In Situ Reaction Mechanism Studies on Atomic Layer Deposition

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ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in auditorium A110 of the Department of Chemistry (A. I. Virtasen Aukio 1) on November 16th, 2012, at 12 o'clock noon.

Helsinki 2012

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ISBN 978-952-10-8399-0 (paperback)
ISBN 978-952-10-8400-3 (PDF)
http://ethesis.helsinki.fi
Helsinki University Printing House
Helsinki 2012

Abstract

Due to certain characteristics unrivalled in thin film deposition technology, atomic layer deposition (ALD) has found great use in microelectronics industry and nanotechnology, in particular. In ALD, thin films are deposited through alternate self-limiting surface reactions. In this thesis, reaction mechanisms of selected ALD processes were studied in situ with a quadrupole mass spectrometer (QMS) and a quartz crystal microbalance (QCM). As a background for the experimental work, a comprehensive review on in situ studies on ALD reaction mechanisms is included. In the introduction, ALD is compared to various chemical thin film deposition techniques and discussed in the context of general inorganic chemistry. Furthermore, studying ALD reaction mechanisms is put into a wider perspective of learning inorganic chemistry.

The $(CpMe)_2Zr(OMe)Me$ – D_2O process that deposits ZrO_2, a high-k oxide, presents clean ligand exchange reactions. The $Nb(OEt)_5$ – D_2O process for another high-k oxide, Nb_2O_5, presents ligand exchange reactions with side-reactions forming Et_2O. The $NbCl_5$ – D_2O process aiming at deposition of the same material is interfered by etching of the film by the precursor. However, $NbOCl_3$ thereby formed may be used as a precursor for deposition of uniform Nb_2O_5 films through ligand exchange reactions.

For deposition of phase-change materials, the $SbCl_3$ – $(Et_3Si)_2Te$ process that deposits Sb_2Te_3, the $GeCl_2{\cdot}C_4H_8O_2$ – $(Et_3Si)_2Te$ process for GeTe and the $SbCl_3$ – $(Et_3Si)_3Sb$ process that deposits Sb, were studied. All these processes were found to constitute ligand exchange reactions.

The $(CpMe)_2Zr(OMe)Me$ – O_3 process that deposits ZrO_2 presents a diversified combustion mechanism. Also for deposition of the noble metal iridium, the combustion processes $Ir(acac)_3$ – O_2 and $Ir(acac)_3$ – O_3 – H_2 and for deposition of the conductive iridium(IV)oxide, the $Ir(acac)_3$ – O_3 process were studied.

Preface

The studies reported in this thesis were carried out in the Laboratory of Inorganic Chemistry at the Department of Chemistry of the University of Helsinki. I am extremely grateful for having had the opportunity to do this thesis as part of a world-leading ALD research group and to be widely enrolled in teaching at the Department of Chemistry at the same time. I want to express my deepest gratitude to the professors Mikko Ritala and Markku Leskelä for giving me this possibility and for all their guidance and support.

I am also grateful to Dr. Antti Rahtu for introducing me to the in situ measurements of ALD processes. Furthermore, I want to acknowledge my additional coauthors, Mr. Timo Hatanpää, Dr. Viljami Pore, Ms. Tiina Sarnet, Doc. Marianna Kemell and Mr. Kenichiro Mizohata. Also, financial support from the Academy of Finland and EU is acknowledged. In addition, the reviewers of this thesis, professor Jaan Aarik and associate professor Ola Nilsen, are gratefully acknowledged.

My warmest gratitude goes to Dr. Pirkko Tilus and Doc. Matti Näsäkkälä who originally inspired me to major in inorganic chemistry. I would also like to thank all the former and present colleagues in the Laboratory of Inorganic Chemistry for a motivating working atmosphere. Especially, Doc. Matti Näsäkkälä, Dr. Jaana Valo, Ms. Miia Mäntymäki and Mr. Mikko Kaipio are thanked the deepest for friendship and numerous stimulating discussions. So is Mr. Yoann Tomczak, who continues in situ measurements.

