CVD and ALD of Group IV- and V-Oxides for Dielectric Applications

BY

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ABSTRACT


Due to the constantly decreasing dimensions of electronic devices, the conventional dielectric material in transistors and capacitors, SiO$_2$, has to be replaced by a material with higher dielectric constant. Some of the most promising candidates are tantalum oxide, Ta$_2$O$_5$, zirconium oxide, ZrO$_2$ and hafnium oxide, HfO$_2$.

This thesis describes new chemical vapour deposition (CVD) and atomic layer deposition (ALD) processes for deposition of Ta$_2$O$_5$, ZrO$_2$ and HfO$_2$ using the metal iodides as starting materials. The layer-by-layer growth in ALD was also studied in real time with a quartz crystal microbalance (QCM) to examine the process characteristics and to find suitable parameters for film deposition.

All the processes presented here produced high-purity films at low deposition temperatures. It was also found that films deposited on Pt substrates generally crystallise at lower temperature, or with lower thickness, than on silicon and single-crystalline oxide substrates. Films grown on MgO(001) and α-Al$_2$O$_3$(001) substrates were strongly textured or epitaxial. For example, monoclinic HfO$_2$ deposited on MgO(001) were epitaxial for deposition temperatures of 400-500°C in ALD and 500-600°C in CVD. Electrical characterisation showed that the crystallinity of the films had a strong effect on the dielectric constant, except in cases of very thin films, where the dielectric constant was more dependent on layer thickness.

Key words: CVD, ALD, Dielectric constant, Tantalum oxide, Ta$_2$O$_5$, Zirconium oxide, ZrO$_2$, Hafnium oxide, HfO$_2$, QCM.

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This thesis comprises the present summary and the following papers, which are referred to in the summary by their Roman numerals.

I  Halide chemical vapour deposition of Ta$_2$O$_5$.
   Katarina Forsgren and Anders Härsta

II  Atomic layer deposition of tantalum oxide thin films from iodide precursor.
   Kaupo Kukli, Jaan Aarik, Aleks Aidla, Katarina Forsgren, Jonas Sundqvist, Anders Härsta, Teet Uustare, Hugo Mändar, and Alma-Asta Kiesler

III  Characterisation of Ta$_2$O$_5$ films prepared by ALCVD.
    Katarina Forsgren, Jonas Sundqvist, Anders Härsta, Kaupo Kukli, Jaan Aarik, and Aleks Aidla

IV  CVD of ZrO$_2$ using ZrI$_4$ as metal precursor.
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V  Atomic layer deposition of zirconium oxide from zirconium tetraiodide, water and hydrogen peroxide.
   Kaupo Kukli, Katarina Forsgren, Jaan Aarik, Teet Uustare, Aleks Aidla, Antti Niskanen, Mikko Ritala, Markku Leskelä, and Anders Härsta

VI  Iodide-based ALD of ZrO$_2$: Aspects of phase stability and dielectric properties.
    Katarina Forsgren, Jörgen Westlinder, Jun Lu, Jörgen Olsson, and Anders Härsta

VII Deposition of HfO$_2$ thin films in HfI$_4$-based processes.
Katarina Forsgren, Jaan Aarik, Aleks Aidla, Jörgen Westlinder, Jörgen Olsson, and Anders Hårsta
Submitted to J. Electrochem. Soc.

VIII In situ preparation of Ti-containing Ta$_2$O$_5$-films by halide CVD.
Katarina Forsgren and Anders Hårsta
1 Introduction

The microelectronics industry is constantly striving towards increased functionality and performance of integrated circuits, that is, to produce faster, smaller and cheaper electronic devices. This is achieved by increasing the density of cells on a chip through reduction of the minimum feature size and the production of more complex circuits. When the feature size is reduced, a lower operating voltage must be applied to maintain a constant electrical field, and this in turn requires the capacitance to increase in order for the device to function properly. Since the capacitance is inversely proportional to the thickness of the isolating layer, this thickness is reduced accordingly. The conventional capacitor material in random access memories and field effect transistors is silicon dioxide, SiO$_2$, and the successful scaling of device dimensions over the past 30 years has lead to the current dielectric thickness of about 2 nm. However, leakage currents are becoming a serious problem at this point, and further scaling would very soon lead to a direct tunneling current through the oxide. In addition, an oxide layer this thin is an insufficient barrier against dopant diffusion. By replacing the SiO$_2$ with a material of higher dielectric constant, the required capacitance can be achieved with a thicker layer, thereby reducing the leakage currents. The scaling towards higher cell densities can thus continue.

The amorphous thermally grown SiO$_2$ currently in use, offers a stable, high-quality interface with silicon, in combination with superior electrical isolation properties, and will thus be very hard to replace. The main requirements for future gate dielectrics are [1]:

i) technology compatible,
ii) homogeneous structure and efficient barrier against penetration of contaminant species,
iii) large bandgap, high dielectric strength and low loss,
iv) large breakdown strength,
v) negligible charge leakage and low interface trap densities,
vi) suitable threshold voltage, and
vii) stable electrical characteristics.

It should be pointed out that there are some distinctions between the requirements for memory and transistor applications. Memory capacitors require extremely low leakage currents and very high capacitance density for charge storage, but the quality of the interface is not as critical. Since the electrical field is not required to penetrate below the bottom electrode, the electrode can consist of metal or nitrided poly-silicon. For a field effect transistor, on the other hand, it is essential that the electrical field penetrates into the Si channel underneath the gate oxide to modulate the carrier transport. It is therefore necessary that the substrate is Si and that the interface between the dielectric and the channel is of very high quality. Transistors have lower demands on leakage current than capacitors, although a high capacitance is still needed [2].

A number of materials have some of the qualities necessary for replacing SiO$_2$, but very few are considered promising in all areas. The materials that have received the most attention are Ta$_2$O$_5$, SrTiO$_3$, TiO$_2$, Al$_2$O$_3$, ZrO$_2$ and HfO$_2$. Among these, Ta$_2$O$_5$, SrTiO$_3$ and TiO$_2$ have the highest dielectric constants, between 25 and 80 in thin films, but are not stable in contact with silicon. Reaction at the interface between film and substrate during the deposition experiment or subsequent heat treatment, may lead to formation of silicon oxide or silicides, that are detrimental to the electrical properties. Ta$_2$O$_5$ and SrTiO$_3$ are still considered for memory applications, but TiO$_2$ is generally characterised by a high leakage current, and can not be used in its pure form. Furthermore, the process integration of the ternary SrTiO$_3$ presents a greater challenge than that of the binary Ta$_2$O$_5$ and TiO$_2$. Al$_2$O$_3$, ZrO$_2$ and HfO$_2$ are thermodynamically stable in contact with silicon [3], and if an interfacial reaction does take place, the result is likely to be silicates, that exhibit intermediate dielectric constants and may even be beneficial for the leakage characteristics. The dielectric constant of Al$_2$O$_3$ is only 8-10, and substituting SiO$_2$ with Al$_2$O$_3$ would thus only be a temporary solution. ZrO$_2$ and HfO$_2$, on the other hand, have dielectric constants of around 20 and offer more long-term solutions.

The electrical properties of a material are determined by a complicated interaction of many factors, most of which will not be discussed here. This thesis describes new chemical vapour deposition (CVD) and atomic layer deposition (ALD) processes for deposition of the high dielectric constant materials Ta$_2$O$_5$, ZrO$_2$, HfO$_2$ and mixed TiO$_2$-Ta$_2$O$_5$ oxide.
There are different contributions to the permittivity of a material depending on the frequency of the applied electrical field as shown schematically in Fig. 2.1 [4]. The current frequency range for transistor (CMOS) operation is indicated in the figure, and it can be seen that the main contributions in this region are electronic and ionic polarizations.

The electronic contribution comes from interaction of the “electron cloud” of an ion with the external electronic field, and ions with a large radius can generally be polarized to a greater extent. The electronic contribution tends to increase the permittivity for oxides of metals with high atomic numbers. The ionic contribution is caused by the displacement of certain ions in the unit cell in response to the applied electrical field. The polarizability can vary between the polymorphic forms of a material, probably due to different density or displacement possibilities. An amorphous body does not exhibit as high a permittivity as a crystalline one since the displacement of the ions is not uniform over any extended volume of material. It has also been found that the addition of a second metal to a certain oxide can enhance the dielectric constant considerably [5, 6, 7]. The exact reason for this effect is not known, however. This is a simplified description, but it is

![Figure 2.1: The frequency dependence of the permittivity [4].](image)
clear that both the nature of the elements and their arrangement in the solid state are of importance for the permittivity.

