticipated that plasma-assisted ALD shows a shorter nucleation delay and smoother Ru films will be obtained than for thermal ALD. From a costs perspective, a TiN-Ru stack electrode is a potential candidate as a bottom electrode for MIM capacitors. The possible oxidation of the TiN substrate during the oxygen-based ALD process of Ru has to be investigated since it might be an issue towards the application.
1.3 Research goals and outline of this report

The aim of this research is to develop a thermal and plasma-assisted ALD processes using O₂ as a reactant for the deposition of Ru thin films, which can be applied as an electrode material in MIM capacitors. During this research the novel Ru precursor, CpRu(CO)₂Et, was investigated to obtain better nucleation properties and to achieve a higher growth per cycle compared to other Ru precursors. Besides the new precursor also the use of an O₂ plasma for ALD of Ru has not been reported before. The main goal of this research can be split up into the following objectives:

- The development of a thermal and plasma-assisted ALD process of Ru using CpRu(CO)₂Et and O₂ as a reactant.
- The examination of the material properties and the quality of the deposited Ru films on TiN substrates with respect to the application envisioned as well as the comparison between films deposited by thermal and plasma-assisted ALD.
- The investigation of the possible oxidation of the TiN substrate due to the use of O₂ gas or O₂ plasma in the ALD process.
- The investigation of the reaction mechanisms of thermal and plasma-assisted ALD to understand similarities and differences from a fundamental point of view.

Besides details about the development of the thermal and plasma-assisted ALD process for Ru Chapter 2 gives also information about the CpRu(CO)₂Et precursor, the type of substrate used, the deposition details, and diagnostics employed in this work. By combining the results obtained from the material properties (Chapter 3) and the reaction mechanism (Chapter 4), a proposal for the growth mechanism of Ru will be given in Chapter 4. Finally in Chapter 5, the general conclusion of this work and an outlook for further research towards the application of Ru as an electrode material in MIM capacitors will be given.
2. Experimental details

The Ruthenium thin films were deposited by thermal and plasma-assisted ALD using \( \text{CpRu(CO)}_2\text{Et} \) with \( \text{O}_2 \) as a reactant. The same reactor was used to develop both processes. This chapter gives a description of the setup, the novel Ru precursor, the substrate material, and the configuration of the cycles for thermal and plasma-assisted ALD of Ru. The diagnostics for determining the material properties of the Ru films are discussed and as well as the quadrupole mass spectrometry experiments to unravel the reaction mechanism.

2.1 Description of the FlexAL ALD reactor

All depositions were carried out on the Oxfords Instruments FlexAL\textsuperscript{®} ALD system [24]. A picture and schematic representation of the FlexAL system are displayed in Figure 2.1. This reactor is commercially available and has already been used to develop several thermal and plasma-assisted ALD processes of different materials such as TiN, HfO\textsubscript{2}, and Al\textsubscript{2}O\textsubscript{3} [25,26].

The reactor consists of a stainless steel reaction chamber connected to a remote plasma source. The plasma is generated by an inductively coupled plasma source that consists of an RF coil wrapped around a quartz tube. A power supply and a matching network can provide plasma powers up to 600 W at a radio frequency of 13.56 MHz. The top valve can separate the plasma source from the deposition chamber to prevent deposition in the plasma source. Different source gases (H\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, NH\textsubscript{3}, Ar, and SF\textsubscript{6}) are available for the process development. In the centre of the chamber a 240 mm ceramic heater is located which temperature range is between 25 - 400 °C. The chamber wall temperature can be controlled separately between 25 - 120 °C. The system is equipped with a load lock that can load wafers with a size of 4” - 8” into the reactor, so the chamber does not need to be vented between depositions. For smaller and odd wafer sizes and shapes, a carrier wafer is required.

Fig. 2.1: Picture and schematic of Oxford Instruments FlexAL ALD system located in the clean room facility of the TU/e.
The FlexAL system can be pumped to a relatively low base pressure of \( \sim 10^{-6} \) Torr. This pressure is reached by a nitrogen-purged 400 l/s turbo molecular pump which is backed by a rotary vane pump located in the sub-fab of the clean room facility. During deposition the pressure in the chamber can be controlled by: a fast (90 ms open-close) butterfly valve (the bottom valve), which is located in front of the turbo pump, and a 100 mTorr capacitance manometer gauge. The operating pressure range of the FlexAL system is 0-100 mTorr. The valves, precursor lines and piping, the turbo pump, the exhaust line between the turbo pump, and the rotary vane pump are all heated to prevent precursor condensation.

Precursor can be delivered into the reactor by independently heated bubblers. The precursor dosing is controlled by a fast ALD valve and the precursor is injected just above the centre of the substrate holder, below the top valve.

### 2.2 Deposition parameters for thermal and plasma-assisted ALD of Ru

The ALD processes developed in this work for the Ru depositions are shown below. For thermal ALD (Fig. 2.2 (a)), the cycle consist of the alternating exposure of the CpRu(CO)₂Et precursor (see Section 2.3) and O₂ gas. The deposition details are summarized in Table 2.1. The top valve was only opened during the reactant step to prevent unwanted deposition of Ru on the quartz tube of the plasma source, which will enhance disturb the ignition of the plasma. The ALD cycle starts with the CpRu(CO)₂Et precursor dosing, by delivering the precursor in the reaction chamber by Ar bubbling. After adequate precursor dosing the reactor chamber was purged to remove residual precursor and reaction products. The O₂ flow was started before opening the top valve to build up some pressure and stabilize the O₂ flow. When the top valve was opened the O₂ gas was directly delivered in the reaction chamber. The pressure during precursor dosing and O₂ gas exposure was kept at \( \sim 30 \) mTorr. At last, the remaining O₂ gas and reaction products were purged away by using Ar gas. The Ru depositions were preformed at a substrate temperature of 400 °C, similar to the preliminary TiN depositions of the substrate in the same reactor.

![Fig. 2.2: Schematic representation of the ALD cycle for depositions of Ru by thermal ALD (a) and depositions of Ru by plasma-assisted ALD (b).](image)
Table 2.1: Deposition parameters for thermal and plasma-assisted ALD of Ru. Differences with respect to the thermal ALD process are highlighted. The depositions details of plasma-assisted ALD of RuO₂ were mentioned for completeness.

<table>
<thead>
<tr>
<th></th>
<th>Thermal ALD</th>
<th>Plasma-assisted ALD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru</td>
<td>Ru</td>
</tr>
<tr>
<td>CpRu(CO)₂Et dosing time</td>
<td>2 s</td>
<td>2 s</td>
</tr>
<tr>
<td>Ar purge time</td>
<td>2 s</td>
<td>2 s</td>
</tr>
<tr>
<td>Ar purge flow</td>
<td>150 sccm</td>
<td>150 sccm</td>
</tr>
<tr>
<td>O₂ gas flow</td>
<td>60 sccm</td>
<td>60 sccm</td>
</tr>
<tr>
<td>O₂ gas exp. time</td>
<td>5 s</td>
<td>2 s</td>
</tr>
<tr>
<td>O₂ plasma exp. time</td>
<td>--</td>
<td>0.8 s</td>
</tr>
<tr>
<td>Ar purge time</td>
<td>2 s</td>
<td>2 s</td>
</tr>
<tr>
<td>Bubbler temperature</td>
<td>90 °C</td>
<td>90 °C</td>
</tr>
<tr>
<td>Ar bubbling gas flow</td>
<td>50 sccm</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Deposition temperature</td>
<td>400 °C</td>
<td>400 °C</td>
</tr>
<tr>
<td>Wall temperature</td>
<td>90 °C</td>
<td>90 °C</td>
</tr>
<tr>
<td>Plasma power</td>
<td>--</td>
<td>100 W</td>
</tr>
<tr>
<td>Chamber pressure</td>
<td>~ 30 mTorr</td>
<td>~ 30 mTorr</td>
</tr>
<tr>
<td>Total cycle time</td>
<td>18.3 s</td>
<td>16.1 s</td>
</tr>
</tbody>
</table>

The ALD cycle for plasma-assisted ALD is displayed in Figure 2.2 (b). The difference between thermal and plasma-assisted ALD lies in the O₂ reactant step where for plasma-assisted ALD a 100 W plasma power was ignited (see Table 2.1). A power of 100 W was selected because for higher plasma powers no deposition of Ru was observed. Before igniting the plasma a sufficient amount of O₂ gas must be present in the deposition chamber. Therefore the O₂ gas was stabilized for 2 s before igniting the plasma. Because the adsorbed CpRu(CO)₂Et precursor also reacts with O₂ gas, it is noted that a thermal component was part of the reactant step of the plasma-assisted ALD cycle. The difference in cycle time between thermal and plasma-assisted ALD of Ru is only due to the duration of the O₂ reactant step, except that the two processes are identical.

The deposition details for the deposition of RuO₂, as described in Section 3.1.3 for a longer O₂ plasma exposure, are also mentioned in Table 2.1 for completeness.
2.3 The novel ruthenium precursor: CpRu(CO)₂Et

Several precursors have been used for the deposition of Ru by ALD and most of them were cyclopentadienyl (C₅H₅ ring structure) based such as RuCp₂, Ru(EtCp)₂, but also precursors such as Ru(thd)₃ have been used before [11-13,18,27]. Most of these precursors were initially designed to be used for CVD processes, which is probably why the Ru growth per cycle is relatively low (0.15 – 1.2 Å/cycle [13,17]). Other disadvantages of these precursors are the nucleation delay and their low vapor pressure (see Figure 2.3).

For the Ru deposition in this work, the metal organic precursor cyclopentadienyl ethyl dicarbonyl ruthenium (SAFC Hitech, abbreviated as CpRu(CO)₂Et, C₉H₁₀O₂Ru) was used. This precursor was not yet commercially available and it was investigated in collaboration with SAFC Hitech. In Figure 2.4 the structural formula of CpRu(CO)₂Et is displayed. The precursor contains two CO groups, an ethyl group (Et, C₂H₅) and a cyclopentadienyl group (Cp, C₅H₅). The Cp group gives thermal stability to the precursor molecule, provides a high vapor pressure and is often used in metal organic precursors, for example Sr(tBu₃Cp)₂ and CH₃CpPt(CH₃)₃ for strontium and platinum depositions. The novel Ru precursor has a higher vapor pressure compared to already existing precursors and was designed to increase the Ru growth per cycle in ALD as well as to enhance the nucleation. Under standard conditions, CpRu(CO)₂Et appears as a yellow crystalline liquid. It has a molecular mass of 251.26 u and a boiling point of 60°C at 0.1mmHg. The precursor was injected into the reactor by bubbling with Ar as carrier gas and the precursor pot was kept at 90 °C. The material safety data sheet (MSDS) of the CpRu(CO)₂Et precursor is displayed in Appendix A.2.

![Fig 2.3: Vapor pressure of the precursor used in this work compared with other metal organic Ru precursors [28].](image)
SAFC Hitech reported a growth rate of 0.95 Å/cycle when using O₂ gas as a reactant for this precursor and nucleation delay was observed for all tested substrates, Si, SiO₂, and Ta/Cu [28]. In a brief study Park et al. reported an ALD process for CpRu(CO)₂Et when using O₂ gas or D₂O. A higher growth per cycle was obtained when using O₂ as a reactant and a short nucleation delay was observed, compared to when using D₂O as a reactant [29]. The CpRu(CO)₂Et was not yet fully characterized for thermal ALD with O₂ gas as a reactant. Moreover, the use of an O₂ plasma as a reactant is investigated for the first time in this work.