I also want to thank all my students over the years for receptiveness. Seeing you learn chemistry is a spring of intellectual resources for me. Special thanks in this respect and for friendship go to those three who have wanted extensive private mentoring from me.

Finally, thanks to my parents and friends for all their support.

Helsinki, October 24th, 2012

Kjell Knapas

List of Publications

This work is based on the following publications which are referred to by their Roman numerals.

I. Knapas, K. and Ritala, M. *Crit. Rev. Solid State Mater. Sci.* accepted

II. Knapas, K. and Ritala, M. *Chem. Mater. 20* (2008) 5698

III. Knapas, K., Rahtu, A. and Ritala, M. *Chem. Vap. Deposition 15* (2009) 269

IV. Knapas, K., Rahtu, A. and Ritala, M. *Langmuir 26* (2010) 848

V. Knapas, K., Hatanpää, T., Ritala, M. and Leskelä, M. *Chem. Mater. 22* (2010) 1386

VI. Pore, V., Knapas, K., Hatanpää, T., Sarnet, T., Kemell, M., Ritala, M., Leskelä, M. and Mizohata, K. *Chem. Mater. 23* (2011) 247

VII. Knapas, K. and Ritala, M. *Chem. Mater. 23* (2011) 2766

The publications are reprinted with the permission from the copyright holders. For publications **I-V** and **VII**, the author has planned the research with the help of the coauthors, performed the research, written the first versions of the papers and completed them with the help of the coauthors. The author also is the corresponding author of those papers. In publication **VI**, the author has performed the reaction mechanism studies and written that part.

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1. Introduction

Atomic layer deposition (ALD), an advanced chemical vapor deposition (CVD) technique, has found many applications in microelectronics industry and nanotechnology because of some important features unrivalled in thin film deposition methodology. In ALD, deposition of a film is realized with alternate saturative surface reactions. With correct precursors and process parameters, uniform and conformal films with the desired composition and thickness are thus directly obtained. This thesis is all about reaction mechanisms in ALD, which are most competently clarified with in situ studies. In this thesis, in situ studies on selected ALD processes were performed with a quadrupole mass spectrometer (QMS) and a quartz crystal microbalance (QCM). The QMS measures the molecules in the gas phase of the reactor and the QCM measures the mass of the film. In addition, a comprehensive review on in situ studies on ALD reaction mechanisms is included as a background for the current work.

In situ studies on reaction mechanisms in ALD have been published mostly during the past fifteen years and are reviewed in publication **I**. There, also the applied experimental methods, including QMS and QCM, are presented in detail. All the results of publications **II-VII** are also included in the review. These are however also summarized in Chapter 3 film material wise. Main emphasis is given to the special challenges encountered with the different processes in these studies. For wider discussion on these and related ALD chemistries, see appropriate sections of the review.[I]

1.1. Chemical reactions as a basis for chemical thin film deposition technologies

Let us consider reactions **1** and **2** where solid ionic compounds are formed. In reaction **1**, lead(II) iodide precipitates when aqueous solutions of lead(II) nitrate and potassium iodide are combined. In reaction **2**, titanium(IV) oxide aerosol ("white smoke") is formed when vapors of titanium(IV) chloride and water are led together. The reactions are quite similar; the only differences between precipitation reactions and aerosol forming gas phase reactions are that the solvent has a different state of aggregation (liquid vs. gas) and the solute particles are different (ions vs. molecules). Sometimes even the same compounds work in both reaction types, e.g. reactions **3-4**.