The dielectric constant increases upon crystallisation, but at the same time, grain boundaries form. In the grain boundaries, the concentration of impurities and defects is higher, and the electrical conductivity is higher than in the “bulk” of the grains. The smaller the grains, the larger the part of the film that consists of grain boundaries. This is normally the reason the leakage current increases when a material goes from the amorphous to the crystalline state. The close connection to the electrical properties is a strong reason to maintain careful control of the phase content of the films.

2.1 Tantalum oxide

In the Ta-O phase diagram, Ta$_2$O$_5$ appears as a line phase, i.e. it has no extended stability region, and should have a well-defined stoichiometry. Orthorhombic [8], monoclinic [9], hexagonal [10] and tetragonal [11] phases of Ta$_2$O$_5$ have been identified, but despite much effort, their respective stability areas are not fully known. There seems to be general agreement that the hexagonal and orthorhombic phases are stable at low temperatures and the monoclinic and tetragonal phases at high temperatures. The orthorhombic $\beta$-Ta$_2$O$_5$ and the hexagonal $\delta$-Ta$_2$O$_5$ structures are closely related:

$$a (\beta$-Ta$_2$O$_5) = \sqrt{3}* a (\delta$-Ta$_2$O$_5) \text{ and } b \beta$-Ta$_2$O$_5) = a (\delta$-Ta$_2$O$_5)$$

The $\delta$-phase is often claimed to be understoichiometric, indicating that Ta$_2$O$_5$ could possibly have a stability region. However, in thin film deposition, the $\beta$-phase of Ta$_2$O$_5$ is the most commonly observed (Fig. 2.2).

Ta$_2$O$_5$ is best known for its high dielectric constant, but it also has other interesting properties like piezoelectricity, protonic conductivity, high refractive index and corrosion resistance. Thin films of Ta$_2$O$_5$ can be used in electroluminescent devices [12], biological and chemical sensors [13, 14], corrosion resistant coatings [15], and anti-reflective coatings [16, 17]. Thin films of Ta$_2$O$_5$ have been produced by laser ablation [18], sputtering [19], evaporation [20], sol-gel [21] and ALD [22], but the most commonly used technique is CVD [23, 24, 25].
Zirconium oxide, $\text{ZrO}_2$, is known to have four different crystal modifications: monoclinic, tetragonal, cubic, and orthorhombic. Due to hysteresis in the transitions and a strong influence of the preparation technique as well as the measurement conditions, the reports on their stability regions differ widely. Therefore, the following data are not to be taken as universal truths. Under atmospheric pressure, the monoclinic low-temperature phase transforms into tetragonal $\text{ZrO}_2$ around 1145°C [26], and the tetragonal phase is stable up to 2370°C where it transforms to cubic $\text{ZrO}_2$ [27]. The high-temperature phases can also be obtained at low temperatures when stabilised by other oxides, for instance $\text{Y}_2\text{O}_3$ or $\text{CeO}_2$ [28, 29], or in materials with small grain sizes, oxygen deficiency or impurities [30]. An orthorhombic phase exists at elevated pressure, and a triple point has been reported for the monoclinic, tetragonal and orthorhombic phases at 600°C and 23 kbar [31]. The homogeneity range for $\text{ZrO}_2$ extends down to 63 atomic percent oxygen [32]. The $\text{ZrO}_2$ phases are unusual in that the structure becomes more symmetric on heating. The true cubic fluorite phase (see Fig. 2.3) is stable above 2450°C, but the monoclinic and tetragonal polymorphs can be described as distorted fluorite structures, with the low temperature phase being the most distorted [33].

$\text{ZrO}_2$ is a material with well-known physical properties that renders industrial applications in many fields. For instance, zirconium oxide has low thermal conductivity, high refractive index and a high dielectric constant and is used in thermal barrier coatings, high-temperature optical filters [34] and oxygen sensors [35]. Some of the techniques that have been used to produce thin films of $\text{ZrO}_2$.

![Figure 2.2: The structure of $\beta$-$\text{Ta}_2\text{O}_5$.]
2.3 Hafnium oxide

Hafnium oxide, HfO$_2$, is very similar to ZrO$_2$ in chemical and physical properties, and the oxides are completely soluble in all proportions in the pseudo-binary system [40]. The HfO$_2$ and ZrO$_2$ phases are isostructural, but there are some differences in atomic positions and transition temperatures, and the hysteresis is considerably smaller for HfO$_2$. For HfO$_2$, the monoclinic to tetragonal transformation takes place between 1620 and 1650°C [40], and the tetragonal to cubic at 2700°C [41]. The triple-point relation is analogous to that found in the ZrO$_2$ system, but located at approximately 1200°C and 15kbar [31]. HfO$_2$ has the same homogeneity range as ZrO$_2$, down to 63 atomic percent oxygen, but the density is higher due to the heavier Hf atom.

As can be expected, HfO$_2$ has the same excellent material properties as ZrO$_2$: extreme chemical and thermal stability, good electrical properties, and a high refractive index, and more or less the same applications result: protective coatings [42], optical coatings [43] and oxygen sensors [44]. Thin films of HfO$_2$ have been produced by laser ablation [45] ion beam sputtering [46], sol-gel [47], ALD [48] and CVD [49].
3 Deposition Techniques

For most thin film applications, the deposition method is a crucial factor in determining the quality and properties of the layer. The process must also be compatible with other fabrication steps, be cost-efficient and suitable for large-scale production. CVD methods have been applied in various fabrication processes for quite some time with great success, and in recent time, the pulsed CVD technique, ALD, has entered the industrial scene. Using CVD techniques, a large variety of materials can be deposited over a wide pressure and temperature range. Dense, well-adherent films can be formed with excellent uniformity over large areas and on complex shapes. With ALD, the composition and thickness of the layer can be controlled down to the atomic level. The different effects that control the film growth in CVD and ALD will be discussed further in the following paragraphs.

3.1 CVD

The name Chemical Vapour Deposition implies the formation of a solid material from the gaseous state by way of a chemical reaction [50]. This reaction normally takes place on, or in the vicinity of, a surface and is activated by some kind of energy. CVD processes can be classified according to i) their activation energy, for instance thermally activated, plasma-enhanced, laser-induced and electron-beam assisted, ii) the nature of the starting material: metalorganic or halide, iii) the process pressure: atmospheric, low-pressure, high-vacuum etc. In addition, conventional, thermal-activation CVD chambers are usually denoted hot-wall or cold-wall reactors, depending on which part is heated. The deposition process can be described as taking place through the following steps (Fig. 3.1):

1. transport of the reactants to the vicinity of the substrate surface
2. diffusion of the reactants to the substrate surface
3. reactant adsorption on the substrate surface
4. surface chemical reaction
5. surface migration and lattice incorporation
6. reaction product desorption
7. diffusion of reaction products away from the substrate surface
8. transport of reaction products outside the deposition zone.

In general, the variables affecting the deposition rate and film properties are the nature of the reactants and their purity, the amount of energy supplied, the substrate temperature, the ratio of reactants, the gas flow rates, the system pressure, the geometry of the deposition chamber and the substrate surface preparation. CVD processes generally have high deposition rates and are suitable for large-scale production at low cost. The choice of starting materials is not very restricted, although some may require high deposition temperatures. In unfortunate cases, where the experimental parameters have not been optimised, reaction can take place in the gas mixture above the substrate, so-called homogeneous nucleation. This leads to formation of powder that, when it falls down on the substrate or the growing film, can cause poor adhesion of the film.

### 3.2 ALD

Throughout this thesis, the name Atomic Layer Deposition, ALD, will be used to describe the technique that was originally called Atomic Layer Epitaxy, ALE.
The term “epitaxy” was abandoned since the deposited films most often are not epitaxial. Another denomination, which emphasizes the relationship with conventional CVD, is Atomic Layer Chemical Vapour Deposition, ALCVD. The ALD technique is based on sequential admission of reactants into the reaction chamber. One reactant at a time is allowed to adsorb to the surface of the substrate or the growing film. After each reactant pulse, the reactor is purged with inert gas to remove superfluous material and to make sure the reactants are separated in time and space. Fig. 3.2 illustrates the growth of a binary compound from binary source materials. The central features for process control are to achieve surface saturation in each reactant pulse, and that no more than one monolayer remains after the purge, since the sequencing alone does not result in a surface controlled deposition. Saturation also makes the thickness proportional to the number of growth cycles instead of to the reactant flux.