2.4 TiN as a substrate for Ru deposition

In the literature the deposition of Ru by ALD was performed on a variety of substrates as Al₂O₃, TaNx, Ta₂O₃, TiN, Si, and SiO₂ [11-13,18,27]. Ru showed a nucleation delay on almost all substrates. In this work, to prevent changing nucleation circumstances during deposition of Ru, all the depositions were performed on a stack of TiN/SiO₂/Si. TiN was chosen because it forms a stable interface with Ru and it is a possible electrode stack used in MIM capacitors [30].

In Figure 2.5 a schematic representation of the starting substrate together with a Ru layer is displayed. The TiN layers were deposited by plasma-assisted ALD in the FlexAl system at a substrate temperature of 400 °C (deposition details can be found in Appendix A.3). The depositions were carried out on a n-type Si wafer with native SiO₂. The typical thickness for the TiN layers was 8 ± 1 nm. The resistivities of the TiN substrates used in this work were slightly varying with an average value of 350 ± 75 μΩ·cm. The roughness of the TiN layers was relatively low, for films below 15 nm a root mean square (RMS) roughness of 0.5 nm was obtained.

Fig. 2.5: The structural formula of the precursor CpRu(CO)₂Et.

Fig. 2.4: The structural formula of the precursor CpRu(CO)₂Et.

Fig. 2.5: Schematic of the Ru/TiN/SiO₂/Si stack after deposition.
2.5 *Ex situ* film characterization of Ru films

The material properties of Ru ALD films were studied at different thicknesses to investigate whether the films meet the electrical requirements set by the application and to study the effect of the novel Ru precursor on the material properties, the nucleation behaviour and film growth. This is why two series of Ru layers were deposited on TiN: 100, 150, 200, 250 and 300 cycles of Ru thermal ALD, and 100, 200 and 300 cycles with plasma-assisted ALD. Material properties such as film composition, microstructure, resistivity, mass density and surface roughness were investigated and the film thickness and the nucleation delay were determined.

The composition of the Ru films was examined by Rutherford backscattering spectroscopy (RBS) performed at the TU/e singletron accelerator employing nominally 2 MeV He\(^{+}\) ions. To examine the layer structure of the samples, time of flight secondary ion mass spectrometry (TOF-SIMS) was performed by a dual beam ION-TOF IV instrument using Cs\(^{+}\) ions of 1 keV for sputtering and Ga\(^{+}\) ions of 25 keV for analysis.

To determine the crystal structure, thickness and mass density of the Ru films X-ray diffraction (XRD) and X-ray reflectrometry (XRR) were performed by a Philips X'Pert MPD diffractometer, equipped with a Cu X-ray source.

The sheet resistance of the TiN substrate and the Ru films was determined with the Signatone four-point-probe (FPP) in combination with a Keithley 2400 Sourcemeter acting as a current source and voltage meter. The resistivity was determined using the sheet resistance and the film thickness obtained by XRR. The sheet resistance was also used as a first test to verify whether the films deposited were conductive or not.

The surface morphology and RMS roughness of the Ru films were determined by atomic force microscope (AFM) measurements performed using a VEECO Dimension 3100 atomic force microscope.

The RBS, XRD, XRR and AFM measurements were carried out by Philips research MiPlaza Materials Analysis and the TOF-SIMS measurements were carried out at Laboratorio Nazionale MDM in Italy.

2.6 *In situ* analysis of the reaction mechanism by QMS

Mass spectrometry was proven to be a suitable tool for ALD process monitoring and reaction mechanism analysis [10,31]. Therefore, to gain understanding of the reaction mechanism of thermal and plasma-assisted ALD of Ru, quadrupole mass spectrometry (QMS) measurements were performed during deposition. The measurements were performed with a MKS Vision 2000C mass spectrometer with a detection range of 1-300 u. It was possible to follow the entire detection range for a given time period or to select certain mass to charge ratio (m/z value) which are followed in time. During QMS measurements ions were identified by their m/z value, which can represent different ions coming from a variety of parent molecules. For example, m/z = 28 can be CO\(^{+}\), C\(_2\)H\(_4\)\(^{+}\) or N\(_2\)\(^{+}\). The CO\(^{+}\) can originate from CO and CO\(_2\). Therefore the interpretation of QMS measurements must be done carefully.
3. Material properties of Ru thin films

The aim of this work is to deposit Ru thin films that fit the material properties required for electrode materials in MIM capacitors. The properties of Ru films obtained by thermal and plasma-assisted ALD have been reported in the literature, for different precursors, reactants, and substrates [10-14,18,27,32]. In this chapter, the work is described in which the effect of the novel CpRu(CO)₂Et precursor on the ALD process was investigated. Thermal and plasma-assisted ALD were compared directly and the same substrate (TiN) and reactant (O₂) were used. The material properties of the films obtained were studied and the films were evaluated with respect to its anticipated application.

3.1 Material properties of Ru films for thermal and plasma ALD

In this work, Ru thin films were successfully deposited by thermal and plasma-assisted ALD when using CpRu(CO)₂Et and O₂ as a reactant on a TiN substrate. In this section the resistivity, mass density and roughness of Ru films (~ 15 nm) deposited by thermal and plasma-assisted ALD are compared. To get an impression of the presence of impurities and the crystallinity, the film composition and microstructure will be discussed in the next sections. Also the influence of the O₂ plasma exposure to these properties will be discussed.

In Table 3.1 a summary is given of the measured properties and a comparison was made with the literature. A high density, high roughness, and low resistivity were observed. For the resistivity and mass density both ALD processes give similar results, however the roughness of the Ru films obtained by plasma-assisted ALD were higher compared to thermal ALD. The mass density of the Ru films obtained by thermal ALD (11 g/cm³) was slightly higher than Ru films obtained by plasma-assisted ALD (10 g/cm³), but the mass densities for both films were lower than the bulk mass density (12.4 g/cm³) [18]. The resistivity was equal for the films obtained by both processes (20 μΩ·cm) and was slightly higher than Ru’s bulk resistivity (7.1 μΩ·cm) [18]. For the mass density and resistivity comparable results were obtained in the literature for ALD processes [11,18]. The roughness of films obtained in this work was relatively high compared to literature [13]. Smoother films were obtained by thermal ALD, while Park et al. reported a higher roughness for thermal ALD. A more detailed description of these properties will be given in Section 3.3.

Table 3.1: Overview of the material properties of Ru film, obtained in this work. For a comparison, material properties of ALD Ru films reported in the literature are also shown.

<table>
<thead>
<tr>
<th></th>
<th>Resistivity [μΩ·cm]</th>
<th>Mass density [g/cm³]</th>
<th>Roughness / Thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FPP</td>
<td>Lit.</td>
<td>XRR</td>
</tr>
<tr>
<td>Thermal ALD (O₂ gas)</td>
<td>20 ± 0.5</td>
<td>20ᵃ</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>Plasma-assisted ALD (O₂ plasma)</td>
<td>20 ± 0.5</td>
<td>12ᶜ</td>
<td>10 ± 1</td>
</tr>
</tbody>
</table>

ᵃ: RuCp₂ with O₂ gas on Al₂O₃ [11],
ᵇ: Ru(EtCp)₂ with O₂ gas on TiN [18],
ᶜ: Ru(EtCp)₂ with NH₃ plasma on TiN [18].
3.1.1 Composition analysis of ALD Ru films

The composition of the deposited films was investigated to confirm that a Ru layer was deposited and to quantify the amount of impurities. The RBS measurements were performed on 22 and 35 nm thick Ru layers deposited by thermal and plasma-assisted ALD, respectively.

The typical RBS spectrum for the 22 nm Ru film obtained by thermal ALD is displayed in Figure 3.1. From the simulations it follows that the contamination of C, O or H in the Ru layer was below the detection limit of < 20% for C and O and < 5% for H. The Ti, N, O, and Si signals are assigned to the substrate. Some contamination of O was observed in the TiN layer due to oxidation of the substrate by the use of O₂ as a reactant for both processes (see section 3.4). The overall composition of the substrate was Ti:N:O = 1:1:1, for both processes. Plasma-assisted ALD showed comparable results to the thermal ALD films and no differences were observed in film composition when using an O₂ plasma as a reactant.

RBS showed that the obtained films are Ru of a high purity. The composition of the substrate indicates that there was some oxidation of the TiN substrate due to the use of O₂ gas or plasma as a reactant.

![Figure 3.1: Film composition of a 22 nm thick Ru film deposited by thermal ALD measured by Rutherford backscattering (RBS). The locations of the most prominent masses are indicated. The broad shoulder below 1.1 eV is caused by the Si substrate.](image-url)
3.1.2 Microstructure of ALD Ru films

The microstructure of the Ru films was determined to investigate whether crystalline Ru was obtained and whether one specific crystal orientation was preferential. A comparison was made between Ru films obtained by thermal and plasma-assisted ALD. The crystallinity of the Ru films was determined by grazing incidence XRD. The measurements were preformed on 22 nm and 35 nm thick films obtained by thermal and plasma-assisted ALD, respectively. To identify the diffraction peaks and to investigate whether a preferential growth direction exists, a comparison was made with the powder spectrum of Ru with a hexagonal crystal structure [36].

In Figure 3.2 the diffraction spectra of the Ru films are displayed for thermal and plasma-assisted ALD. When looking to the two spectra no differences are observed in the positions and intensities of the diffraction peaks. The positions of the peaks and the intensity ratios for the two experimental spectra coincide with the powder spectrum of hexagonal Ru. This shows that for both processes polycrystalline Ru films were obtained with no preferential growth direction.

Preferential growth can occur at high substrate temperatures as reported in the literature. Aaltonen et al. reported preferential growth in the (002) direction at a substrate temperature of 350 °C when using O₂ gas as a reactant [11]. Park et al. showed also the (002) preferential direction when using NH₃ plasma as a reactant at a substrate temperature of 300 °C [13]. For a hexagonal closed packed structure as Ru the (002) direction is the most thermodynamically stable crystal orientation. However, in this work the Ru films were deposited at 400 °C and no preferential orientation was observed, for thermal or plasma-assisted ALD.

![Fig. 3.2: Microstructure of Ru films deposited by thermal and plasma ALD, with thicknesses of 22 nm and 35 nm respectively, as determined with grazing incidence X-ray diffraction (XRD). The data was vertically shifted for clarity. The top graph shows the diffraction spectrum of a hexagonal Ru powder sample [36].](image-url)
3.1.3 Influence of increasing the O₂ plasma exposure time

Knoops et al. showed for plasma-assisted ALD of platinum (Pt) that tuning the O₂ plasma exposure time can be used to deposit Pt (0.5 s) or PtO₂ (5 s) films [9]. To examine whether, also RuO₂ could be deposited, the influence of the O₂ plasma exposure time during the deposition of Ru was investigated. A film was deposited by extending the O₂ plasma exposure time from 0.8 to 6 s. To characterize the deposited material, the crystallinity was investigated by grazing incidence XRD and compared with the powder spectrum of RuO₂ and Ru. The film composition was determined by RBS.

The crystallinity of a 25 nm thick film obtained by this experiment is displayed in Figure 3.3. The spectrum was compared to the powder spectra of RuO₂ and Ru. The positions of the diffraction peaks coincide with the powder spectrum of polycrystalline rutile RuO₂. The intensity ratios of the measured spectrum were not perfectly coinciding with the powder spectrum [36]. The intensity of the (101) diffraction peak for RuO₂ was much higher compared to the intensities of the other peaks. This indicates a preferred orientation of the RuO₂ crystallites, in the (101) direction. Also the (101) orientation from Ru’s reference powder spectrum could be distinguished in the measured spectrum indicating also the presence of Ru crystallites.