$$Pb(NO_3)_2(aq) + 2\ KI(aq) \rightarrow PbI_2(s) + 2\ KNO_3(aq) \qquad (1)$$

$$TiCl_4(g) + 2\ H_2O(g) \rightarrow TiO_2(s) + 4\ HCl(g) \qquad (2)$$

$$CdCl_2(aq) + H_2S(aq) \rightarrow CdS(s) + 2\ HCl(aq) \qquad (3)$$

$$CdCl_2(g) + H_2S(g) \rightarrow CdS(s) + 2\ HCl(g) \qquad (4)$$

When reactant solutions or vapors are simply mixed, the products are usually powders and the processes are called precipitation and aerosol synthesis. However, under proper reaction conditions, the same reactions can deposit thin films on solid substrates. Such processes are called chemical bath deposition (CBD, aqueous process) and chemical vapor deposition (CVD, gas phase process). To achieve the best possible control over the thin film growth, the reactions can furthermore be divided into alternate half-reactions by exposing the substrates to one reactant (precursor) at a time. Ideally the half-reactions are self-limiting (saturative) surface reactions, e.g. reactions **5-6** for reaction **2**. These sequential processes are called successive ionic adsorption and reaction (SILAR, aqueous process) and atomic layer deposition (ALD, gas phase process). The relations between different technologies are further illustrated in Table **1**.

$$2\ \text{–OH(s)} + \text{TiCl}_4\text{(g)} \rightarrow \text{–O}_2\text{TiCl}_2\text{(s)} + 2\ \text{HCl(g)} \tag{5}$$

$$\text{–O}_2\text{TiCl}_2\text{(s)} + 2\ \text{H}_2\text{O(g)} \rightarrow \text{–O}_2\text{Ti(OH)}_2\text{(s)} + 2\ \text{HCl(g)} \tag{6}$$

Table 1. Solution and gas phase processes for formation of solid ionic compounds.

Supply of reactants	Simultaneous		Alternate
Product	Powder	Thin film	
Aqueous phase	Precipitation	Chemical Bath Deposition (CBD)	Successive Ionic Layer Adsorption and Reaction (SILAR)
Gas phase	Aerosol synthesis	Chemical Vapor Deposition (CVD)	Atomic Layer Deposition (ALD)

As a conclusion, normal reactions of inorganic chemistry form the basis of also ALD. Counterparts to e.g. etching reactions caused by ALD precursors can also be found in general inorganic chemistry. Compare e.g. the etching reaction discussed in section 3.2, reaction **7**, to reaction **8** where mercury(II) iodide, first precipitated by potassium iodide, dissolves in excess reagent.

$Nb_2O_5(s) + NbCl_5(g) \rightarrow 5\ NbOCl_3(g)$ (7)

$HgI_2(s) + 2\ KI(aq) \rightarrow K_2[HgI_4](aq)$ (8)

1.2. SILAR and ALD process steps in light of general inorganic chemistry

SILAR and ALD cycles consist of four steps: exposing the substrates to the first precursor, purging the substrates from excess precursor and byproducts, exposing the substrates to the second precursor, and purging again. Each precursor goes self-limiting half-reactions with the surface on its turn. The sum of the half-reactions is the process reaction, the overall chemical reaction that forms the basis of the process.

Division of a chemical reaction into separately occurring half-reactions is not unique to SILAR and ALD: the same is done in ion exchange and in galvanic cells. However, in a galvanic cell the redox half-reactions take place simultaneously in separate vessels, but in SILAR and ALD the half-reactions take place sequentially on the same substrate. Thus, the half-reactions are continuous and separated in space in a galvanic cell but step-wise and separated in time in SILAR and ALD.

In general inorganic chemistry, a self-limiting surface reaction is found in ion exchange. A cation exchange resin can e.g. convert a sodium chloride solution to a hydrogen chloride solution. At the same time the resin is converted from hydrogen ion form to sodium ion form. If this process is carried out e.g. for quantitative analysis of sodium through subsequent acid-base titration, the resin has to be purged thoroughly with deionized water after running the sodium chloride solution through it. Otherwise only a small fraction of the original sodium is found because most of the hydrogen ions released from the resin are still in the column that holds the resin, in the solution filling and encapsulating the resin particles. Similar purges are also extremely important in SILAR and ALD between the exposures of the substrate to the different precursors to avoid uncontrolled growth and film defects caused by mixing of the precursors.