The minimisation of electronic circuits requires an atomic level accuracy in thin film deposition that is inherent in the ALD technique. The separate pulsing of the source materials and layer by layer growth also makes ALD an excellent tool for producing complex and layered coatings. Other advantages are that the separation of the reactants eliminates the risk for gas-phase reactions, and that lower deposition temperatures can be used in ALD than in CVD. However, the choice of precursors for ALD is generally more limited, than in CVD, see section 3.3, the processes are inherently slow, and large-scale production is not very easy to accomplish. On the other hand, with atomic level control of thickness, uniformity and composition, the use of ALD processes in industrial fabrication can still be cost-efficient. The reactions in ALD have traditionally been thermally activated, but other energy sources like plasmas and lasers are now coming into use.
3.3 Precursors for CVD and ALD

Unlike physical film deposition techniques like sputtering and evaporation, the chemical processes CVD and ALD are very dependent on the properties of the source materials. Chemical and physical properties determine which materials will be possible to use for deposition, as well as the properties of the resulting films. Since the film growth in CVD and ALD processes is based on somewhat different principles, the demands on suitable starting materials are slightly different. Both techniques can utilize materials that are gases, liquids or solids at room temperature, as long as they are stable enough to be evaporated or sublimated, and have high enough vapour pressures. Gaseous compounds are the most easy to handle, and can also be supplied at a controllable rate by simply using a mass flow controller. The evaporation rate of liquid and solid sources, on the other hand, is determined by temperature, surface area and carrier gas flux. In all classes of materials, it is of course preferable to avoid the ones that are poisonous, explosive or flammable for the sake of personal safety, and also to avoid corrosive or etching media for the sake of the equipment.

In ALD, it is essential that the precursors adsorb to the surface, since otherwise no growth can be achieved. Uniform, self-limiting growth demands uniform saturation, for which it is important that the precursors are stable at the process temperature. Decomposition on the surface or incomplete exchange reactions can cause loss of saturation and incorporation of impurities in the film. The need for thermal stability usually limits the ALD processes to a narrower working range than with CVD. Furthermore, the activation energy for surface reaction should be low, and since the reactants are separated in time and space, the risk for gas-phase reactions is eliminated, which facilitates the use of more reactive source materials than in CVD. With more reactive source materials, lower deposition temperatures can be used.

Each CVD precursor does not need to adsorb to the surface in order for film growth to occur, and it is not necessary that it is stable on the surface. However, the precursors should not be too reactive, since a certain reaction threshold is needed to avoid reactions in the gas phase and for the deposition to occur uniformly over the surface.

3.3.1 Previous work

The metal sources that have been used in deposition of Ta₂O₅, ZrO₂ and HfO₂ by CVD and ALD are metal halides and metalorganics, and in some cases, nitrate compounds. Among these, both liquid and solid materials are available.
3.3 Precursors for CVD and ALD

Table 3.1: Precursors utilised in previous works.

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursors in CVD</th>
<th>Precursors in ALD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta₂O₅</td>
<td>TaCl₅ [49, 53, 25]</td>
<td>TaCl₅ [22, 54, 55]</td>
</tr>
<tr>
<td></td>
<td>Ta(OC₂H₅)₅ [56, 23, 57]</td>
<td>Ta(OC₂H₅)₅ [58, 59]</td>
</tr>
<tr>
<td></td>
<td>Ta[N(CH₃)₂]₅ [60]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(BuN)-Ta(NEt₂)₃ [61]</td>
<td></td>
</tr>
<tr>
<td>ZrO₂</td>
<td>ZrCl₄ [62, 63, 64]</td>
<td>ZrCl₄ [65, 54, 59]</td>
</tr>
<tr>
<td></td>
<td>Zr(NO₃)₄ [66, 67]</td>
<td>Zr[OC(CH₃)₃]₄ [68]</td>
</tr>
<tr>
<td></td>
<td>Zr(acac)₄ [56, 34, 30]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr(NEt₂)₄ [69]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr[OC(CH₃)₃]₄ [70]</td>
<td></td>
</tr>
<tr>
<td>HfO₂</td>
<td>HfCl₄ [71]</td>
<td>HfCl₄ [72, 73, 54]</td>
</tr>
<tr>
<td></td>
<td>Hf(acac)₄ [49]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hf(thd)₄ [49]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hf(NO₃)₄ [67]</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1 is a compilation of precursors that have been used in CVD and ALD of the respective oxides. It appears that for Ta₂O₅, Ta(OC₂H₅)₅ is the most common precursor in both CVD and ALD. For ZrO₂ and HfO₂, the chlorides are almost the only sources used in ALD, whereas a number of metalorganics have been used in CVD. The chlorides are the outstandingly most popular halide precursors, and there are only a few examples where other halides have been used. With chloride sources, there is a risk for etching reactions with the substrate, the growing film or the reactor, and in CVD rather high deposition temperatures are usually required. The metalorganic precursors seldom etch the substrate, and the growth temperatures are low. However, a common problem for chloride and metalorganic starting materials is that chloride or carbon impurities, respectively, often are incorporated into the films. For example, Ta₂O₅ films containing 2% Cl [52], and HfO₂ films containing 5% Cl [39], have been grown by ALD using the respective chloride, and ZrO₂ films containing 15% C [34] have been grown by CVD using zirconium acetylacetonate. Nitrate precursors have been used in CVD of ZrO₂ and HfO₂ at low temperatures, apparently leaving no impurities in the films, but they may not be completely safe to handle.

Metal iodides have earlier proven to be suitable precursors for deposition of thin films of for example Bi₂Sr₂CaCu₂O₈₊ₓ [74], Bi₄Ti₃O₁₂ [75] and TiO₂ [76] by CVD and TiO₂ by ALD [77, 78]. The CVD processes employed O₂ as the
only oxygen source, and in ALD, O\(_2\) [78] or H\(_2\)O\(_2\) [77] was used. The group IV- and V-metal iodides are all solids at room temperature, but the thermal stability is good and the vapour pressure high enough to give a reasonable evaporation rate [79, 80]. According to literature, TaI\(_5\) [81] and ZrI\(_4\) [49] react with oxygen already at 100\(^\circ\)C to form their respective oxides. Information about the reactivity of HfI\(_4\) is scarce, but it is usually said to have similar properties to TiI\(_4\) and ZrI\(_4\) [82]. Based on the said reactivities and results from previous studies, it should be possible to deposit of Ta\(_2\)O\(_5\), ZrO\(_2\) and HfO\(_2\) using iodide sources at low temperatures. It also points to the possibility of using O\(_2\) as single oxygen source, at least in CVD, thereby minimising the number of elements involved. In most chloride processes, H\(_2\)O must be introduced to remove the chlorine in the form of HCl.
4 Experimental

4.1 CVD experiments

The films were deposited in a horizontal hot-wall CVD reactor consisting of two concentric quartz tubes (Fig. 4.1). The reactor is heated by a four-zone furnace that allows careful adjustment of the temperature profile. The solid metal source is evaporated from an open boat in the inner tube and a flow of inert gas is used for transporting the vapour into the deposition zone. The oxygen source is supplied by the outer tube directly to the deposition zone, where the inner tube ends. The flow of reactants can be controlled by the evaporation temperature and carrier gas flow. All gas flows are monitored by mass flow controllers and a throttle valve is used for maintaining a constant pressure of 10 torr in the chamber. Argon (99.9999%) was used as carrier gas with a flow of 150 sccm, and oxygen (99.998%) was supplied as the single oxygen precursor with a rate of 175 sccm and was diluted with an additional 100 sccm of argon. The linear gas flow velocity was 105 cm·s⁻¹ and the air leak rate into the system (1·10⁻⁶ Pa·m³·s⁻¹) corresponds to an air contamination level of less than 1 ppm.

![Diagram of CVD reactor](image)

**Figure 4.1:** Schematic illustration of the CVD reactor.
Metal source (purity) | $T_{evap}$ (°C) | $T_{reactor}$ (°C) | Substrates | Paper no. |
--- | --- | --- | --- | --- |
TaI$_5$ (99%) | 275 | 300-800 | Si(100) Pt/Ti/SiO$_2$/Si, MgO (001) | I |
ZrI$_4$ (99.5%) | 200 | 400-700 | Si(100) Pt/Ti/SiO$_2$/Si | IV |
HfI$_4$ (99%) | 300 | 300-700 | Poly-Si MgO (001) | VII |

<table>
<thead>
<tr>
<th>Ti-Ta-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaI$_5$ (99%)</td>
</tr>
<tr>
<td>Ti$_4$ (99%)</td>
</tr>
</tbody>
</table>

Table 4.1: Process parameters for the CVD experiments.