RBS measurements showed that the RuO₂ film was slightly Ru rich with a composition of Ru:O = 1.1:2. No traces of C or H were present in the RuO₂ layer (below detection limit, C < 20 %, H < 5%). This is an indication that Ru crystallites were present in the RuO₂ film. Thus, it is shown that for Ru ALD with a long O₂ plasma exposure time RuO₂ can be obtained, comparable to ALD of Pt [9]. Comparing to the literature no plasma-assisted ALD process was reported for RuO₂. For thermal ALD of RuO₂ no preferential growth was observed [14,33].

Fig. 3.3: Microstructure of RuO₂ film determined by grazing incidence X-ray diffraction (XRD). The 25 nm film was deposited by plasma-assisted ALD with an increased O₂ plasma exposure of 6 s. The top graph shows the diffraction spectrum of RuO₂ powder spectrum (open squares) and the strongest diffraction line in the hexagonal Ru powder spectrum (closed circle). The broad peak between 60° and 80° can be assigned to the crystalline Si substrate.
3.2 Thickness increase of Ru per ALD cycle

To investigate the effect of the novel Ru precursor on the ALD process performance, the ALD growth as a function of the number of cycles was studied for thermal ALD. A comparison of the growth per cycle, nucleation delay and surface coverage during one ALD cycle was made between thermal and plasma-assisted ALD.

For thermal ALD, five samples were deposited and characterized; i.e. films grown with 100, 150, 200, 250, and 300 ALD cycles (see Section 2.5). The thickness as a function of the number of cycles was measured by XRR. To check whether the measurements were not affected by the high surface roughness (see Section 3.3.1), the amount of deposited atoms (at/cm²) as a function of the number of cycles was measured by RBS. A comparison was made with plasma-assisted ALD by depositing three samples (with 100, 200, and 300 ALD cycles). The large uncertainty for the 300 cycles of plasma-assisted ALD data point (see Figure 3.4) is due to unusual behavior during deposition revealed by QMS monitoring, compared to the other samples.

In Figure 3.4 the thickness increase and the amount of deposited atoms of the Ru films as function of the number of cycles are displayed. As expected for an ALD process, both thermal and plasma-assisted ALD showed a linear increase in thickness. This was confirmed by both XRR and RBS. To obtain the growth per cycle of the Ru films, the data was fitted linearly. Thermal and plasma-assisted ALD both showed the same growth per cycle of 1.0 Å/cycle and $7.4 \times 10^{14}$ atoms/cm²·cycle as determined by XRR and RBS respectively. Assuming a linear behavior at the start of film growth as well, the nucleation delay is given by the intersection of the linear fit with the x-axis. For thermal ALD growth starts after ~ 80 cycles while for plasma-assisted ALD the growth starts after ~ 40 cycles. This is observed for both XRR and RBS.

Comparing to the literature, Aaltonen et al. showed a growth per cycle of 0.45 Å/cycle for thermal ALD when using RuCp₂ and O₂ gas as a reactant [11]. For thermal ALD the growth per cycle obtained in this work was twice as high. This was probably due to the precursor used, Ru(EtCp)₂ or RuCp₂, the two Cp ligands caused probably more steric hindrance compared to the precursor used in this work. For plasma-assisted ALD when using Ru(EtCp)₂ and an NH₃ plasma, Kwon et al. showed a growth per cycle of 0.38 Å/cycle [18]. Therefore, it is concluded that the growth per cycle was not only influenced by the used reactant but also by the precursor used.

![Fig. 3.4: Ru growth as a function of the number of ALD cycles for Ru films deposited by thermal and plasma ALD investigated in terms of by thickness (a) and the Ru areal density (b). Each data point represents a separate deposition.](image-url)
Kwon et al. showed that ALD of Ru when using Ru(EtCp)$_2$ and an NH$_3$ plasma had a shorter nucleation delay compared to the films obtained using the same precursor and O$_2$ gas on a TiN substrate [32]. This work also showed a shorter nucleation delay on TiN with plasma-assisted ALD than with thermal ALD. The faster nucleation is likely related to the more reactive species provided in the plasma.

The Ru surface coverage, expressed in monolayers per cycle (ML/cycle), was investigated to make a comparison with previous work. From the thickness increase and amount of deposited atoms per cycle, the surface coverage was calculated by two different approaches (Appendix A.2). In the first approach the surface coverage was calculated using the amount of deposited atoms per cycle, obtained by RBS, and the bulk mass density. In the second approach, the thickness increase per cycle, obtained by XRR, and the vertical lattice constant of Ru’s primitive cell (see Figure 3.5) were used to calculate the surface coverage. The films obtained by thermal and plasma-assisted ALD were polycrystalline Ru (see Section 3.1.2), the surface coverage was estimated by using the maximum and minimum vertical lattice constant.

In ALD, even in saturated conditions, the surface coverage during a cycle is in general below 1 ML/cycle, for example due to steric hindrance by the precursor molecules or due to the number of available reactive surface sites [8]. So, a surface coverage below 1 ML/cycle was expected. Since the same growth per cycle was obtained for thermal and plasma-assisted ALD, the surface coverage is equal for both processes. A maximum surface coverage of 0.43 ± 0.05 ML/cycle was obtained when using RBS together with the bulk mass density and the assumption of isotropic material. A similar result of 0.43 ± 0.05 ML/cycle was obtained when using XRR with the minimum vertical lattice constant. A minimum surface coverage of 0.23 ± 0.05 ML/cycle was obtained when using XRR and the maximum vertical lattice constant. Aaltonen et al. reported a growth per cycle of 0.2 ML/cycle for Ru films having the (002) orientation obtained when using RuCp$_2$ and O$_2$ gas on Al$_2$O$_3$ [10]. This was calculated by using the thickness increase per cycle (0.45 Å/cycle) and the vertical lattice, constant corresponding to the (002) orientation of the crystallites. The surface coverage in this work lies above surface coverage obtained by Aaltonen, which was not surprising since the growth per cycle in this work was also higher. As mentioned earlier, this can be assigned to the different precursor used.
3.3 Material properties of Ru films for different thicknesses

The Ru films (~ 15 nm) obtained by thermal and plasma-assisted ALD have comparable material properties (see Section 3.1). However, the nucleation delay of the Ru films is different for the two processes and could therefore influence the material properties (see Section 3.2). Therefore, the material properties of the Ru films such as roughness, mass density, and resistivity were investigated with respect to film thickness. In addition, the industrial application of Ru as an electrode material sets the requirements of low costs. Therefore, it is relevant to know the minimum thickness of the Ru films at which material properties still meet the specifications for MIM capacitors.

3.3.1 Surface morphology and roughness of Ru ALD films

Smooth films are required for implementing Ru films in MIM capacitors. To obtain the best electrical properties a well defined interface between the dielectric and electrode material is required. The surface roughness for thermal ALD, when using O2 gas as a reactant, is already well studied [13,18]. Besides the reactant, also the precursor used influences the surface roughness, therefore the film morphology of the films using the CpRu(CO)2Et precursor was investigated.

To examine the surface morphology and root mean square (RMS) roughness of the Ru films AFM measurements were performed on Ru layers with different thicknesses (see Section 2.5). For every sample two scans of 5 x 5 μm were performed and averaged. The TiN substrate had a RMS roughness of less than 0.5 nm. The final roughness of the Ru films was relatively high; therefore the influence of the substrate’s roughness to the final surface roughness was negligible.

The film morphology of the Ru films obtained by thermal and plasma-assisted ALD is displayed in Figure 3.6. It is clear that the surface morphology of comparable films (~ 15 nm in thickness) is quite different, the difference between thermal and plasma-assisted ALD is striking. For the film obtained by thermal ALD small grains were evenly distributed over the surface, whereas for the films obtained by plasma-assisted ALD some bigger, dominant grains were observed with smaller grains in between. Also the distance between the grains was bigger for plasma-assisted ALD films. The film nucleation determines the final film morphology. Besides the difference in nucleation delay also the formation of nucleation sites is different on TiN for thermal ALD compared to plasma-assisted ALD.

![Fig. 3.6: Film morphology for Ru films deposited by thermal ALD (a) with a thickness of 15 nm and 5 nm RMS roughness, and plasma-assisted ALD (b) with a thickness of 16 nm and 10 nm RMS roughness. Notice the difference in height scale.](image)
The roughness of the films (shown in Fig. 3.6) confirms the difference for both ALD processes, 5 and 10 nm roughness for 15 and 16 nm thick Ru films obtained by thermal and plasma-assisted ALD, respectively. This suggests that the initial growth mechanism of Ru determines the roughness and surface morphology of the entire film.

Therefore, the RMS roughness was investigated as a function of thickness and is shown in Figure 3.7. The errors in the thick Ru films were affected by some bigger grains present at one of the scan positions. More scans at different positions and scan sizes could give a better statistical outcome. Figure 3.7 shows that thermal ALD provides smoother films for all thicknesses, although the roughness was still relatively high compared to previous work, 3.1 and 0.7 nm RMS roughnesses for 50 nm thick Ru films obtained by thermal and plasma-assisted ALD, respectively [18]. The evolution of the surface roughness scales linearly with thickness. For the application the roughness should be as low as possible, therefore the Ru film should be as thin as possible. Also the roughness development mechanism must be understood such that the roughness development can be suppressed, for example by decreasing the substrate temperature.

Park et al. showed that ALD of Ru using an NH₃ plasma provides smoother films compared to thermal ALD using O₂ gas [13] and claimed that the low roughness was due to the good nucleation for plasma-assisted ALD in this case. However, in the present work fast nucleation was observed for plasma-assisted ALD, compared to thermal ALD (see Section 3.2), a high roughness was observed. Therefore, it can be concluded that the difference in surface roughness was not only due to the nucleation delay itself, but also due to the chemistry during the precursor and reactant exposure.
3.3.2 Mass density evolution with Ru film thickness

In Section 3.1 was shown that for ~ 15 nm thick Ru films a slightly higher mass density was obtained for thermal ALD compared to plasma-assisted ALD. For the application, it is investigated at which thickness the highest mass density was obtained. The difference in nucleation, for thermal and plasma-assisted ALD, and the presence of oxygen in the Ru layer (see Section 3.4), could influence the mass density at different thicknesses.

For each ALD process, the mass density was calculated from XRR measurements for different Ru thicknesses (see Section 2.5). Appendix B.2 shows an example of a typical XRR spectrum and its fit. The relatively big error in the measurement was caused by the high surface roughness (see Section 3.4.2) and the complex layer structure of the substrate (see Section 3.4). For films below 10 nm the error was even bigger because the Ru layers were relatively thin and no well defined interface between Ru and TiN was present.

As seen in Figure 3.8, all samples deposited by plasma-assisted ALD were less dense compared to films deposited by thermal ALD, which could be due to the presence of oxygen in the Ru films (see section 3.3.2). On the other hand, almost all films had a mass density lower than Ru’s bulk density of 12.4 g/cm$^3$, which can be related to the high surface roughness. In the XRR fit it was difficult to model the surface roughness. The Ru surface layer was assumed homogenous but is in reality a mixture of Ru and voids. Because the films obtained by plasma-assisted ALD contained more voids, related to a higher roughness, compared to thermal ALD the average electron density was lower. For thermal ALD the electron density was 3.000 ± 0.005 e/Å$^3$ and for plasma-assisted ALD the electron density was 2.800 ± 0.005 e/Å$^3$ compared to 3.25 e/Å$^3$ for bulk Ru. Thus, a higher roughness together with the presence of oxygen in the layers leads to a lower average electron density, which also reflects in a lower mass density.