1.3. Studying ALD reaction mechanisms in the context of learning inorganic chemistry

The task of clarifying mechanisms of ALD processes resembles significantly the work done by the chemists of previous generations in explaining the behaviors of different elements together with reagents in aqueous solutions. This work, essential for the utilization of the elements in the form of relatively pure compounds, eventually enabled the expansion of the chemical industry into one of the most influential branches man kind has seen.

The exploration of chemistry generally aims towards balanced reaction equations. In order to achieve them, one first has to know all the reactants and products. Let us think about the effect of ammonia on metal ions in solutions. Some metals will not react at all but others will form precipitates. The constitution of these precipitates is not hard to guess, provided that the alkaline nature of ammonia is already known. Then a great number of qualitative and quantitative trials and more or less accurate balanced equations for the precipitation reactions are obtained. However, a few of the obtained precipitates will dissolve in excess ammonia. Here, the confusion of what happened was greater. Relatively early though, first by Leopold Gmelin in 1822,[1] crystals could be obtained from such solutions, and it became evident that even after recrystallization these substances contained both the metal, ammonia and the anion of the acid originally used to dissolve the metal. So the substances were compounds of these constituents and after quantitative analysis, balanced equations were once again obtained. How exciting times the early chemists must have had! Of course, a satisfying explanation as to the constitution of the ammine complexes came much later, in 1893 by Alfred Werner with the coordination bond.[1]

From reaction equations, that provide only depictions of happenings in nature, science advanced to answer questions as what is the difference between different metals that dictates whether a precipitate with ammonia does not form at all, forms and persists, or forms and redissolves. Then it is also examined how the attack of ammonia molecules on hydroxide precipitates proceeds.

The work described above goes still on with other reagents. Actually from the aqueous ammonia solution reactions one does not have to move on further than to liquid ammonia in order to find reactions that are currently being investigated.[2] The work also goes on in the special conditions provided by methods of modern materials science. Chemical thin film deposition techniques provide unique circumstances for chemical reactions to take place and therefore require new chemistry research. Understanding the reactions in deposition processes is essential in utilizing the techniques as efficiently and broadly as possible.

Meanwhile, the reactions of elements in aqueous solutions are used all over the world in teaching the basic concepts of inorganic chemistry. These reactions have been selected as prototypes of all the reactions inorganic chemistry involves. With a good picture of these, very complicated reactions in other media can be understood too, since the basic phenomena are the same. This is equally true for the reactions in biological processes as for modern materials science. Without more simple examples preceding, complicated reactions in these branches of science could be impossible to conceive. After all, the understanding of the aqueous chemistry of iron did not start with the role of iron in oxygen transport in the human body, but with iron minerals dissolving in acid and iron hydroxide precipitates forming with alkali from these solutions.

In teaching, especially the qualitative analysis chart exercises have proved useful in the beginning, since they provide a way of revising knowledge of chemical reactions by doing, seeing and thinking without cramming at all. On the other hand, by cramming without any observations of actual reactions, this area of science could be quite difficult to master. Indeed, the analysis chart teaches in a way that challenges even the best methods of modern didactics. The same is true for complexometric titrations that in the next stage provide first understanding of coordination chemistry. Classical analysis in general provides a possibility for the student to travel the same way and make the same observations and conclusions that were originally made by researchers. This path is a fairly safe and direct one.

With respect of the traditional analysis chart based on precipitation of chlorides, sulfides and carbonates, presented originally by Carl Remigius Fresenius in 1841 in the form depicted in Table **2**, also other interesting observations can be made. With many alternative charts presented in literature, the original one, that goes back almost 200 years, has survived. It also differs from all its challengers in a sense that it is almost perfectly generic, i.e. an ion precipitating in a certain group will generally precipitate in all the groups to follow as well. From this feature not evident from the chart itself it follows that when one proceeds with the groups, the chemistry of the ions becomes in a certain sense simpler. Therefore, the ions of the last group (K^+, Na^+) usually do not precipitate, do not hydrolyze, do not form complexes and do not oxidize or reduce. Generally they do not react at all. They are just as they are, happy and silent. On the other hand, the ions of the first group (Pb^{2+}, Ag^+, Hg_2^{2+}, Tl^+) do all the above even more frequently than one usually would hope.