4.2 ALD experiments

The experiments were performed in a hot-wall flow-type ALD reactor that can be fitted with a quartz crystal microbalance (QCM) mass sensor for *in situ* monitoring. The reactor consists of an outer stainless steel tube, lined with a quartz tube, and an inner quartz tube that connects the precursor evaporation zone with the deposition zone (Fig. 4.2). The gases are fed through valves controlled by microprocessors that allow the flows to be switched on and off in less than 0.1 s. The metal source was evaporated from a silica crucible and carried to the substrates by a flow of inert gas. The evaporation rate of the metal source was controlled by the choice of evaporation temperature. An aqueous solution of H$_2$O$_2$ (30% H$_2$O$_2$) was used as oxygen precursor for deposition of Ta$_2$O$_5$ and ZrO$_2$, and deionised water for deposition of HfO$_2$. The liquids were kept in an external container at 20°C, and the partial pressure of H$_2$O and H$_2$O$_2$ was regulated by a needle valve. Nitrogen (99.999%) was used as both carrier and purge gas, and with a total reactor pressure of 250 pascal, the linear flow rate was 5 m/s. The film growth characteristics were studied in real time by QCM monitoring with the susceptor placed in the reaction zone instead of the substrate holder. The QCM consists of a quartz crystal connected to an electrical circuit and a read-out unit. The crystal has a certain vibration frequency, and when gases adsorb to its surface and it becomes heavier, the vibration frequency is reduced. The reduction in frequency is recorded as a gain in mass. Analogously, desorption leads to increased vibration.
frequency, which is recorded as a loss of mass.

![Schematic illustration of the ALD reactor.](image)

**Figure 4.2:** Schematic illustration of the ALD reactor.

<table>
<thead>
<tr>
<th>Metal source (purity)</th>
<th>$T_{\text{evap}}$ ($^\circ$C)</th>
<th>$T_{\text{reactor}}$ ($^\circ$C)</th>
<th>Substrates</th>
<th>Paper no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TaI$_5$ (99%)</td>
<td>245</td>
<td>250-400</td>
<td>Si(100)</td>
<td>II,III</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt/Ti/SiO$_2$/Si</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgO (001)</td>
<td></td>
</tr>
<tr>
<td>ZrI$_4$ (99.5%)</td>
<td>240</td>
<td>250-500</td>
<td>Si(100)</td>
<td>V,VI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt/Ti/SiO$_2$/Si, Poly-Si, $\alpha$-Al$_2$O$_3$(001)</td>
<td></td>
</tr>
<tr>
<td>HfI$_4$ (99%)</td>
<td>205</td>
<td>225-500</td>
<td>Poly-Si, Si(100)</td>
<td>VII</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>MgO (001)</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.2:** Process parameters for the ALD experiments.

### 4.3 Film characterisation

The phase composition of the films was examined with X-ray diffraction (XRD), and depending on the character of the film, different analysing modes were used. For thin films of random orientation, using a low incidence angle, so-called Grazing Incidence, is usually suitable. It makes the analysis more surface sensitive and
helps raising the peak intensities and avoiding overlap with substrate peaks. For thicker films, standard θ-2θ scans are more appropriate. Also, strongly textured or epitaxial films must be analysed in θ-2θ mode, since atomic planes that are parallel to the substrate cannot be observed in Grazing Incidence. In case of strongly textured films, Rocking Curve (ω-scan) analysis can be performed to investigate the film quality. In Rocking Curve, the Bragg angle is kept constant while varying the incidence angle, and the full width at half maximum (FWHM) value of the resulting peak, gives an indication of the film quality. A small FWHM value indicates the possibility of epitaxy, which can be confirmed by a ϕ-scan. A ϕ-scan is done by recording the intensity from a plane non-parallel with the surface, while rotating the sample around its normal, where ϕ denotes the rotational angle. Comparing ϕ-scans performed for both the film and the substrate reveals the in-plane relationship between them. In some cases, Raman spectroscopy was used as a compliment to the phase analysis by XRD, since Raman has higher sensitivity for short-range order.

The purity and composition of the films were analysed by X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence spectrometry (XRFS). In XPS, the analysis was performed after removing the surface contamination and the topmost layers of film by sputtering with Ar⁺ ions, and in some cases, depth profiling was performed. Surface morphologies were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Film thicknesses were determined in different ways depending on the thickness range of the films: Large film thicknesses were determined by surface profilometry over a step in the film or by measuring the cross-section of the film in SEM. Ellipsometry or X-ray reflection (XRR) was used for thinner films. For the electrical characterisation, capacitors were fabricated by depositing metallic contacts on top of the films. Leakage currents in the films were measured as a function of voltage. Capacitance was measured as a function of voltage or frequency, and the dielectric constants of the films were calculated from

\[ \varepsilon_r = (\varepsilon_0 \cdot \text{A} \cdot \text{C}) / \text{d} \]

where  
\( \varepsilon_r \) = relative permittivity  
\( \varepsilon_0 \) = permittivity of vacuum  
A = area of contact  
C = capacitance  
d = film thickness

Some films were studied by transmission electron microscopy (TEM) to evaluate the quality of the interface between film and substrate.
5 Deposition of Tantalum Oxide

5.1 CVD

The orthorhombic $\beta$-Ta$_2$O$_5$ [8] phase was obtained without post-deposition annealing in the temperature range 300-800°C. The films were texture free on Si(100) substrates, but showed preferential growth in the c-axis direction on MgO(001) substrates. X-ray diffracograms for films deposited at 600°C can be seen in Fig. 5.1.

![X-ray diffractogram](image)

**Figure 5.1:** X-ray diffractograms for Ta$_2$O$_5$ films deposited at 600°C.

No iodine could be detected in the films for any of the deposition temperatures by XRFS (the detection limit for iodine is about 0.01%). Furthermore, the films were continuous and had a very smooth surface as can be seen in the AFM micrograph in Fig. 5.2 for a film grown on Si(100) at 600°C.

The deposition rate was found to be strongly dependent on the reactor temperature. The oxide thickness increased with 1 $\mu$m/h at 600°C, but lowering the
Deposition of Tantalum Oxide

reactor temperature to 500°C reduced the growth rate to about 0.5 µm/h. At 300°C, the growth rate was found to be very low, about 0.015 µm/h, and this was the reason for not attempting an even lower deposition temperature. At the other extreme, 800°C, the deposition rate was again substantially reduced, probably due to thermal decomposition of TaI₅ before reaching the deposition zone. From the SEM cross-section of a film deposited at 600°C shown in Fig. 5.3, it can be seen that the oxide has grown with a dense, columnar structure and forms a sharp interface with the Si(100) surface.

Electrical characterisation of a film deposited at 600°C indicated the value of the dielectric constant to be 25.8 with no measurable temperature dependence between 24 and 90°C. However, a relatively high dc conductivity was simultaneously observed, which was believed to be caused by hydrogen incorporated into the film during deposition or from water uptake upon storage in air. A more detailed study of the electrical behaviour of a film deposited at 600°C film has been published elsewhere [83].

In most other studies, the electrical characteristics are given for annealed films. However, Burte and Rausch [84] performed measurements both before and after thermal treatment of the amorphous films. They found that the dielectric constant increased from 24.5 to 32 while the leakage current decreased consid-

Figure 5.2: AFM micrograph of a Ta₂O₅ film deposited on Si(100) at 600°C.
5.2 In situ monitoring

There are numerous examples of investigations reporting that annealing helps to improve the electrical characteristics, but for most industrial applications, high process temperatures should preferentially be avoided.

It is interesting to note that pure, crystalline $\beta$-Ta$_2$O$_5$ films can be produced already at 300°C, using TaI$_5$ as precursor in CVD. In studies employing other tantalum precursors, the lowest deposition temperature where crystalline Ta$_2$O$_5$ has been obtained by thermally activated CVD has been reported to be 625°C [85]. In most cases, however, some sort of thermal treatment above 700°C is required for crystallisation.