![Fig. 3.8: Mass density of Ru as a function of film thickness deposited by thermal and plasma-assisted ALD determined by XRR.](image-url)
Kwon et al. reported a mass density of 8.7 g/cm$^3$ and 12.03 g/cm$^3$ for thermal and plasma-assisted ALD with Ru(EtCp)$_2$, respectively [18,27]. For plasma-assisted ALD no impurities were detected, for thermal ALD carbon and oxygen incorporation was observed [18,27]. Comparable to the results in this work, higher mass densities were obtained when less impurities were present in the Ru layer. The choice of the film thickness for the Ru electrode material in MIM capacitors is not limited by the mass density, because no clear differences were observed in mass density at different thicknesses.

### 3.3.3 Ru resistivity as a function of film thickness

For the application of Ru as an electrode material for MIM capacitors, it is important to obtain Ru films with a high conductivity at low thicknesses. The resistivity of Ru ALD films was therefore measured for different thicknesses. The resistivity of the TiN ALD film was $\sim 350 \mu\Omega\cdot\text{cm}$, compared to a resistivity of 7.1 $\mu\Omega\cdot\text{cm}$ for bulk Ru. The sheet resistance was measured at five points on the Ru wafer using FPP, after which the resistivity was calculated using the film thickness obtained by XRR (see Section 3.2).

In Figure 3.9 is shown that the resistivity decreases with thickness and saturates around 20 $\mu\Omega\cdot\text{cm}$ for Ru films above a thickness of 20 nm. The data shows comparable results for thermal and plasma ALD. The conductivity of the layer was apparently only a function of the film thickness and independent of the ALD process. The measured resistivities were always higher than the bulk value of Ru most probably because of the presence of contaminations in the Ru layer (see Section 3.4.2), which made the layers less conducting.

When comparing the resistivity with the literature, Kwon et al. reported a resistivity of 12 $\mu\Omega\cdot\text{cm}$ and Park et al. reported a resistivity of 14 $\mu\Omega\cdot\text{cm}$ for plasma-assisted ALD when using an NH$_3$ plasma [13,18]. Aaltonen et al. reported resistivities below 20 $\mu\Omega\cdot\text{cm}$ for thermal ALD with O$_2$ gas [11]. All the films, including ours, have low resistivities; however, they remain higher than the Ru bulk value of 7.1 $\mu\Omega\cdot\text{cm}$. For implementing Ru as an electrode material in MIM capacitors a resistivity at maximum 300 $\mu\Omega\cdot\text{cm}$ was required. The Ru films obtained in this work fit this requirement.

![Fig. 3.9: Resistivity as a function of thickness for Ru films deposited by thermal and plasma-assisted ALD. The resistivity was determined by FPP and using the XRR thickness. The error represents the standard deviation in the sheet resistance measurements.](image-url)
3.4 Substrate oxidation and film nucleation

The use of O\textsubscript{2} as a reactant in the ALD process might lead to oxidation of the substrate. The oxidation of the TiN substrate during thermal and plasma-assisted ALD was studied by examining the sheet resistance, the formation of interfacial oxide layers, and the film composition. Depositions on different dielectric oxides were carried out to compare the nucleation behavior of Ru growth between thermal and plasma-assisted ALD.

3.4.1 Sheet resistance of Ru with respect to the TiN substrate

The exposure of O\textsubscript{2} gas or plasma to the TiN substrate can lead to substrate oxidation. In this section the substrate oxidation due to O\textsubscript{2} gas exposure was compared to the oxidation by O\textsubscript{2} gas and plasma. To determine the sheet resistance as a function of thickness, the sheet resistance was measured on the TiN substrate and after the Ru deposition.

The relative sheet resistance as a function of the number of ALD cycles is displayed in Figure 3.10. All the values in Figure 3.10 were normalized by the sheet resistance of the TiN starting substrate to emphasize the change in sheet resistance due to the deposition. For thermal ALD no clear change in sheet resistance was observed after 50 or 100 ALD cycles. For thermal ALD, the sheet resistance drops due to nucleation of the Ru film after 150 cycles. For plasma-assisted ALD the relative sheet resistance increased after 50 ALD cycles. This was probably due to oxidation of the TiN substrate by the O\textsubscript{2} plasma. After 100 ALD cycles the sheet resistance drops and decreased further due to Ru deposition. If the sheet resistance after 50 cycles was compared for thermal and plasma-assisted ALD it is observed that for plasma-assisted ALD a higher sheet resistance was obtained. The increase of the sheet resistance was likely caused by the oxidation of the TiN prior to the start of Ru growth. The oxidation was consequently more intense during plasma-assisted ALD than during thermal ALD.

![Relative sheet resistance](image)

Fig. 3.10: Relative sheet resistance determined by FPP of Ru with respect to the sheet resistance of the TiN substrate as a function of the number of ALD cycles. The same data set was used as in Fig. 3.9.
To confirm the hypothesis that the TiN substrate was more oxidized during plasma-assisted ALD the TiN substrate was exposed to only O₂ gas and O₂ plasma. For O₂ gas exposure (250 s, equivalent to 50 cycles of thermal ALD of Ru) no clear change in sheet resistance was observed for the TiN substrate (625 Ω/□). For O₂ gas in combination with plasma exposure (100 s O₂ gas plus 90 s O₂ plasma, equivalent to 50 cycles of plasma-assisted ALD of Ru), the sheet resistance increased to 1030 Ω/□, the same behavior was observed after 50 plasma-assisted ALD cycles (see Figure 3.10). Therefore, it was assumed that the TiN substrate was mainly oxidized by O₂ plasma. The oxidation of the substrate was faster and more intense during plasma-assisted ALD which could also lead to the formation of interfacial layers between the substrate and the deposited Ru.

3.4.2 Formation of interfacial layers by oxidation

To investigate the oxidation of the TiN substrate, the layer structure and film composition were studied for thermal and plasma-assisted ALD of Ru. The film composition was determined by RBS measurements on the TiN substrate, prior to deposition, and on Ru films deposited by thermal and plasma-assisted ALD. The layer structure was determined by TOF-SIMS. To investigate the evolution of the oxidation, measurements were performed after 100 and 300 ALD cycles of thermal and plasma-assisted ALD.

From RBS it was observed that the TiN substrate contained oxygen after the Ru deposition, due to oxidation by the reactant (see section 3.1.1). No difference in film composition was observed by RBS before and after deposition of Ru, the technique was not sensitive enough. Before the Ru deposition the composition for the TiN layer was Ti:O:N = 1:1:1. This oxidation was probably due to the exposure to the ambient air. After thermal and plasma-assisted ALD of Ru the film composition of the TiN layer was equal. Because of the high detection limit for oxygen (< 20%) RBS only was not sufficient enough to observe differences in substrate oxidation; therefore TOF-SIMS measurements were performed to obtain a qualitative picture.

![Fig. 3.11: Film composition as a function of sputter time obtained by TOF-SIMS of a 2 nm thick Ru layer on TiN deposited by thermal ALD (a), and a 6 nm thick Ru layer on TiN deposited by plasma-assisted ALD (b). Both films were deposited by 100 ALD cycles.](image-url)
Figure 3.11 shows the film composition as function of the sputter time for a Ru layer deposited by 100 cycles of thermal and plasma-assisted ALD. For both thermal and plasma-assisted ALD, two peaks of the TiO signal were present in the TiN layer. This indicates that oxygen was present at the Ru-TiN interface, and at the TiN-SiO₂ interface. The oxygen found at the bottom interface is believed to come from the native SiO₂ of the substrate. No differences in oxygen content were observed in the TiN layer between thermal and plasma-assisted ALD.

The film composition as function of the sputter time for a Ru layer, deposited by 300 cycles of thermal and plasma-assisted ALD, is displayed in Figure 3.12. Again two peaks were observed in the TiO signal for thermal ALD. No difference in oxidation of the TiN layer was observed after 100 or 300 cycles of thermal ALD. A low penetration depth of oxygen into the substrate was observed, due to the O₂ gas. For plasma-assisted ALD one broad peak was observed for the TiO signal. Oxygen was present in the whole TiN layer due to the O₂ plasma, which means a larger penetration depth of oxygen into the substrate due to the plasma. For plasma ALD a high intensity was observed for the RuO signal, which means that the Ru contained more oxygen compared to thermal ALD. The amount of oxygen in the Ru layers was less than 20% because it could not detected by RBS.

It can be concluded that for both processes the TiN substrate was oxidized by the O₂ reactant. For thermal ALD only the top layer of the TiN contained oxygen. The O₂ plasma incorporated oxygen more efficiently into the surface for plasma-assisted ALD and eventually oxygen was present in the complete TiN layer. Besides more oxygen present in the TiN layer for plasma-assisted ALD, also more oxygen was observed in the Ru layer itself. Schematic overviews of the layer structure of Ru deposition by thermal and plasma-assisted ALD on TiN are displayed in Figure 3.13.

![Fig. 3.12: Film composition as a function of sputter time obtained by TOF-SIMS of a 22 nm thick Ru layer on TiN deposited by thermal ALD (a), and a 35 nm thick Ru layer on TiN deposited by plasma ALD (b). Both films were deposited by 300 ALD cycles.](image)
Fig. 3.13: Schematic overview of the layer structure after deposition of a thick (> 20 nm) Ru layer on TiN for thermal ALD (a) and plasma-assisted ALD (b).

3.4.3 Thermal and plasma-assisted ALD of Ru on different substrates

As mentioned in Chapter 1, the motivation of this work is to implement Ru as an electrode material for MIM capacitors. Different oxides are potential candidates as dielectric materials. Therefore the deposition of Ru on different oxides and its nucleation properties were investigated for thermal and plasma-assisted ALD.

Depositions of Ru were carried out simultaneously on TiO$_2$, SrTiO$_3$, native SiO$_2$, thermal SiO$_2$, and Al$_2$O$_3$ substrates by 200 ALD cycles for both thermal and plasma-assisted ALD. Before and after deposition the sheet resistance was measured by FPP to indicate whether there was growth of Ru and to get an indication of the difference in nucleation delay, as shown in Table 3.2.

For all substrates the sheet resistance was lower after deposition of Ru by plasma-assisted ALD, compared to thermal ALD. This was an indication that plasma-assisted ALD of Ru nucleates faster than thermal ALD on all the substrates investigated. A process with the smallest amount of ALD cycles is desirable in industry, to reduce precursor consumption. With this requirement only, TiO$_2$ or Al$_2$O$_3$, deposited by plasma-assisted ALD, would be the best materials in combination with Ru electrodes, but the $k$-value of the dielectric also determines the quality of the MIM stack. Compared to SrTiO$_3$ (STO), TiO$_2$ and Al$_2$O$_3$ have much lower $k$-values and therefore STO is most promising dielectric for MIM capacitors.

<table>
<thead>
<tr>
<th>Used Substrate</th>
<th>$k$-value$^a$</th>
<th>Sheet resistance before deposition ($\Omega/\square$)</th>
<th>Sheet resistance after 200 cycles</th>
<th>Substrate before deposition</th>
<th>After 200 cycles thermal ALD</th>
<th>After 200 cycles plasma-assisted ALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native SiO$_2$ (2 nm)</td>
<td>3.9</td>
<td>$\sim 33 \cdot 10^3$</td>
<td>$\sim 18 \cdot 10^3$</td>
<td>$\sim 2.4 \cdot 10^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal SiO$_2$ (450 nm)</td>
<td>3.9</td>
<td>$\sim 1 \cdot 10^8$</td>
<td>$\sim 1 \cdot 10^8$</td>
<td>$\sim 4.5 \cdot 10^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$ (45 nm)</td>
<td>9</td>
<td>$&gt; 20 \cdot 10^3$</td>
<td>$&gt; 30 \cdot 10^3$</td>
<td>$\sim 8.4 \cdot 10^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ (43 nm)</td>
<td>80</td>
<td>$&gt; 80 \cdot 10^3$</td>
<td>$\sim 60 \cdot 10^3$</td>
<td>$\sim 2.3 \cdot 10^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>STO (32 nm)</td>
<td>300</td>
<td>$&gt; 70 \cdot 10^3$</td>
<td>$\sim 28 \cdot 10^3$</td>
<td>$\sim 10 \cdot 10^3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a: Maximum values from Wilk et al.[35]*
3.5 Conclusion

Depositions of Ru films by thermal and plasma-assisted ALD when using CpRu(CO)$_2$Et as precursor in combination with O$_2$ as a reactant were performed successfully. For both processes polycrystalline material with no preferential growth direction was obtained containing some oxygen impurities due to the O$_2$ reactant. For plasma-assisted ALD similar material properties were obtained comparing to thermal ALD. When extending the O$_2$ plasma exposure time for plasma-assisted ALD RuO$_2$ was obtained.