I hope that this has given a clear picture of the role of reaction knowledge in chemistry, of why reactions are studied in teaching and research, and how knowledge of one reaction can help to predict the outcome of another. I have also tried to show that there is a continuum from the very first lab exercises during the university freshman autumn to this thesis and beyond. Studying ALD reaction mechanisms is not that different from studying the behaviors of the elements in aqueous solutions or e.g. the search for indicators and masking agents for complexometric titrations. Although we do not yet have an ALD reaction chart, and perhaps never will, ALD processes are grouped in the conclusions chapter of the review[I] according to their dominating mechanisms.

Table 2. The analysis chart presented by Carl Remigius Fresenius in 1841.[3]

Group	Separation	Ions
6	A precipitate with HCl	Pb^{2+}, Ag^{+}, Hg_2^{2+}
	A precipitate with both H_2S and $(NH_4)_2S$	The former and Hg^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}
5	A precipitate with H_2S soluble in $(NH_4)_2S$	Sb^{3+}, Sn^{2+}, Sn^{4+}, As^{3+}, As^{5+}, Pt^{4+}, Au^{3+}
4	No precipitate with H_2S but a sulfide precipitate with $(NH_4)_2S$	Fe^{2+}, Fe^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}
3	No sulfide precipitate but a hydroxide precipitate with $(NH_4)_2S$	Al^{3+}, Cr^{3+}
2	No precipitate with neither H_2S nor $(NH_4)_2S$ but a precipitate with K_2CO_3	Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}
1	No precipitate with neither H_2S, $(NH_4)_2S$ nor K_2CO_3	Na^{+}, K^{+}, NH_4^{+}

2. Experimental

All the studies **II-VII** were performed with the ALD-QMS-QCM instrument setup located at the chemistry department of the University of Helsinki and shown in Figures **1-2** and depicted schematically in Figure 2 of publication **I**. The setup has been built in the late 1990s.[4] The heart of the setup is a modified hot-wall flow-type F-120 SAT ALD reactor manufactured by ASM Microchemistry Ltd. Pulsing of precursors evaporated inside the reactor is accomplished with inert gas valving. Typically 3500 cm^2 of soda lime glass surface is applied as substrates for the film deposition. Downstream of the substrates are located a Maxtek TM 400 QCM with a sampling rate of 20 Hz and a 50-200 μm sampling orifice for the QMS. The QMS is a Hiden HAL/3F 501 RC. Electron-impact ionization with an ionization energy of 70 eV and a Faraday cup detector are applied. The QMS chamber is differentially pumped with a turbomolecular pump backed by a mechanical pump. With the orifice in between, the pressure reduction from 3 mbar in the ALD reaction chamber to 10^{-5} mbar range in the QMS chamber is thereby accomplished. Both the QCM and the sampling orifice of the QMS are at the same temperature as the substrates.

QMS and QCM in general are discussed in publication **I**. In the following, the operational manners normally used in papers **II-VII** are enlightened.