5.2 In situ monitoring

The deposition kinetics were investigated by recording the mass signal during relatively long deposition cycles (Fig. 5.4). During the TaI$_5$ pulse, $t_1$, the mass increased sharply and stabilised at a certain level, $\Delta m_1$. The stabilisation of the QCM signal indicates that the precursor adsorption is saturative and the process thereby self-limiting. During the $\text{H}_2\text{O-H}_2\text{O}_2$ pulse, a mass decrease, denoted $\Delta m_2$, was recorded, and after completion of the growth cycle, the mass of the deposited layer was observed as $\Delta m_0$. For temperatures in the range 240-325°C, the mass sensor signal remained stable after saturation had been reached, but at higher temperatures, the mass decreased continuously during extended TaI$_5$ exposures (Fig. 5.4). The loss of mass was enhanced by increasing the temperature, and concurrently, $\Delta m_0$ decreased. At sufficiently long pulse times and high substrate temperatures, $\Delta m_0$ became negative, indicating that some of the previously

Figure 5.3: SEM cross-section of a Ta$_2$O$_5$ film deposited on Si(100) at 600°C for 5h.
deposited material was removed by etching reactions with TaI₅. The etching reaction was, however, noted to be slower than in the TaCl₅-H₂O precursor system [86].

At source temperatures (Tₛ) above 245°C, the TaI₅ adsorption stabilised and remained fairly insensitive to further changes in Tₛ. During the subsequent studies, Tₛ was kept at about 245°C. The amount of tantalum oxide deposited in each cycle, Δm₀, increased rapidly with the TaI₅ pulse length, t₁, between 0.5 and 1 s (Fig. 5.5). Upon further increases in t₁, the Δm₀ value continued to increase but at a considerably lower rate. This non-saturative increase in mass might be attributed to thermal decomposition of the metal precursor. The same kind of behaviour has been observed, for instance, in the TiI₄-H₂O₂ precursor system in the temperature range 200-400°C [87], and in the Ta(OH₂)₅-H₂O system at temperatures above 300°C [58]. During the first purge period, t₂, a considerable mass decrease was observed (Fig. 5.4), the magnitude of which increased with temperature. This effect was attributed to the release of I₂, formed by precursor decomposition, which was also confirmed by the fact that Δm₀ was not significantly affected by variations in t₂. Therefore, the purging process could not include desorption of Ta-containing surface species.

At the same time, Δm₀ only had a weak correlation with the growth temperature and was actually decreasing with increasing temperature. This indicated that the contribution of the etching effects to the growth rate was more signifi-
5.2 In situ monitoring

![Graph](image)

**Figure 5.5:** Dependence of the growth rate, $\Delta m_0$, on the length of the TaI$_5$ pulse, $t_1$, H$_2$O$_2$ exposure time, $t_3$, and second purge time, $t_4$. The first purge period, $t_2$, was kept constant at 2 s.

can be compared with this influence of thermal decomposition of the precursor during $t_1$. The growth rate was not noticeably affected by the length of the H$_2$O-H$_2$O$_2$ pulse, $t_3$, but it was affected by the vapour pressure of the liquid. For this reason, the H$_2$O-H$_2$O$_2$ dose was kept relatively high in the subsequent experiments to ensure rapid completion of the exchange reactions.

Assuming that the ALD-grown oxide surface is terminated with OH-groups after the end of each water pulse, the subsequent TaI$_5$ adsorsbs to the hydroxylated surface through an exchange reaction. Calculating the mass exchange ratio from QCM data recorded at different temperatures gives $\Delta m_0$ values ranging from 0.333 to 0.345, without clear correlation with growth temperature. These values correspond quite well to a situation where TaI$_5$ reacts with one OH-group during $t_1$, according to

$$|\text{Ta-OH} + \text{TaI}_5(g) \rightarrow |\text{Ta-O-TaI}_4 + \text{HI}(g)$$

For the deposition of sample films, the TaI$_5$ exposure time was set to 2 s in order to achieve a fairly high degree of saturation, while minimizing the effects of etching and precursor decomposition. Although the growth rate was rather independent of the purging time, both the first, $t_2$, and second purge, $t_4$, were chosen to be as long as 2 s to ensure reliable separation of the precursors. The oxygen precursor pulse was also set to 2 s.
5.3 ALD

It was concluded that the growth rate was influenced both by reactor temperature and substrate (Fig. 5.6). For Si(100) and MgO(100) substrates the deposition rate decreased with increasing temperature which can be explained by a certain degree of etching of the growing film by the oncoming TaI₅ [88]. This trend agrees with the results from the QCM studies. For the Pt substrate, the thickness was the same at the lower temperatures, but starting at 350°C, the growth rate increased drastically with the temperature. At 300°C, the deposition rate was approximately 0.8 Å per cycle, independent of the substrate, but for Pt it increased to 3 Å per cycle at 400°C. XPS analysis showed that the deposited films were iodine-free for all reactor temperatures and all substrates.

The substrate also had a strong influence on the crystallisation temperature of the films. The films grown on Si(100) substrates were found to be amorphous in the whole temperature interval 250-400°C. Films on MgO(100) substrates started to crystallise at 350°C, and at 400°C strongly [001]-textured Ta₂O₅ had formed (Fig. 5.7). For Pt substrates, there were no signs of crystallisation of the films at 325°C and below, but above this temperature, randomly oriented Ta₂O₅ had formed. The strongest XRD peaks can be assigned to either the hexagonal δ-phase [10] or the orthorhombic β-Ta₂O₅ [8], but while the peaks at d-values of
1.82 Å and 1.80 Å both can be indexed as orthorhombic, only the 1.82 Å peak fits with the hexagonal phase. Thus, the Ta$_2$O$_5$ phase is identified as the orthorhombic $\beta$-phase.

Surface studies by SEM and AFM revealed that the amorphous films were extremely smooth. Rms values of 0.5 nm were measured for films on Si(100) and MgO(100) substrates, and 1.7 nm for films on Pt. The crystalline phase grew as large grains that increased the surface roughness considerably, and depending on the substrate, different shapes were observed. For Si(100) at 400°C, large outgrowths were found embedded in the amorphous matrix with random distribution over the surface. The shape of these outgrowths indicated that they were crystalline, but no crystalline phase could be detected by XRD. The [001]-texture of the Ta$_2$O$_5$ on MgO(100) at 400°C caused grains of hexagonal shape to grow out of the film (Fig. 5.8). The randomly oriented Ta$_2$O$_5$ deposited on Pt at 350 and 400°C had a different appearance which can be seen in the SEM micrograph displayed in Fig. 5.8. The increased surface topography of the films grown on Pt leads to increased surface area for adsorption, which seems to be the reason for the enhanced growth rate on Pt above 350°C.

Electrical characterisation was performed for films deposited on Pt substrates. The capacitance measurement failed for the 250°C film, but it was found that the samples of amorphous films deposited at 300 and 325°C had dielectric constants of approximately 26, whereas the crystallised Ta$_2$O$_5$ films at 350 and 400°C both...
gave the value 66. These are very high dielectric constants for pure, as-deposited Ta$_2$O$_5$, and other ALCVD studies [59] have reported values of 25 for weakly crystallised films. It is known that the crystallisation enhances the permittivity, and in addition, with the Pt substrate, no interfacial oxide can form, lowering the total permittivity. However, it can not be ruled out that interfacial charge trapping affects the measurements [89].

Figure 5.8: SEM micrographs of Ta$_2$O$_5$ grown at 400°C on Pt substrate (left) and MgO(001) (right).
6 Deposition of Zirconium Oxide

6.1 CVD

From the X-ray diffraction studies, it was concluded that all films deposited on Si(100) were crystalline as-deposited and consisted of the monoclinic ZrO\(_2\) phase [90]. The films were strongly textured with preference for the 002, 020 and 200 reflections, but the 020 reflection was usually the strongest. Fig. 6.1 shows a typical X-ray diffractogram where the very strong 020 reflection indicates that the film has a strong [020] texture. However, the \(\omega\)-scan full width at half maximum (FWHM) value for the 020 reflection was as high as 15\(^\circ\), ruling out the possibility of epitaxial growth.