The use of the novel precursor caused a higher growth per cycle and a relatively high surface roughness, comparing the results of those of thermal ALD of Ru to the literature. The low resistivity was only a function of thickness. The resistivity saturates around 20 $\mu$Ω·cm. For implementing Ru as an electrode material in MIM capacitors a resistivity at maximum 300 $\mu$Ω·cm was required. The Ru films obtained in this work fit this requirement.

The use of O$_2$ as a reactant causes incorporation of oxygen in the Ru layer and oxidation of the TiN substrate. The oxidation was more intense for plasma-assisted ALD compared to thermal ALD. For some applications oxidation of the substrate is an undesired side effect. The presence of oxygen in the Ru layer reduces the mass density below the Ru bulk density. Because more oxygen was present for Ru films obtained by plasma-assisted ALD a lower mass density was obtained compared to Ru films obtained by thermal ALD.

The surface morphology of Ru films obtained by thermal and plasma-assisted ALD was different. The RMS roughness of the plasma-assisted ALD films was higher than for thermal ALD. For the application the roughness must be as low as possible. Because the roughness decreases linearly with thickness there must be chosen for a Ru thickness that fits the electrical properties. The resistivity for a 5 nm thick film was ~ 30 $\mu$Ω·cm and fits the requirements for Ru as an electrode material.

The differences in roughness can be related to a difference in the initial growth mechanism for thermal and plasma-assisted ALD, because the film nucleation determines the final film morphology. Besides the disadvantage of a high surface roughness the benefit of the plasma lies in the reduction of the nucleation delay, which is shorter for plasma-assisted ALD compared to thermal ALD.
4. Reaction mechanism of thermal and plasma-assisted ALD of Ru

The reaction mechanism of thermal ALD of Ru using O₂ as a reactant is already relatively well understood [10,12,37]. Compared to thermal ALD, the reaction mechanism of plasma-assisted ALD of Ru has not really been studied yet. Therefore, the reaction mechanism of plasma-assisted ALD of Ru from CpRu(CO)₂Et with O₂ as a reactant was investigated and compared to the reaction mechanism of thermal ALD. In order to do so, quadrupole mass spectrometry (QMS) was used to identify the reaction products being formed during the surface reactions.

4.1 Reaction mechanism for thermal ALD of Ru

The reaction mechanism of thermal ALD of Ru and Pt (platinum) with O₂ gas as a reactant was studied extensively by Aaltonen et al., using QMS [10,37]. The reaction mechanism proposed for thermal ALD of Ru using bis(cyclopentadienyl)-ruthenium (RuCp₂) and O₂ gas is illustrated in Figure 4.1.

![Fig. 4.1: Schematic overview of the reaction mechanism of thermal ALD of Ru. The surface reactions during the RuCp₂ precursor dosing (a) and during the O₂ gas exposure (b) are illustrated. Both surface reactions produce CO₂ and H₂O as reaction products [37].](image)

The ALD cycle starts with the RuCp₂ precursor adsorption on the Ru surface, which contains chemisorbed oxygen from the previous O₂ reactant exposure. This chemisorbed oxygen oxidatively decomposes the ligands of the precursor forming H₂O and CO₂ as reaction products. Because a limited amount of chemisorbed oxygen is present at the surface, the ligands are only partially oxidized. Some unreacted ligands remain on the surface after the precursor exposure. In the second half cycle the catalytically active Ru surface dissociates the molecular oxygen from the gas phase to atomic oxygen at the surface. The adsorbed oxygen then reacts with the remaining ligands of the chemisorbed precursor and forms H₂O and CO₂ as reaction products. The remaining oxygen left on the surface after the O₂ exposure will be used for the combustion reaction during the precursor adsorption in the next ALD cycle.

In the ALD process using RuCp₂, the ligands combusted to mainly H₂O and CO₂. For the same ALD process when using tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium (Ru(thd)₃) and O₂ gas, CO and H₂ were also detected together with H₂O and CO₂ [12]. Thus, the reaction taking place on the Ru surface depends on the chemical nature of the precursor ligands. Therefore, the reactions of ALD using CpRu(CO)₂Et will also be studied with QMS in the following sections.
4.2 Characterization of the CpRu(CO)$_2$Et precursor molecule

Before determining the reaction products during ALD of Ru, it is necessary to gain knowledge about the CpRu(CO)$_2$Et precursor molecule. In the mass spectrometer the precursor molecule splits up into different fragments due to dissociative ionization. The measurement of these fragments results in a characteristic pattern of lines identifying the CpRu(CO)$_2$Et molecule, the so-called cracking pattern. It is noted that the cracking pattern gives therefore also quantitative information about the bonding strength of the different ligands within the precursor molecule. Because CpRu(CO)$_2$Et is a newly developed precursor, no cracking pattern was available for this molecule in the National Institute of Standards and Technology (NIST) database [38]. To facilitate identification of the fragments of CpRu(CO)$_2$Et from the QMS signal, the cracking patterns of RuCp$_2$ and Et from the NIST database were used [38].

To measure the cracking pattern, CpRu(CO)$_2$Et vapor was injected in the deposition chamber of the FlexAL system (see Section 2.1). The pressure in the chamber was kept at ~ 10 mTorr by closing the bottom and top valve. The molecular weight of the intact CpRu(CO)$_2$Et precursor molecule is 251.25 u. Therefore, all fragments can be detected by acquiring a mass scan from $m/z$ = 1 to 300. Since, the intensities of the lower masses ($m/z$ = 1 to 50) were relatively high compared to the higher masses, the $m/z$ = 50 to 300 range was scanned with a higher sensitivity. The cracking pattern for CpRu(CO)$_2$Et is shown in Figure 4.2.

![Fig. 4.2: Cracking pattern of the CpRu(CO)$_2$Et precursor molecule compared with the cracking patterns of Et and RuCp$_2$, obtained from the NIST database [38]. The background signal of the mass spectrometer and deposition chamber was subtracted from the spectrum.](image)

The measured cracking pattern confirms the complex structure of the precursor molecule (see Figure 2.2) and a small amount of the intact molecule ($m/z$ = 252) was present in the cracking pattern. The different ligands can be identified by comparing the QMS signal to the cracking patterns of RuCp$_2$, Et, and the molecule structure of CpRu(CO)$_2$Et (see Figure 2.2). It is noted that RuCp$_2^+$ ($m/z$ = 231) itself is not a fragment of the CpRu(CO)$_2$Et precursor, but the cracking pattern of RuCp$_2$ is part of the cracking pattern of RuCp$_2$. The $m/z$ = 28 and its surrounding $m/z$ values (24 until 30) correspond to the cracking pattern of the Et group (see Appendix C.2). Besides a contribution of the intact Et$^+$, $m/z$ = 28 also contains signal of CO$^+$. Because the contribution of Et$^+$ was clearly dominating for $m/z$ = 28, the CO$^+$ signal was difficult to distinguish from the Et$^+$ signal.
To identify the remaining \( m/z \) values, the cracking pattern was compared to the possible combinations of ligands present in the precursor (see Appendix C.1). The \( m/z \) values corresponding to \( \text{Ru(CO)}_2^+ (m/z = 157) \), \( \text{RuCOEt}^+ (m/z = 158) \), and \( \text{Ru(CO)}_2\text{Et}^+ (m/z = 186) \) were not observed in the cracking pattern. This suggests that the Ru-Et and Ru-CO were broken up first, and the Ru-Cp bond stayed intact the longest. Therefore, the Ru-Cp bond was indicated as the strongest bond within the precursor molecule. When looking to the high intensity of \( m/z = 28 \) it can be concluded that the Ru-Et bond is weak. It was difficult to speculate on the bonding strength of the CO ligand with the precursor molecule because the detection of \( m/z = 28 \) was dominated by the Et group. From chemical bonding theory it becomes clear that the Ru-CO and Ru-Et bonds were indeed weaker than the Ru-Cp bond [39].

It is not always possible to identify all \( m/z \) values of a cracking pattern especially when the spectrum of lines is complex. Additional \( m/z \) values can be explained by species present in the precursor included during its synthesis and there are always lines that stay unidentified. This characterization gave not only information about the bonding strengths of the precursor ligands, but also showed that \( m/z = 28 \) was the most dominant signal. Therefore, this mass signal is considered to be suitable to monitor the precursor during the ALD process.

### 4.3 Determination of the reaction products formed during ALD of Ru

The reaction products during both thermal and plasma-assisted ALD are identified in this section by real time QMS measurements during the ALD process. To distinguish between the contributions of the precursors (\( \text{CpRu(CO)}_2\text{Et} \) and \( \text{O}_2 \)) and the process gases from the reaction products formed during the ALD process, the substrate was also exposed to the precursor and reactant only [40]. Subsequently, the reaction products can be determined by comparing the signals measured during the ALD cycle with the signals measured during the cycles without precursor or reactant exposure. A wide \( m/z \) range was followed in time with QMS and the contributions of the signal for the different experiments are shown in Figure 4.3.

![Fig. 4.3: Contributions of the QMS signal during the precursor and reactant step for an ALD cycle, a cycle with only precursor dosing, and a cycle with only \( \text{O}_2 \) gas/plasma exposure [40].](image)
The experiments were carried out on a thick (> 30 nm) Ru substrate to exclude contributions due to initial growth. To cancel out start up effects, the deposition chamber and substrate were conditioned for 200 cycles before every experiment. Measuring the entire m/z range at once results in an insufficient time resolution (0.02 s), therefore the range was split up in measurements of four m/z values at a time (resolution, 0.15 s). The m/z = 40 (Ar\textsuperscript{+}) was followed during every measurement as a reference signal.

As an example for the typical measurement, Figure 4.4 shows m/z = 18, 28, 32 and 44, during a thermal and plasma-assisted ALD cycle, and during the exposure to precursor and reactant only. During the precursor and reactant only measurements no change in intensity for m/z = 18 and 44 was observed, which indicates that the measurements were not affected by so-called pressure effects. All the m/z values show changes during the O\textsubscript{2} exposure of the ALD cycle (Fig. 4.4 (a, b)). Since the cycle with only O\textsubscript{2} gas exposure (Fig. 4.4 (e, f)) showed only a change in intensity for m/z = 32 (O\textsubscript{2}\textsuperscript{+}), it can be concluded that the changes in m/z = 18, 28 and 44 during the ALD cycle can be directly assigned as ALD reaction products. A similar behavior was observed during the CpRu(CO)\textsubscript{2}Et dosing (Fig. 4.4 (c, d)).
When the procedure described above was applied to the time resolved measurements of \( m/z = 1 \) until 50, the following lines were identified as ALD reaction products: \( m/z = 12, 16, 17, 18, 22, 28, \) and 44. These \( m/z \) values correspond to the cracking pattern of H\(_2\)O and CO\(_2\) (see Appendix C.2). The assignment of \( m/z = 28 \) was more difficult since it includes different contributions. It can represent C\(_2\)H\(_4^+\) from the precursor, or CO\(^+\), which can originate from the precursor, as a cracking product of CO\(_2\) or it can be due to CO production.