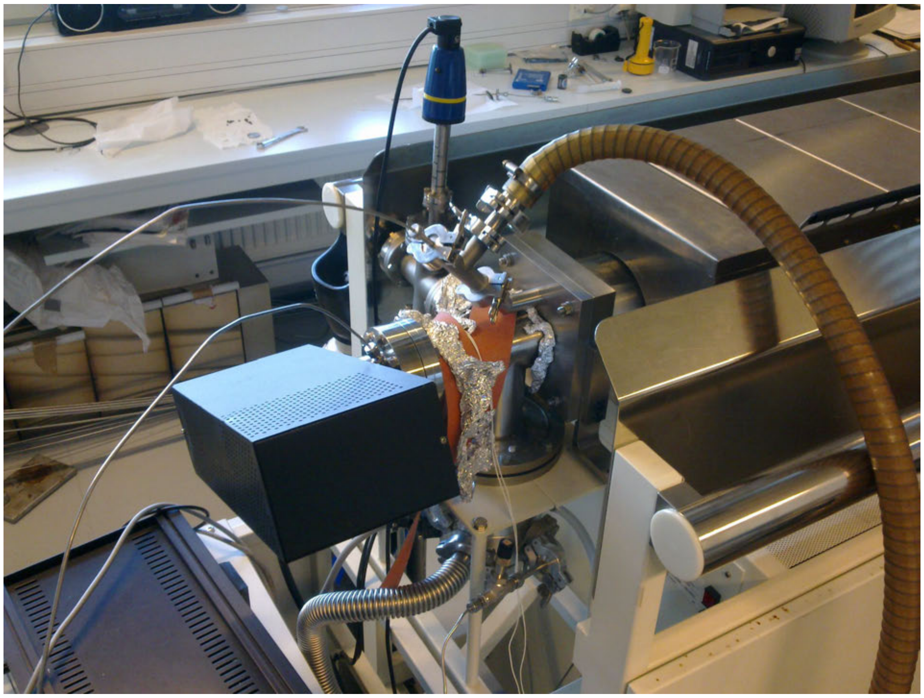

Figure 1. The ALD-QMS-QCM instrument setup used in this study. The black box at the end of the reactor is the electronic unit of the mass spectrometer.

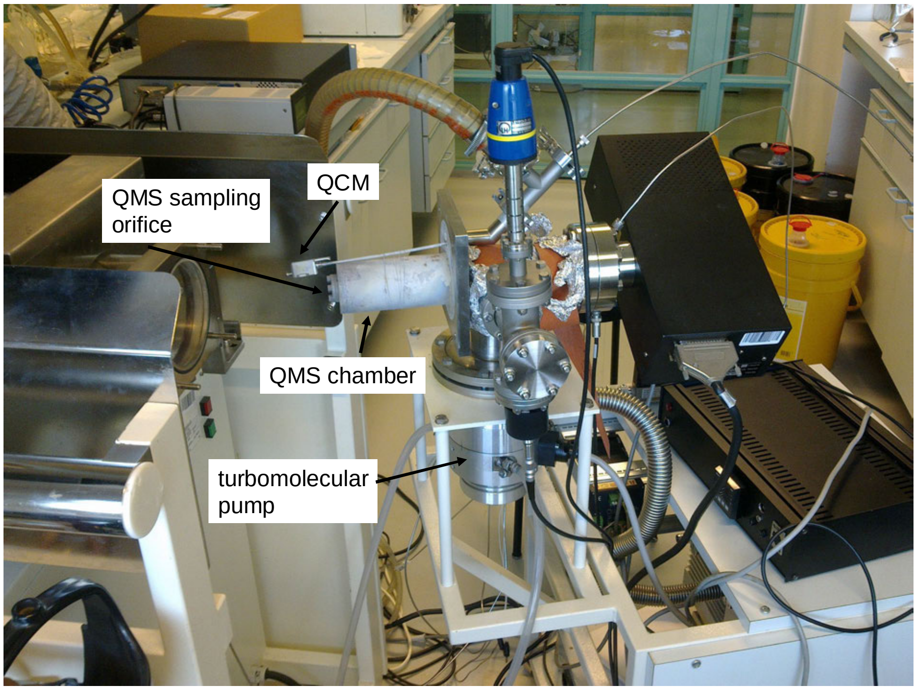

Figure 2. The parts downstream of the substrates pulled out of the reactor.

2.1. Quadrupole mass spectrometry

With the QMS, the volatile byproducts of the ALD processes were investigated. In most such measurements, the non-metal precursor was first pulsed five times (reference pulses), then the precursors were pulsed ten times alternately (i.e. ten cycles of the ALD process were run), and finally the metal precursor was pulsed five times (reference pulses). Over this pulsing sequence, usually only one *m/z* value was followed at a time with the QMS because of its limited measuring rate. The data obtained consists of peaks during the pulses. In a general case, peaks appear during both precursor pulses in the ALD process. In an ideal case, there should not however appear any peaks when the same precursor is pulsed repeatedly. In most practical cases, however, background signals were seen during these reference pulses.