![X-ray diffractogram for a ZrO\(_2\) film deposited on Si(100) at 500\(^\circ\)C.](image)

**Figure 6.1:** X-ray diffractogram for a ZrO\(_2\) film deposited on Si(100) at 500\(^\circ\)C.

According to XRFS analysis, the films were iodine-free, even for the lowest deposition temperatures. The deposition temperature was found to have a
strong influence on the growth rate with a maximum of 0.3 \( \mu m/h \) at 500\(^{\circ}\)C. The reduction in growth rate at higher temperatures cannot be explained by reaction kinetics. One possible explanation is that the depletion of the gas mixture increases with temperature, causing a steeper thickness gradient and displacement of the actual deposition zone. It is also possible that iodine-containing species etch the growing oxide to some extent, an effect that is likely to be larger at elevated temperatures. Another point that has to be considered is that ZrI\(_4\) has a boiling point of approximately 600\(^{\circ}\)C, and some authors claim that the molecule is dissociated at 650\(^{\circ}\)C [79]. If this is the case, part of the ZrI\(_4\) should decompose or react before the deposition zone is reached, thereby reducing the deposition rate for the highest temperatures.

Surface morphology studies using AFM showed that the deposition temperature had no significant effect on the surface roughness or grain size of the films. Continuous films with smooth surfaces were grown at all temperatures, and from the micrograph in Fig. 6.2 the average grain size can be estimated to 0.3 \( \mu m \).

A dielectric constant of 18 was calculated from the capacitance measured at 1 Mhz for a film deposited on Pt(2000Å)/Ti(200Å)/SiO\(_2\)(800Å)/Si(100) substrate at 500\(^{\circ}\)C. Measurement of the electrical resistance of the same film gave a conductance value of 145 \( \mu \Omega^{-1} \). These values are within the range of what
6.2 In situ monitoring

QCM studies revealed that ZrI₄ had to be evaporated at temperatures above 235°C to achieve film deposition at an appreciable rate. The ZrI₄ adsorption was detected as an increase in the QCM signal, denoted $\Delta m_1$ (Fig. 6.3), during the ZrI₄ exposure. The signal continued to increase up to 40 s, which shows that the adsorption of ZrI₄ was not completely self-limiting in this temperature range. This kind of behaviour is analogous to that observed for adsorption of TiI₄ on a TiO₂ surface treated in H₂O-H₂O₂ flux [92]. In both cases, the effect may be explained by the decomposition of metal iodide on the oxide surface. With increasing exposure time, the rate of the mass change decreased significantly: about two times higher mass increase was obtained during the first 5 s than in the following 35 s. One can thus rely on the surface coverage with iodide species to be close to the maximum value already after the first few seconds.

Using long purge times between the ZrI₄ and H₂O-H₂O₂ exposures caused the film mass to decrease by an amount denoted $\Delta m_p$ in Fig. 6.3. This is probably due to the desorption of iodine released in the ZrI₄ decomposition process. Desorption of ZrI₄ itself can probably be ruled out since no decrease in the mass increment per complete ALD cycle was observed upon the prolongation of the purge time from 2 to 10 s. During the H₂O-H₂O₂ pulse, the film mass decreased abruptly by $\Delta m_2$ (Fig. 6.3). This decrease was related to an exchange reaction between the -ZrIₓ adsorbed on the surface and the oncoming oxygen precursor, where the heavy iodine is replaced by oxygen or -OH groups. When the cycle is completed, a new layer with the mass $\Delta m_0$ has formed. A H₂O-H₂O₂ pulse of 2 s was long enough to recover the adsorption capability of the surface towards ZrI₄ and achieve stable growth in a series of repeated ALD cycles (Fig. 6.4), and was therefore used in further studies.

As could be expected, the mass increment $\Delta m_0$ as a function of ZrI₄ pulse
Figure 6.3: QCM signal recorded during an extra long ZrO₂ growth cycle.

Figure 6.4: Consecutive ZrO₂ growth cycles using 2-2-2-2 s pulses.
duration, did not saturate. After a steep increase for pulse times between 0.4 and 1.0 s, an almost linear increase in $\Delta m_0$ with a considerably lower but constant rate was observed. Extending the ZrI$_4$ pulse duration from 2 to 10 s made the value of $\Delta m_0$ increase by a factor of 1.8. To avoid the contribution from the ZrI$_4$ decomposition, probably responsible for this increase, ZrI$_4$ pulses of 2 s were used for the deposition of the films for post-deposition studies. A more complete saturation of the mass increment per cycle was achieved by increasing the oxygen precursor pulse duration. The value of $\Delta m_0$ increased by a factor of 1.3 when the exposure time of H$_2$O-H$_2$O$_2$ increased from 2 to 10 s. The QCM studies also showed that purge periods of 2s were sufficiently long to remove gaseous products from the reactor and to avoid overlap between the precursor pulses.

6.3 ALD

6.3.1 Temperature series

The XPS analysis showed that small amounts of iodine, 1.3-0.8 atomic %, were incorporated into films deposited at 250 to 350°C, but for higher temperatures, no contamination was found in the films. Films deposited on both Si(100) and Pt substrates at temperatures between 250 and 500°C were crystalline. Fig. 6.5 shows how the diffractograms for films deposited on Si(100) change with temperature, but the same trends apply for films on Pt. Peaks that are characteristic of monoclinic ZrO$_2$ [93] were detected in the whole temperature interval (d-values of approximately 3.14, 2.84, 2.62, 2.32, 2.19, 1.84 and 1.65 Å). The remaining peaks in the diffractogram, at d = 2.93, 2.58, 2.54, 2.10, 1.80, 1.69, 1.55 and 1.53 Å, could all be attributed to the tetragonal phase [94], and the ones in bold print also to the cubic phase [95]. The intensity of the peaks at 2.54 and 1.53 Å first increases and then decreases abruptly with increasing temperature. At the same time, the intensity of the peaks at 2.58 and 1.55 Å that clearly do not belong to cubic ZrO$_2$, increases strongly with deposition temperature, starting from 300°C.

These trends could indicate a change in phase content, from cubic to tetragonal, with increasing temperature, but it could also reflect a change of orientation of the tetragonal grains with deposition temperature. Indeed, Raman spectroscopy studies verified that tetragonal ZrO$_2$ had formed even at the lowest temperatures. A few peaks of both tetragonal and monoclinic phase [96] appeared already at 275°C, and the number as well as the intensity of the peaks increased with temperature.

The deposition rate reaches a sharp maximum of 1.25 Å/cycle at 275°C, and decreases to approximately 0.7 Å/cycle for the higher temperatures. No differ-
Figure 6.5: X-ray diffractograms for ZrO$_2$ films deposited on Si(100) at different temperatures.

ence can be seen in the deposition rate on Pt and Si(100) substrates, and the SEM studies showed that the surface microstructure is practically identical for films deposited on the two substrates. The surface morphology changes with temperature as can be seen from the SEM micrographs of Fig. 6.6.

Figure 6.6: SEM micrographs of films grown on Si(100) substrate at 300°C and 500°C.
TEM studies performed on films deposited on Si(100) at 325 and 500°C showed that an amorphous layer of approximately 2 nm has formed at the substrate/film interface of both samples, see Fig. 6.7 for the 500°C film. EDS analysis points to the composition of this layer to be SiO$_2$. The grains are randomly oriented for both temperatures, and in low-magnification cross-sections of the whole films (not shown here), it was observed that large equi-axed grains have formed at 325°C whereas a columnar structure has developed at 500°C.

### 6.3.2 Thickness series

Films of thicknesses between 3 and 30 nm were deposited at an average rate of 0.09 nm/cycle. No significant differences in deposition rate based on substrate or temperature could be seen. The growth rate at 275°C was apparently not as high as was found previously (see above), and even though a small offset towards lower temperature would easily reduce the growth rate, this cannot fully explain the discrepancy between the two results.

From XRD studies, it could be concluded that not only the temperature, but also the substrate influences the crystallisation. The ZrO$_2$ films crystallised at lower thicknesses on Pt substrates than on poly-Si and α-Al$_2$O$_3$(001), an effect that was stronger at the lower temperature. At 275°C, the same tetragonal reflections appeared as for the thicker films deposited at the same temperature, i.e.
d = 2.93, 2.54, 1.80 and 1.53 Å. For deposition at 325°C, the first peaks were the same as for 275°C, but with increasing thickness, the tetragonal reflections at d = 2.58 and 1.55 Å, as well as monoclinic reflections appeared. For both temperatures, films deposited on α-Al₂O₃(001) substrates exhibited only one strong reflection at d=2.54 Å, which was assigned to the (110) plane of tetragonal ZrO₂. Rocking curve (ω-scan) analysis of this peak gave full-width-at-half-maximum (FWHM) values of about 4.5° for both deposition temperatures. Consequently, the films have a strong texture, but are probably not epitaxial.