The cracking pattern of CO\(_2\) shows that the \( I_{co} / I_{co^+} \) intensity ratio is 0.1 (Appendix C.2). From the measurements, for the total ALD cycle the \( I_{co} / I_{co^+} \) ratio was above 0.4 and 0.7, for thermal and plasma-assisted ALD respectively. This comparison reveals that \( m/z = 28 \) can have a contribution from the cracking of CO\(_2\) but also points to other products.

In addition, during the precursor dosing of the total ALD cycle no other contributions related to the cracking pattern of C\(_2\)H\(_4\) were observed besides \( m/z = 28 \). Compared to only precursor dosing the shape of the \( m/z = 28 \) was different during the ALD cycle (see Figure 4.4 (c,d)). It can be concluded that \( m/z = 28 \) corresponds mainly to CO\(^+\) during the ALD cycle, although the contribution of Et from the precursor to \( m/z = 28 \) cannot be totally excluded.

The H\(_2\)O, CO, and CO\(_2\) species can be assigned as the main reaction products for thermal and plasma-assisted ALD for CpRu(CO)\(_2\)Et with O\(_2\) gas or plasma as a reactant. In Figure 4.4 becomes clear that for plasma-assisted ALD almost all reaction products were produced during the O\(_2\) gas exposure, before the plasma exposure. It can be concluded that plasma-assisted ALD contains a thermal component during the reactant exposure. No additional reaction products were observed for plasma-assisted ALD compared to thermal ALD.

The graphs in Figure 4.4 show that for thermal and plasma-assisted ALD:

- Large amounts of H\(_2\)O and CO\(_2\) were produced during the precursor dosing.
- Production of CO during the precursor dosing.
- Large amounts of CO and CO\(_2\) were produced during the O\(_2\) reactant exposure.
- Low production of H\(_2\)O during the O\(_2\) reactant exposure.

Aaltonen et al. reported H\(_2\), CO, CO\(_2\), and H\(_2\)O to be the dominant reaction products for thermal ALD of Ru, when using metal organic precursors as RuCp\(_2\) and Ru(thd)\(_3\) and O\(_2\) gas as a reactant [10,37]. This work showed that H\(_2\)O, CO and CO\(_2\) were the reaction products for thermal and plasma-assisted ALD when using CpRu(CO)\(_2\)Et with O\(_2\) as a reactant. As mentioned in Section 4.1, the production of the reaction products depends on the chemical nature of the Ru precursor. Since the same precursor was used and the plasma-assisted ALD process contained a thermal component, it was not surprising that the addition of a plasma to the process provides no additional reaction products. In Figure 4.4 the reaction products were showed in a logarithmic scale, so small differences in the signal intensity were difficult to observe. In the next section the differences in the amount of produced reaction products were investigated by a quantitative comparison, for thermal and plasma-assisted ALD.
4.4 Production of H$_2$O, CO and CO$_2$ during thermal and plasma-assisted ALD

In the previous section H$_2$O, CO and CO$_2$ were identified as the reaction products for thermal and plasma-assisted ALD of Ru, when using CpRu(CO)$_2$Et and O$_2$. Because the growth per cycle (in Section 3.2) is equal for thermal and plasma-assisted ALD, the same amount of precursor was combusted during one ALD cycle for each process. By a quantitative comparison of the reaction products possibly more insight can be obtained about the nature of the combustion reactions during thermal and plasma-assisted ALD, and a comparison can be made. To determine the amount of reaction products, the values $m/z = 18$, 28, 32 and 44 (representing H$_2$O$^+$, CO$^+$, O$_2$$^+$ and CO$_2$$^+$, respectively) were followed by QMS during an ALD cycle. The area under the peaks of these $m/z$ values scales with the amount of H$_2$O, CO, (production and cracking of CO$_2$) and CO$_2$ produced.

![Fig. 4.5: Time dependent plot of deposition cycle of thermal ALD (a) and plasma-assisted ALD (b). Reaction products and reactant gas were measured by QMS and displayed in a linear scale to compare reaction products quantitatively. For thermal ALD the substrate was exposed to O$_2$ gas for 5 s, whereas for plasma-assisted ALD the 2 s O$_2$ gas exposure was followed by a 0.8 s O$_2$ plasma step. Because of the high intensity of $m/z = 32$ a break in the y-axis was added.](image)

Figure 4.5 shows one ALD cycle of each process in a linear scale to make differences in intensity visible. Besides reaction products, also the O$_2$ reactant was shown to indicate the reactant and the plasma steps. For plasma-assisted ALD, the 2 s of O$_2$ gas exposure were followed by a 0.8 s O$_2$ plasma step. The figure showed that for both processes, almost all reaction products were produced during the first 2 seconds of the O$_2$ exposure. For plasma-assisted ALD this means that, the combustion reactions took place before the plasma was ignited. No additional amount of reaction products were produced during the O$_2$ plasma exposure itself (see Figure 4.4).

The combustion of the precursor ligands can occur by complete or incomplete combustion. In the case of complete combustion by O$_2$ the hydrocarbons will be converted to H$_2$O and CO$_2$, which is displayed in Equation 4.1.

$$2C_xH_y + \frac{1}{2}(4x + y)O_2 \rightarrow 2xCO_2 + yH_2O$$  \hspace{1cm} (4.1)
In the case of incomplete combustion the hydrocarbons will also be converted to CO instead of H₂O and CO₂ only. Because H₂O, CO and CO₂ were identified as reaction products, the precursors ligands are combusted by incomplete combustion.

In Figure 4.5, it becomes visible that the \( \frac{I_{CO}}{I_{H_{2}O}} \) ratio for the total ALD cycle was equal to 2.5 for thermal and plasma-assisted ALD. This implies that the same complete combustion of CₓHᵧ took place for both processes.

For plasma-assisted ALD, the signal for \( m/z = 28 \), which was assigned to CO production, was more intense for the total ALD cycle (\( \frac{I_{CO}}{I_{CO_{2}}} = 0.7 \)), compared to thermal ALD (\( \frac{I_{CO}}{I_{CO_{2}}} = 0.4 \)). For plasma-assisted ALD the higher CO production during the CpRu(CO)₂Et dosing (\( \frac{I_{CO}}{I_{CO_{2}}} = 0.6 \)) is caused by the addition of a plasma to the ALD process. At the end of the ALD cycle the plasma provides atomic oxygen, which can be adsorbed on the Ru surface. Thus, before the new cycle starts more chemisorbed oxygen is available for the incomplete combustion of the precursor, leading to more CO⁺ during the precursor adsorption. In Section 3.4.2 TOF-SIMS measurements already showed that Ru films obtained by plasma-assisted ALD contain more oxygen compared to thermal ALD. Besides the higher CO production during the O₂ exposure (\( \frac{I_{CO}}{I_{CO_{2}}} = 0.8 \)) a higher consumption of \( m/z = 32 \) (O₂⁺) was observed as a dip in the \( m/z = 32 \) line (see Appendix C.3). The oxygen consumed was used for the production of CO, by incomplete combustion. For thermal ALD also O₂⁺ consumption was observed but less than for plasma-assisted ALD.

In Section 3.2 it was shown that thermal and plasma-assisted ALD of Ru give the same growth per cycle. This means that the same amount of precursor reacted during a complete ALD cycle. The amount of precursor ligands combusted into CO₂ was identical for thermal and plasma-assisted ALD but more CO was produced during plasma-assisted ALD, especially during the O₂ reactant exposure. As a consequence the additional carbon, produced during incomplete combustion in thermal ALD, leaves the surface in a different form, probably as CₓHᵧ instead of CO₂.
4.5 QMS measurements of complex phenomena

In the previous sections it was shown that QMS is a suitable tool to investigate the reaction mechanism of ALD processes, with the notion that the interpretation of QMS data is generally challenging. In this section some interesting but complex QMS measurements are shown to illustrate the possibilities of this technique for understanding ALD processes, such as the detection of chemisorbed oxygen on the Ru layer and the nucleation delay for thermal and plasma-assisted ALD of Ru on TiN.

Chemisorbed oxygen

In Section 4.4 it was concluded that chemisorbed oxygen was present at the Ru surface after the reactant exposure, which is investigated by the following experiment. Directly after the deposition of a thick (>30 nm) Ru ALD film the substrate was exposed to 40 cycles of only CpRu(CO)2Et precursor. After each set of 10 ALD cycles spectroscopic ellipsometry (SE) measurements were performed to investigate there was Ru growth. In Figure 4.6 the m/z = 18 (H2O+), 28 (CO+, C2H4+) and 44 (CO2+) followed by QMS are shown to investigate if reaction products were formed due to the presence of chemisorbed oxygen on the Ru layer.

For the first 20 cycles, signals of the m/z = 18, 28, and 44 were observed during the precursor dosing, while no deposition of Ru was observed by SE (see Appendix C.5). The presence of m/z = 18, 28 and 44 could be due to the combustion of the precursor by chemisorbed oxygen left on the Ru layer after the ALD deposition. Another possible reason could be parasitic CVD reaction on the reactor wall. After ~20 cycles the m/z = 18 and 44 signals decreased to noise level, meaning that all the chemisorbed oxygen was consumed. The m/z = 28 signal still showed the cycle like behavior after ~30 cycles, with a relatively low intensity, which could be due to the CO+ and Et+ ligands from the precursor molecule due to its cracking in the mass spectrometer.

![Fig. 4.6: Time resolved mass signals during the first 40 cycles of only precursor dosing on a Ru surface after Ru deposition by plasma-assisted ALD, the same behavior was observed for thermal ALD.](image)

Fig. 4.6: Time resolved mass signals during the first 40 cycles of only precursor dosing on a Ru surface after Ru deposition by plasma-assisted ALD, the same behavior was observed for thermal ALD.
Nucleation delay

Both thermal and plasma-assisted ALD showed a nucleation delay for the growth of Ru on TiN (see Section 3.2). To investigate the nucleation delay, QMS measurements were performed during the first 50 ALD cycles of Ru on TiN, which was deposited just before the Ru deposition in the same reactor.

Figure 4.7 shows that \( m/z = 18, 28, \) and 44 stabilized after \( \sim 50 \) cycles. The \( m/z = 28 \) could be assigned to different species: \( \text{C}_2\text{H}_4^+ \) from the precursor, \( \text{N}_2^+ \), from the reactant used in the previous TiN deposition, but it can also be \( \text{CO}^+ \) as a reaction product, coming from the precursor, or from the cracking of \( \text{CO}_2 \). This makes the interpretation of the \( m/z = 28 \) signal difficult. Even if the behavior of the \( m/z = 28 \) was different, the measurements were reproducible for thermal and plasma-assisted ALD. However, the origin of this difference remains unclear.

The \( m/z = 18 \) and 44 start at noise level for both processes. For thermal ALD the \( m/z = 18 \) (\( \text{H}_2\text{O}^+ \)) and \( m/z = 44 \) (\( \text{CO}_2^+ \)) signals showed cycle like behavior immediately at the start of the deposition. The signals stabilized after \( \sim 30 \) cycles (~400 s), which does not coincide with the nucleation delay of ~80 cycles as determined by a linear fit of the XRR data in Section 3.2. For plasma-assisted ALD it was observed that \( m/z = 18 \) and 44 started at the noise level and subsequently started increasing after \( \sim 15 \) ALD cycles (~150 s). After \( \sim 40 \) cycles (~400 s) the production of all \( m/z \) values measured was fully developed. This coincides with the nucleation delay of ~40 cycles as determined by a linear fit of the XRR data in Section 3.2. Although these observations appear to be consistent for plasma-assisted ALD, it is surprising that the nucleation delay does not coincide for thermal ALD. An explanation could be that besides the contribution of the reaction products also the reactor wall influences the measurements. Although the interpretation of the data remains challenging, QMS proves itself to be a very useful and sensitive tool pointing out that the nucleation behavior might be more complex than expected initially.