The byproducts were identified and then quantified. The quantification of the data began by determining the areas of all the peaks in the pattern. Then the areas of the three last non-metal precursor reference pulse peaks were averaged. That average was subtracted from the areas of the non-metal precursor pulse peaks during the ALD process. Similarly, the areas of the three last metal precursor reference pulse peaks were averaged and the average subtracted from the areas of the metal precursor pulse peaks during the ALD process. The so obtained background corrected byproduct signals during the pulses of the ALD process were then summed for each ALD cycle. Then the signal during the metal precursor pulse was divided with this sum still for each ALD cycle. Finally, these ratios were averaged for the eight last ALD cycles. This single, finally obtained value was taken as the quantitative result for that measurement. It depicts which fraction of that byproduct was released during the metal precursor pulse as compared to a complete ALD cycle and gives thus direct information of the reaction mechanism. For thorough discussion on the background correction, see section 2.1 of publication **I**.

Sometimes a particular measurement was repeated during the same measurement session. In all cases, however, the reactor was reloaded with precursors many times and all the measurements repeated, because only such measurements can be considered genuine parallel measurements. The results of all the parallel measurements were averaged and also their numbers (N) and error margins (standard deviations) were reported in the papers.

2.2. Quartz crystal microbalance

The change in the piezoelectric resonance frequency of the quartz crystal is proportional to the mass change. For QCM measurements, usually ten cycles of the ALD process were run. The resonance frequency changes during each metal precursor pulse and during each ALD cycle were determined. The frequency change during each metal precursor pulse was then divided with the frequency change during the corresponding complete ALD cycle. This ratio is the same as the ratio of the corresponding mass changes. Finally, these ratios were averaged for the eight last ALD cycles and this single value was taken as the quantitative result for that measurement. Then again the measurement was repeated many times after reloading the reactor. The results were averaged and reported as in the case of QMS data.

3. Results and Discussion

3.1. ZrO_2

Two processes that deposit the high-k oxide ZrO_2 were studied.[II] In these, the heteroleptic precursor $(CpMe)_2Zr(OMe)Me$ was used together with water[5] and ozone[6] at 350 °C. In the half-reactions of the water process, there are three unknowns when ligand exchange reactions are assumed: the relative amounts of the three different ligands released in protonated (deuterated with D_2O) form during the metal precursor pulse as compared to a complete ALD cycle. These unknowns can be determined from the QMS data as easily as for processes that use homoleptic precursors. On the other hand, from the QCM data only one equation can be obtained which uniquely defines the mechanism only with homoleptic precursors. With the process under discussion, QCM was used for cross-checking the mechanism derived from the QMS data, reactions **9-10**. The match was found to be reasonable.

$$2.3\ \text{–OD(s)} + \text{(CpMe)}_2\text{Zr(OMe)Me(g)} \rightarrow \text{–O}_{2.3}\text{Zr(CpMe)}_{0.9}\text{(OMe)}_{0.6}\text{Me}_{0.2}\text{(s)}$$

$$+\ 0.8\ \text{MeD(g)} + 0.4\ \text{MeOD(g)} + 1.1\ \text{DCpMe(g)} \qquad (9)$$

$$\text{–O}_{2.3}\text{Zr(CpMe)}_{0.9}\text{(OMe)}_{0.6}\text{Me}_{0.2}\text{(s)} + 2\ \text{D}_2\text{O(g)} \rightarrow \text{–O}_2\text{Zr(OD)}_{2.3}\text{(s)}$$

$$+\ 0.2\ \text{MeD(g)} + 0.6\ \text{MeOD(g)} + 0.9\ \text{DCpMe(g)} \qquad (10)$$