The SEM studies showed that films on Pt and poly-Si substrates developed very similar microstructures with increasing thickness, and the appearance of the 30 nm thick films were already very similar to that of the thicker films. A minor effect of the growth temperature could be seen in that the films deposited at 325°C had somewhat larger grains and higher roughness than at 275°C. Independent of temperature and thickness, the films deposited on α-Al₂O₃ (001) were extremely smooth and are barely visible in the SEM.

Fig. 6.8 shows the dielectric constant as a function of film thickness, where the values vary between 2.5 and 17 for thicknesses between 3.5 and 20 nm. The dielectric constant appears to be higher for films grown at 325 than at 275°C, and also somewhat enhanced for Pt substrates, but the data points are too few for conclusions to be drawn. However, the film thickness has a strong influence on the permittivity, regardless of temperature and substrate. The leakage currents in the films were difficult to determine reproducibly and no general trends could be seen. Excellent reproducibility was, however, obtained for a 10 nm thick film grown on Pt at 275°C for which a leakage current of 1 μA/cm² at 1 MV was measured.

The breakdown voltage for this film was 4 MV/cm. The instability in the leakage currents could possibly be caused by oxygen vacancies in the oxide, which would also have a stabilizing effect on the tetragonal phase.
Figure 6.8: Dielectric constant of ZrO$_2$ films as a function of thickness, temperature and substrate.
7 Deposition of Hafnium Oxide

7.1 CVD

The film thickness measurements showed that the growth rate increased exponentially with temperature, from 0.5 nm/min at 300°C to 90 nm/min at 700°C. XPS analysis showed that films deposited at 300°C contained about 0.8 atomic % iodine, and very small amounts (~0.1 atomic %) were also detected in films deposited at 400 and 500°C. From the diffraction studies, it was found that monoclinic HfO₂ [97] had grown on poly-Si and MgO(001) substrates in the whole temperature range 300-700°C. Deposition on poly-Si resulted in poly-crystalline films with a preference for the [001] orientation that became more pronounced with temperature. Films on MgO showed a general preference for the [001], [010] and [100] orientations, but the contributions from the different orientations varied with temperature (Fig. 7.1). For 300°C, the films were only partly crystallised, with broad peaks of very low intensity.

The 500 and 600°C films gave very strong 0k0 reflections, and rocking curve analysis of the 020 peak gave FWHM values of approximately 1.4 and 1.8 degrees, respectively. For 700°C, the overlapping peaks made Rocking Curve analysis impossible, but a comparison of the results from θ-2θ and GIXRD scans showed that the (0k0) planes were exclusively oriented parallel with the surface, in contrast with the other planes. ϕ-scans were performed for the (024) plane of MgO and the (041) plane of HfO₂ for the 500 and 600°C films, resulting in four peaks from the film coinciding with the peaks from the substrate. This shows that an epitaxial relationship exists between the HfO₂ and the substrate: the a-axis of HfO₂ is parallel with the a- or the b-axis of the MgO. Due to low peak intensity in the θ-2θ scan, no attempts were made to analyze the orientational relationships for the film deposited at 400°C.

The development of the microstructure of the films as a function of temperature and substrate was studied by SEM. Fig. 7.2 a) and b) show micrographs of films deposited at 400 and 600°C on MgO substrates. At 400°C, spherical crystallites with small diameters are visible and the surface is very smooth. In
Figure 7.1: θ-2θ X-ray diffractograms for HfO$_2$ films deposited on MgO substrates, at 400-700°C with the φ-scan for 600°C in the inset.

contrast, the films deposited at 600°C consist of oblong crystallites, whose ordering was strongly influenced by the substrate. On MgO, the crystallites are oriented in one of two possible directions, 90° rotated from each other, while on poly-Si, they are randomly oriented. This structure was developed gradually with increasing temperature and is the most obvious in the thick films grown at 700°C, where the crystallites have grown to about 200 nm long needles (not shown here).

The dielectric constant increased rather sharply from 10.5 for the 300°C film to 17 for the 400°C film, but was almost constant between 400 and 700°C where it reached a value of 19 (Fig. 7.3). This shows that the dielectric constant is dependent on the crystallinity of the film. For films that have almost the same thickness, the 300°C film that is only partly crystallised has a much lower permittivity than the crystalline films. No obvious trends can be seen for the leakage currents measured for the different growth temperatures. However, as an example, a leakage current density of 0.1 $\mu$A/cm$^2$ at 1 MV/cm and a breakdown field above 1.5 MV/cm was measured for the 300°C film.
**Figure 7.2:** SEM micrographs of HfO$_2$ films deposited on MgO(001) substrates at a) 400°C and b) 600°C.

**Figure 7.3:** Dielectric constant of HfO$_2$ as a function of deposition temperature.
7.2 In situ monitoring

The QCM studies revealed that a HfI$_4$ vapour pressure sufficiently high for ALD-type growth at acceptable exposure times, was obtained at HfI$_4$ source temperatures exceeding 195-200°C. Fig. 7.4 shows a typical behavior of the QCM signal recorded at $T_G = 300^\circ$C during a relatively long ALD cycle. The most significant amount of HfI$_4$ is adsorbed in the beginning of the pulse, but the film mass continues to increase at exposure times reaching 20 s. The mass decreases during the subsequent purge, indicating desorption of some species from the film surface.

![Figure 7.4: QCM signal recorded in an HfO$_2$ ALD cycle during long exposure and purge times.](image)

However, as can be seen in Fig. 7.5, the amplitude of this mass decrease, $\Delta m_p$, does not influence the mass increment per complete ALD cycle, $\Delta m_0$. Consequently, the amount of hafnium released during the purge can not be considerable and the mass decrease is most probably due to desorption of iodine from the surface species formed during the HfI$_4$ pulse. Exposure of the surface to H$_2$O (Fig. 7.4 and 7.5) causes an abrupt decrease of the film mass. Such response to the oxygen precursor is typical for ALD processes in which a halide and water vapor are used as precursors [73, 87] and is explained by substitution of the heavy iodine ligands with much lighter oxygen atoms and/or hydroxyl groups. As a result of the exchange reaction, a new layer of oxide with the mass $\Delta m_0$ has formed and a relatively stable surface is obtained (Fig. 7.4).
The mass increment $\Delta m_0$ depends on the HfI$_4$ pulse duration as well as on the oxygen precursor pulse duration, but both dependencies saturate when sufficiently long pulses are used. The relatively high source temperature of HfI$_4$ (205°C) limits the range of substrate temperatures that can be used because the adsorption of the metal precursor does not saturate when the substrate temperature is lower than the source temperature.

By comparing calculated $\Delta m_0/\Delta m_1$ ratios with experimental values, the average I/Hf ratio in the adsorbate layer formed during the HfI$_4$ pulse can be estimated. The obtained I/Hf ratios are 1.9, 2.0 and 2.3 at 220, 260 and 290°C, respectively. This increase in the I/Hf ratio with temperature could be an effect of decreasing concentration of surface hydroxyl groups with increasing temperature. For comparison, the ligand/metal ratios, which were determined for the surface intermediate layer formed during the HfCl$_4$ pulse in the HfCl$_4$-H$_2$O process, were 2.4, 2.5 and 3.0 at substrate temperatures of 225, 300 and 400°C, respectively [73]. Thus, these QCM results show that HfI$_4$ decomposes more easily than HfCl$_4$.

### 7.3 ALD

The growth rate determined from film thickness measurements was $0.075 \pm 0.007$ nm per cycle, and was independent of the deposition temperature in the range
225-500°C. Small amounts of iodine were detected in the films deposited at 225 and 300°C, 0.85 and 0.35 atomic % respectively, but the films deposited at higher temperatures were free from contamination.

The films grown at 225°C were mainly amorphous, whereas those grown at 300-500°C were crystalline and consisted mainly of monoclinic HfO₂ [97]. The diffractograms for films deposited on poly-Si substrates at 400 and 500°C also contained a peak at about 2θ = 30.4°, that could be attributed to orthorhombic [17], tetragonal [98], or cubic [99] HfO₂, but the peak was not possible to identify unambiguously.