Fig. 4.7: Time resolved mass signals recorded during the first 50 cycles on a TiN substrate for thermal (a) and plasma-assisted (b) ALD of Ru. Reaction products measured by QMS are displayed.
4.6 Discussion on the growth mechanism of Ru

When combining the insight into reaction mechanism (see Section 4.4) with the results on the material properties (see Chapter 3) a preliminary growth mechanism of Ru can be proposed. In Table 4.1 a comparison is made between the observations for the material properties of Ru films obtained by thermal and plasma-assisted ALD.

Table 4.1: Comparison of Ru film properties obtained by thermal and plasma-assisted ALD.

<table>
<thead>
<tr>
<th></th>
<th>Thermal ALD of Ru</th>
<th>Plasma-assisted ALD of Ru</th>
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<tbody>
<tr>
<td>Nucleation delay</td>
<td>~ 80 cycles</td>
<td>~ 40 cycles</td>
</tr>
<tr>
<td>Roughness / Thickness</td>
<td>5 nm / 15 nm</td>
<td>10 nm / 16 nm</td>
</tr>
<tr>
<td>Film morphology</td>
<td>Small grains, evenly distributed on surface</td>
<td>Large dominant grains surrounded by smaller grains</td>
</tr>
<tr>
<td>Oxygen content Ru and TiN</td>
<td>Less O incorporated</td>
<td>More O incorporated</td>
</tr>
</tbody>
</table>

Compared to plasma-assisted ALD Ru films obtained by thermal ALD had a longer nucleation delay, smoother films, different film morphology and less oxygen incorporated in the Ru layer and TiN substrate. Section 4.4 showed that when using plasma-assisted ALD for the deposition of Ru more chemisorbed oxygen was available on the Ru surface for the combustion of the precursor ligands.

A schematic of the proposed growth mechanism of Ru is shown in Figure 4.8 to address the similarities and differences of the thermal and plasma-assisted ALD processes. The nucleation of the Ru films is affected by the presence of chemisorbed oxygen on the surface provided by O₂ gas or O₂ plasma in the ALD process. During plasma-assisted ALD, nucleation sites are created faster as a result of a more efficient chemisorbtion of oxygen on the entire TiN surface and, consequently, the film growth starts earlier.

Fig. 4.8: Schematic representation of the growth mechanism during the first ALD cycles of thermal and plasma-assisted ALD of Ru. The CO ligand was not included in the picture because it was unknown when the CO group was combusted.
Even after formation of initial nucleation sites, the development of the Ru grains is slow in thermal ALD. This can be related to the limited catalytic activity of the nucleation sites due to the absence of Ru bulk properties. As a consequence, more nucleation sites are created rather than existing grains develop. Since atomic oxygen is provided in the gas phase during plasma-assisted ALD, oxygen chemisorbs on the surface much more efficiently compared to thermal ALD. The growth is, however, preferential on the existing Ru nucleation sites. As a consequence, mainly these sites continue growing after creation.

The difference in nucleation of thermal and plasma-assisted ALD has an effect on the roughness development of the Ru films (Figure 4.8). In thermal ALD, the grains are more evenly distributed over the surface resulting in smoother films. Large dominant grains are formed during plasma-assisted ALD and that results in rougher films. For sufficiently thick Ru films, the growth relies on the catalytic behavior of the film. The same growth per cycle and material properties were, therefore, obtained for thermal and plasma-assisted ALD.

4.7 Conclusion

The reaction products of thermal and plasma-assisted ALD of CpRu(CO)$_2$ with O$_2$ as a reactant were determined using QMS. In addition to the reaction products proposed by Aaltonen et al., using RuCp$_2$ and O$_2$ gas, also CO was identified as a reaction product. The addition of a plasma to the ALD process results in no additional reaction products compared to thermal ALD, which was not surprising because the same precursor was used and most reaction products were already produced during the first seconds of the O$_2$ gas exposure. However, more CO was produced during plasma-assisted ALD due to a more efficient chemisorption of oxygen on the Ru surface.

The investigation of the reaction mechanism confirmed observations made during the material properties study. As a result, a proposal for the Ru growth mechanism could be made, explaining the nucleation delay and the high roughness of the Ru film.
5. General conclusions and outlook

The capacity density of MIM capacitors can be increased by using ultra high-$k$ materials, such as SrTiO$_3$ (STO) and high work function electrode materials. The work reported in this thesis focused on the development of ALD Ru processes in order to meet the requirements on material quality and growth control for the metal electrode. Thermal and plasma-assisted ALD using the novel precursor CpRu(CO)$_2$Et and O$_2$ as a reactant were studied. The material properties of the Ru films were characterized extensively for growth on TiN substrates. Both ALD processes resulted in similar Ru material properties and high purity, polycrystalline Ru films were obtained with a high mass density and a low resistivity. Also a high growth per cycle was obtained, which is a benefit over previous Ru ALD processes reported in the literature. The Ru films satisfy the thickness and electrical requirements for electrode materials in MIM capacitors.

The plasma-assisted ALD process improved the film nucleation; however it also led to films with higher surface roughness compared to thermal ALD. The difference in roughness and film morphology indicated a difference in nucleation behavior. The insights into the reaction mechanism were combined the oxidation of the TiN substrate during film growth. From this it was concluded that more chemisorbed oxygen was present at the Ru surface during the plasma-assisted ALD process. This aspect is likely responsible for the reduced nucleation delay and more pronounced roughness development of the plasma-assisted ALD Ru films.

For the thermal and plasma-assisted oxygen-based ALD processes, the roughness of the Ru films was too high for industrial application. In future experiments possibilities of reducing the surface roughness have to be investigated. Since the film nucleation seems to determine the final roughness of the Ru films, immediate nucleation must be established which could be achieved by a pre-treatment of the TiN substrate with an O$_2$ plasma. In that way, chemisorbed oxygen could be available before the start of the deposition in order to combust the precursors ligands immediately at the start of the ALD process. Besides improving the nucleation, also the deposition at a lower substrate temperature can be investigated in order to obtain smoother films, as reported in other studies.

For the integration of Ru into MIM capacitors, the conformality of the Ru films has to be established for high aspect ratio trenches. Moreover, a Ru-STO-Ru MIM stack deposited by the oxygen-based ALD process must be tested to determine the electrical properties of the MIM stack.
Acknowledgments

First of all I want to thank my first supervisor Noémi Leick. You were always optimistic, full of ideas and pulling me in the right direction when necessary. Thanks for everything. I want to thank Erwin Kessels. You were interested in new results and open for discussion. But in the first place thanks for making me enthusiastic about ALD and PMP. Erik Langereis, thanks for reading and correcting draft versions of my thesis, making wonderful pictures, and for supervising and supporting me during Noémi’s maternity leave.

Special thanks goes to, Luca Lamagna for the TOF-SIMS measurements and the pleasant and scientific teamwork during your three months stay at PMP. Wytze Keuning for the support on the FlexAL. Fred Roozeboom, Dick van Oers, Peter Graat, and René Beerends, for the XRR, XRD, RBS, AFM measurements and the interpretation of the data. Simon Rushworth for sending expensive Ru precursor when we emptied the bubbler ...again. The (ex-) inhabitants of the students room for the pleasant time and all the ridiculous challenges.

At last I want to thank, Jan-Willem, my boyfriend. I complained a lot about my graduation project during the last 15 months, but you kept on supporting me. Within approximately four months I make it up to you.
Bibliography


[28] SAFC Hitech within MaxCaps project, private communication.


### Appendix A

#### A.1 Literature overview ALD of Ru

*Table A.1: Literature overview of ALD processes for Ru deposition using different precursors, reactants and substrates for thermal and plasma-assisted ALD.*

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Reactant</th>
<th>Substrate temp. [°C]</th>
<th>Substrate</th>
<th>Growth [Å/cycle]</th>
<th>Resistivity [μΩ·cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuCp$_2$</td>
<td>O$_2$ gas$^a$</td>
<td>225-350</td>
<td>Ir, SiO$_2$, Al$_2$O$_3$, TiO$_2$, HfO$_2$</td>
<td>0.12 – 1.2</td>
<td>14 - 35</td>
</tr>
<tr>
<td></td>
<td>NH$_3$ plasma$^b$</td>
<td>300</td>
<td>SiO$_2$</td>
<td>0.9</td>
<td>--</td>
</tr>
<tr>
<td>Ru(EtCp)$_2$</td>
<td>O$_2$ gas$^c$</td>
<td>270 - 300</td>
<td>SiO$_2$, Ta$_2$O$_5$</td>
<td>1 – 1.8</td>
<td>15 - 16</td>
</tr>
<tr>
<td></td>
<td>NH$_3$ plasma$^d$</td>
<td>230 - 300</td>
<td>TiN, WNC, SiO$_2$</td>
<td>0.25 – 0.8</td>
<td>12 - 35</td>
</tr>
<tr>
<td>Ru(acac)$_3$</td>
<td>H$_2$ gas$^e$</td>
<td>340</td>
<td>SiO$_2$</td>
<td>0.02 - 0.07</td>
<td>--</td>
</tr>
<tr>
<td>Ru(thd)$_3$</td>
<td>O$_2$ gas$^f$</td>
<td>250 – 350</td>
<td>Ir, Al$_2$O$_3$</td>
<td>0.15 – 0.36</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>C$<em>{16}$H$</em>{22}$Ru</td>
<td>O$_2$ gas$^g$</td>
<td>220</td>
<td>SiO$_2$, TiN</td>
<td>0.86 - 1</td>
<td>36</td>
</tr>
</tbody>
</table>

*a: Aaltonen et al. [11,17], Park et al. [16], and Park et al. [20]*  
*b: Park et al. [13]  
*c: Kwon et al. [14], Choi et al. [15], and Park et al. [16]  
*d: Park et al. [13], Kwon et al. [14], and Yim et al. [21]  
*e: Igumenov et al. [22]  
*f: Aaltonen et al. [12,17]  
*g: Eom et al. [23]
A.2 Material safety data sheet of CpRu(CO)$_2$Et

**MATERIAL SAFETY DATA SHEET**

**Date of Issue:** September 2005  
**Revision:** 05/001  
**ID:** RUCCOE

**CYCLOPENTADIENYL ETHYL DICARBONYL RUTHENIUM**

**1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND COMPANY.**

**Product Name**  
Cyclopentadienyl Ethyl Dicarbonyl Ruthenium

**Formula**  
C$_5$H$_5$Ru

**Company Identification**  
See header

**2. COMPOSITION INFORMATION ON INGREDIENTS**

**Substance/Preparation**  
Cyclopentadienyl Ethyl Dicarbonyl Ruthenium

**Components/Impurities**  
None

**EC No.**  
None

**CAS No.**  
None

**3. HAZARDS IDENTIFICATION**

**Harmful by inhalation and if swallowed**

**4. FIRST AID MEASURES**

**Skin**  
In case of contact, immediately wash skin with soap and copious amounts of water.

**Eyes**  
In case of contact, flush contaminated eyes with large quantities of water for at least 15 minutes. Hold eyelids open to ensure complete flushing.

**Inhalation**  
If inhaled, remove to fresh air. If breathing is difficult, give oxygen. If breathing has stopped, apply artificial respiration. Medical assistance should be sought immediately. Keep victim warm and quiet.

**Ingestion**  
If swallowed, wash out mouth with water provided person is conscious. Call physician.

**5. FIRE-FIGHTING MEASURES**

**Extinguishing Media**  
Water spray, carbon dioxide, dry chemical powder, or appropriate foam.

**Exposure Hazards**  
Emits toxic fumes under fire conditions.

**Special Protective Equipment for Fire-Fighters**  
Self-contained breathing apparatus, face shield and safety goggles, safety shoes and fire resistant gloves.

**6. ACCIDENTAL RELEASE MEASURES**

**Personal Precautions**  
Evacuate area. Use appropriate protective equipment. Wear self breathing apparatus, rubber boots, and heavy rubber gloves.

**Environmental Precautions**  
Try to stop release, if safe to do so. For fire-fighting measures see section 5.

**Clean up methods**  
Sweep up, place in a bag and hold for waste disposal. Avoid raising dust. Ventilate area and wash spill site after material pickup is complete.

**7. HANDLING AND STORAGE**

**Handling**  
Avoid contact and inhalation. Do not get in eye, on skin or clothing.

**Storage**  
Protect containers from physical damage. Do not allow temperatures to exceed (125F) 51C. Store away from flammable material.

**8. EXPOSURE CONTROLS/PERSONAL PROTECTION**

**Exposure Controls**  
OSHA or ACGIH: Not established

**OES and MEL:**  
None established. Ensure adequate ventilation.

**Personal Protection**  
Self-contained breathing apparatus, rubber gloves, safety goggles, safety shoes and fire-resistant garments. Safety shower and eye wash station.

**9. PHYSICAL AND CHEMICAL PROPERTIES**

**MW:**  
251.26

**Boiling Point:**  
60°C @ 0.1mmHg

**Melting Point:**  
NA

**Appearance:**  
Yellow crystalline Liquid

**10. STABILITY AND REACTIVITY**

**Materials to avoid**  
Avoid strong oxidising agents

**Hazardous Decomposition Products**  
CO, CO$_2$

**11. TOXICOLOGICAL INFORMATION**

**Signs and symptoms of exposure**  
To the best of our knowledge, the chemical, physical and toxicological properties have not been thoroughly investigated.

**Routes to exposure**  
Multiple routes: May be harmful by inhalation, ingestion, or skin absorption. May cause irritation.
12. ECOLOGICAL INFORMATION
This product does not contain any class I or class II ozone depleting chemicals.

13. DISPOSAL CONSIDERATIONS
Regional and National regulations should be followed during waste disposal. Contact an SAFC Hitech representative for disposal of container and any unused quantities.

14. TRANSPORT INFORMATION

ADR
UN No 3291
CLASS: 6.1
PG III
Marine pollutant No
Proper Shipping Name: (Metal carbynyls, Liquid NOS Cyclopentadienyl (Ethyl dicarbonyl Ruthenium)

IMDG
UN No 3291
CLASS: 6.1
PG III
Marine pollutant No
Proper Shipping Name: (Metal carbynyls, Liquid NOS Cyclopentadienyl (Ethyl dicarbonyl Ruthenium)

DOT
UN No 3291
CLASS: 6.1
PG III
Marine pollutant No
Proper Shipping Name: (Metal carbynyls, Liquid NOS Cyclopentadienyl (Ethyl dicarbonyl Ruthenium)

IATA
UN No 3291
CLASS: 6.1
PG III
Proper Shipping Name: (Metal carbynyls, Liquid NOS Cyclopentadienyl (Ethyl dicarbonyl Ruthenium)

15. REGULATORY INFORMATION
Classification
Xn Harmful
Risk Phrases
R22: Harmful by inhalation and if swallowed
S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37/39: Wear suitable protective clothing, gloves and eye/face protection

16. OTHER INFORMATION
Ensure operators understand the harmful nature of the product. Before using this product, it is recommended that a risk assessment and safety study be carried out. Further information on the use of this product can be obtained from the Technical Product Manager at the nearest SAFC Hitech facility.

SAFETY NOTICE: In order to provide our customers with the highest quality material and maintain our high standards of safety, the surface temperature of the bubbler may be monitored during the transportation of our products using a templatel. Templatel is a temperature-monitoring strip which will indicate the temperature during shipment. The strip will turn black at one of the four ratings shown if the temperature is reached (normally a silver centre). If the temperature monitor is changed, please notify an SAFC Hitech representative immediately and we will assist you in the proper measures to be taken. We ask for your co-operation in our efforts of quality assurance and safety. If you have any questions or comments, please contact an SAFC Hitech representative. We thank you for your co-operation. Your assistance is greatly appreciated.

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United States: Chemtrec (800) 424 9300
Other International Countries: Chemtrec (703) 527 3887
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### A.3 Deposition parameters plasma-assisted ALD process for TiN

Table A.1: Most important deposition parameters for plasma-assisted ALD of TiN on SiO$_2$/Si. The substrate was exposed to 300 s of H$_2$N$_2$ plasma prior to the TiN deposition.

<table>
<thead>
<tr>
<th>ALD step</th>
<th>TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>TiCl$_4$</td>
</tr>
<tr>
<td>Precursor exposure time</td>
<td>2 x 40 ms</td>
</tr>
<tr>
<td>Plasma composition</td>
<td>H$_2$:N$_2$ (30:4)</td>
</tr>
<tr>
<td>Plasma exposure</td>
<td>20 s</td>
</tr>
<tr>
<td>Plasma power</td>
<td>500W</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>400 °C</td>
</tr>
<tr>
<td>Cycle time</td>
<td>41.08 s</td>
</tr>
<tr>
<td>Growth per cycle</td>
<td>0.5 Å/cycle</td>
</tr>
<tr>
<td>Typical thickness used</td>
<td>8 ± 1 nm</td>
</tr>
</tbody>
</table>
Appendix B

B.1 Two approaches using growth per cycle obtained by XRR and RBS for surface coverage calculations.

a. Surface coverage calculation using bulk density:

The surface coverage [ML/cycle] in one ALD cycle can be calculated using the growth per cycle from RBS [atoms/cm²-cycle], the bulk mass density \( \rho_m [g/cm^3] \), Avogadro’s number \( N_A [1/mol] \), and the atomic mass of Ru \( A_{Ru} [g/mol] \). This is displayed in equation B.1.

\[
\text{Surface coverage} = \frac{GPC_{RBS}}{\left( \rho_m \cdot \frac{A_{Ru}}{N_A} \right)^{\frac{1}{2}}} \quad \text{(B.1)}
\]

b. Surface coverage calculation using XRR growth rate:

The surface coverage [ML/cycle] in one ALD cycle can be calculated using the growth per cycle from XRR [Å/cycle] and the vertical lattice constant, \( \lambda [\text{Å}] \). This is displayed in equation B.2.

\[
\text{Surface coverage} = \frac{GPC_{XRR}}{\lambda} \quad \text{(B.2)}
\]

The results of the calculations by the different approaches are displayed in Table B.1.

*Table B.1: Calculated growth per cycle for different approaches using bulk mass density and XRR growth per cycle.*

<table>
<thead>
<tr>
<th></th>
<th>Growth per cycle (ML/cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBS and bulk density</td>
<td>Average</td>
</tr>
<tr>
<td>Growth rate and ( \lambda )</td>
<td>Min ( \lambda )</td>
</tr>
<tr>
<td></td>
<td>Max ( \lambda )</td>
</tr>
</tbody>
</table>
B.2 Measured and simulated data of XRR measurement of Ru on TiN

In the XRR fit an assumption of the layer structure and materials must be made. XRR measurements deliver the total electron density. From the simulated data the mass density and film thickness can be extracted.

B.3 Measured and simulated data of RBS measurement of TiN substrate

In the RBS fit an assumption of the layer structure and materials must be made. The film composition and amount of deposited atoms can be extracted.
Appendix C

C.1 Ion complexes resulting from dissociative ionization of CpRu(CO)₂Et

Table C.1: Different ion complexes of ligands from CpRu(CO)₂Et and their m/z values.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>CO⁺</td>
</tr>
<tr>
<td>29</td>
<td>Et⁺</td>
</tr>
<tr>
<td>65</td>
<td>Cp⁺</td>
</tr>
<tr>
<td>101</td>
<td>Ru⁺</td>
</tr>
<tr>
<td>129</td>
<td>RuCO⁺</td>
</tr>
<tr>
<td>130</td>
<td>RuEt⁺</td>
</tr>
<tr>
<td>157</td>
<td>Ru(CO)₂⁺</td>
</tr>
<tr>
<td>158</td>
<td>RuCOEt⁺</td>
</tr>
<tr>
<td>166</td>
<td>CpRu⁺</td>
</tr>
<tr>
<td>186</td>
<td>Ru(CO)₂Et⁺</td>
</tr>
<tr>
<td>194</td>
<td>CpRuCO⁺</td>
</tr>
<tr>
<td>195</td>
<td>CpRuEt⁺</td>
</tr>
<tr>
<td>222</td>
<td>CpRu(CO)₂⁺</td>
</tr>
<tr>
<td>223</td>
<td>CpRuCOEt⁺</td>
</tr>
<tr>
<td>251</td>
<td>CpRu(CO)₂Et⁺</td>
</tr>
</tbody>
</table>
C.2 Cracking patterns for molecules related to Ru ALD process

![Graph showing cracking patterns for H₂O, CO, CO₂, and C₂H₂ from the NIST data base.]

Fig. C.1: The cracking patterns for H₂O, CO, CO₂, and C₂H₂ from the NIST data base.

C.3 Comparison m/z = 32 during ALD cycle and only O₂ gas/plasma

![Graphs comparing m/z = 32 intensity for O₂ gas/plasma only and O₂ gas/plasma during thermal ALD and plasma ALD.]

Fig. C.2: Comparison between O₂ gas/plasma only and O₂ gas/plasma during thermal (a) and plasma (b) ALD to illustrate O₂ consumption.

If the profiles of m/z = 32 (O₂⁺) during an ALD cycle and O₂ gas only are compared. A lower intensity was observed at the beginning of the ALD cycles that can be addressed to O₂ consumption due to the ALD process. For plasma-assisted ALD it was even more clear compared to thermal ALD.
C.4 Original plots time resolved reaction products for ALD of Ru

Fig. C.3: Time resolved mass signals recorded during thermal (a) and plasma-assisted (b) ALD of Ru. To identify the reaction products, the cycles with (c,d) only precursor, and (e,f) only reactant are also shown without shifting the data. The dotted line indicates the ignition of the plasma.

In Figure 4.4 the measured $m/z$ values were shifted vertically by a multiplication factor for clarity. This can give rise to confusion of the absolute intensities of the signals. For a proper comparison of the line intensities of the different mass signals, the uncorrected (original) data is displayed in Figure C.3.
C.5  Pseudo dielectric function during only precursor dosing on Ru

![Graph showing pseudo dielectric function](image)

*Fig C.4: Pseudo dielectric function of the substrate measured by spectroscopic ellipsometry after Ru deposition, 10 and 20 cycles of only CpRu(CO)2Et precursor exposure.*

The pseudo dielectric function is representing the dielectric properties of the total layer structure of the sample. Changes in the pseudo dielectric function indicate a thickness increase of the Ru layer or another modification of the substrate. After 10 cycles a small change in the pseudo dielectric function was observed possible related to a monolayer of precursor adsorption. This change cannot be modeled with the dielectric properties of Ru. After 20 cycles of only precursor exposure no changes were observed comparing to the measurement after 10 cycles. From that it is concluded that there was no significant growth of Ru on the substrate after only precursor exposure. This is also an indication that there is no decomposition of the precursor due to the high substrate temperature of 400 °C.