The substrate had a very strong influence on the texture of the growing HfO₂. On poly-Si, the films were poly-crystalline with a slight preference for the [001] orientation, whereas on MgO, only reflections originating from the (0k0) planes were detected (Fig. 7.6). Rocking curve analysis of the 020 peak for the 400 and 500°C films on MgO gave FWHM values of approximately 1 degree, indicating the possibility of epitaxy. ϕ-scans were performed for the (024) plane of MgO and the (041) plane of HfO₂, see the inset in Fig. 7.6. for the 500°C film. Both the 400 and 500°C films gave four peaks that coincided with the substrate peaks. This shows that there is an epitaxial relationship such that the a-axis of HfO₂ is parallel with either the a- or the b-axis of the substrate. Due to low peak intensity in the θ-2θ scan, no attempts were made at analyzing the orientational relationships for the film deposited at 300°C.

Figure 7.6: X-ray diffractogram for a HfO₂ film deposited on MgO at 500°C. The inset shows the ϕ-scan for the same film.
The SEM-studies of the surface microstructure showed that extremely smooth films were deposited at all temperatures. The poly-Si substrate in itself is rough compared to the MgO surface, but the films deposited on MgO and poly-Si had the same microstructural features. All the films had a small and very uniform grain size of approximately 15 nm. TEM analysis of films deposited on Si(100) at 500°C showed that a 2-3 nm thick layer of amorphous SiO$_2$ had formed at the film-substrate interface, Fig. 7.7. The films were crystalline throughout the thickness and consisted of randomly oriented monoclinic HfO$_2$.

The dielectric constant of the films was found to increase with temperature, from 10 at 225°C to 18 at 500°C (Fig. 7.8). Since the film thicknesses are equal, but the crystallinity of the oxide increases with growth temperature, it can be concluded that the permittivity is dependent on the crystallinity. Typical DC current-voltage (I-V) characteristics are shown in Fig. 7.9, where it can be seen that the leakage current increases with the deposition temperature, except for the 500°C film. The breakdown voltage increases strictly with decreasing deposition temperature, and reaches very high values for the low temperature films. It is also worth noting that the leakage mechanism is fairly similar for all the films.
**Figure 7.8:** Dielectric constant of HfO$_2$ as a function of growth temperature.

**Figure 7.9:** Current-voltage characteristics of HfO$_2$ films deposited on poly-Si at 225-500°C.
8 Deposition of Mixed TiO$_2$-Ta$_2$O$_5$ Films

Thin films of mixed tantalum and titanium oxides have been produced by sputtering [100, 7], sol-gel [5], but none of these have reached as high permittivity as the bulk material [6]. One of the techniques that have not previously been used for deposition of mixed Ti-Ta oxides is conventional CVD.

8.1 CVD

According to XRFS analysis, the films deposited at 500°C had compositions in the range 5-100% titanium, and at 600°C in the range 40-65% titanium. XPS depth profiles of the films show a certain titanium enrichment towards the surface which could be due to a lower surface energy for TiO$_2$. No iodine residues could be detected at the surface or after sputtering.

Both the Ti/Ta ratio and the deposition temperature had a strong influence on the crystallinity of the films. Films deposited at 500°C were amorphous for compositions up to 50% titanium, but higher titanium content resulted in crystalline TiO$_2$ (anatase). However, the anatase XRD peaks were displaced towards higher d-values (lower angle) than in the literature, indicating that the cell parameters were enlarged due to solid solution with the larger Ta atom. It should be noted that pure Ta$_2$O$_5$ grown from TaI$_5$ has been found to be crystalline at this temperature [101]. The X-ray diffractograms for pure TiO$_2$ and the solid solution (approximately 80% Ti) are shown in Fig. 8.1 a) and b) respectively. Films containing approximately 50% titanium deposited at 600°C contained a mixture of crystalline β-Ta$_2$O$_5$ and anatase, see Fig. 8.1 c). The same displacement of the anatase peaks is observed as for the 500°C films, whereas the positions of the β-Ta$_2$O$_5$ peaks remain at literature values [102].

SEM studies of the surface microstructures revealed a dependence on titanium concentration that correlates with the phase content. The amorphous films are relatively smooth with no special features, but upon crystallisation of the
films, different shapes are observed (Fig. 8.2).

![Diffractograms](image)

**Figure 8.1:** Diffractograms for a) pure TiO$_2$ grown at 500°C, b) TiO$_2$ with Ta in solid solution grown at 500°C, and mixed film, 50% Ti grown at 600°C.

![SEM micrographs](image)

**Figure 8.2:** SEM micrographs of films containing a) 80% Ti deposited at 500°C, b) pure TiO$_2$ deposited at 500°C.

It was found that the dielectric constant was connected to the phase content and the film thickness. For films deposited at 500°C, amorphous films (5-50% Ti) had dielectric constants of approximately 35, irrespective of the composition. For films of crystallised anatase with tantalum in solid solution the dielectric constant was approximately 60, again without composition dependency. For pure anatase, the values were around 70. For comparison, 600°C films containing
about 50% titanium in a mix of crystallised $\beta$-Ta$_2$O$_5$ and anatase had a dielectric constant of about 20. The increase in dielectric constant with increasing titanium concentration appears to be related directly to the phase content, which in turn is controlled by the composition. Within these phase stability regions, the layer thickness had a strong influence on the dielectric constant.

The dielectric constants calculated for these films correlate well with those of Umezawa et al. [7], who found that the dielectric constant of thin films of Ti-Ta oxide increased from 30 to 70 when the titanium concentration was increased from 10 to 90%. Gan et al. [100] studied thin films of $(\text{TiO}_2)_x-(\text{Ta}_2\text{O}_5)_{1-x}$ prepared by sputtering and found that 8% TiO$_2$ gives a maximal dielectric constant of 30 for as-deposited films. High-temperature anneal induced crystallisation of the films and enhanced the permittivity but the maximum, now 55, was still found at 8% Ti.
9 Concluding remarks

This thesis describes the basic features of iodide-based CVD- and ALD-processes for deposition of Ta₂O₅, ZrO₂ and HfO₂. These processes have been studied for the first time, and the process parameters have therefore not yet been optimised. Already at this stage, however, it is clear that the iodide precursors offer the possibility to deposit pure, crystalline films at lower temperatures than most other processes. In the CVD processes, this is done using O₂ as the only oxygen source, whereas H₂O is usually needed in chloride-processes to remove Cl in the form of HCl. It is preferable to avoid introducing hydrogen into the process since HI that is formed might etch the film, and hydrogen can be incorporated into the films which affects the electrical properties. Recently, it was shown that TiO₂ can be deposited by ALD using TiI₄ and O₂ [87]. Work is currently in progress to prove that O₂ can be used in ALD of Ta₂O₅ as well [103]. A reason for the lower contamination levels in iodide processes compared with the very popular chloride processes can be found in the formation enthalpies. The metal iodides have lower formation enthalpies, and thereby lower thermal stabilities that lead to easier removal of the ligands in chemical reactions. The difference in thermal stability also means that the energy gain on going from a metal iodide to the oxide is larger than going from the chloride to the same oxide. The energy that is released can be used for crystallisation of the oxide, which would therefore require a lower temperature when using an iodide precursor than when using a chloride [104].

The metal iodides used in this work are very similar both in their chemical reactions and thermal stabilities, but there are some differences in the process characteristics. For TaI₅ and ZrI₄, the growth rate in CVD increases up to a certain point, and then decreases with increasing temperature. In ALD using TaI₅, the growth rate decreases slightly with temperature, and for ZrI₄ there is a maximum and then decreasing growth rate with increasing temperature. HfI₄, on the other hand, gives a growth rate in CVD that increases monotonically with temperature and in ALD that is constant with temperature. It thus appears that HfI₄ is more stable and can more easily give self-limiting growth in ALD.
Although ZrO$_2$ and HfO$_2$ are predicted to be stable in contact with silicon, it was shown that an interfacial layer of SiO$_2$ had formed in the ALD experiments. A SiO$_2$ layer has most likely formed in the Ta$_2$O$_5$ samples as well, but no TEM analysis has been performed to confirm this. The SiO$_2$ can form either in the beginning of the deposition experiment, when the substrate surface has not been completely covered and is exposed to oxygen-containing species, or later in the experiment since oxygen diffuses rather easily in both ZrO$_2$ and HfO$_2$. It is also possible that the interfacial layer formed in a solid state reaction between the film and the substrate, but in that case, the ZrO$_x$ formed in the reaction must have reoxidised to ZrO$_2$. The series connection with the SiO$_2$ layer lowers the total dielectric constant and must somehow be avoided for future applications.
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Eject!
Bibliography