Clarifying the mechanism of the corresponding ozone process turned out to be challenging. Prior to this investigation only very few detailed in situ reaction mechanism studies on ozone processes had been published.[7] During the study, it turned out that the byproducts and especially the times of their releases were not exactly as expected. Also, the half-reactions were not uniquely defined with the usual measurements. The most important byproducts were, as expected, CO_2 and H_2O. However, most interestingly about 20% of both of them were released during the $(CpMe)_2Zr(OMe)Me$ as compared to a complete ALD cycle. In addition, some MeH and HCpMe were released during the $(CpMe)_2Zr(OMe)Me$ pulse. Some ligands were obviously combusted already during the $(CpMe)_2Zr(OMe)Me$ pulse, but on basis of the mentioned data, it is impossible to say which ones. The mentioned data are however all that are obtained when measuring just the ALD reactions themselves as has traditionally been done in ALD-QMS studies.

In order to get a more precise picture of the process under discussion, special surface probing experiments were performed. The idea with such experiments is to measure the relative amounts of certain surface species with the help of specific probe molecules that react with these surface species in unambiguous manners. The products of these reactions are quantified with QMS. Ligands remaining on the surface after the $(CpMe)_2Zr(OMe)Me$ pulse were probed with D_2O, and hydroxyl groups remaining on the surface after the O_3 pulse with $ZrCl_4$. In addition, the amounts of MeH and HCpMe released during the $(CpMe)_2Zr(OMe)Me$ pulse in the O_3 process were quantified with the help of the D_2O pulse. To my knowledge, this is the first time this kind of surface intermediate probing has been used to study ALD processes.

Altogether eight QMS results have been mentioned in the previous paragraph. With six unknowns in the half-reactions, these together with the QCM result give three equations more than necessary for solving the unknowns. When determining the unknowns, all experimental results were taken into account and the errors in them leveled. As a result, half-reactions **11-12** were obtained. Because the numbers in the equations are given with an accuracy of one decimal, the equations as given are not exactly balanced. In the $(CpMe)_2Zr(OMe)Me$ half-reaction, three elementary processes take place: 1) reactions with surface hydroxyl groups release some ligands in protonated form, 2) surface active oxygen O^* eliminates some ligands as CO_2 and H_2O, and 3) the H_2O thereby formed releases some more ligands in protonated form. In the O_3 half-reaction, the remaining ligands are eliminated as CO_2 and H_2O and the surface hydroxyl groups and active oxygen restored. Active oxygen is usually oxygen at oxidation state zero, in this case most likely neutral oxygen atoms (oxygen radicals) bonded to surface zirconium ions. The study under discussion was the first one to report chemisorbed active oxygen playing a role in an oxide ALD process.

$$0.3\ –OH(s) + 5.1\ –O^*(s) + (CpMe)_2Zr(OMe)Me(g) \rightarrow –Zr(CpMe)_{0.8}(OMe)_{0.5}Me_{0.4}O_{1.3}(s)$$
$$+ 0.6\ MeH(g) + 0.9\ HCpMe(g) + 1.9\ CO_2(g) + 0.9\ H_2O(g) \qquad (11)$$

$$–Zr(CpMe)_{0.8}(OMe)_{0.5}Me_{0.4}O_{1.3}(s) + 21.7\ O$$
$$\rightarrow –ZrO_2O^*_{5.1}(OH)_{0.3}(s) + 5.9\ CO_2(g) + 4.7\ H_2O(g) \qquad (12)$$

3.2. Nb_2O_5

Two processes explored earlier for ALD of the high-k oxide Nb_2O_5 were studied. In these processes, $NbCl_5$[III] and $Nb(OEt)_5$[IV] were used together with water mainly at 250 °C. The first process deposits highly non-uniform and irreproducible films.[8] These problems had earlier been suspected to be due to an etching effect of $NbCl_5$ on Nb_2O_5 which had also been demonstrated with etching experiments. In this study, the etching and deposition mechanisms were studied in situ.

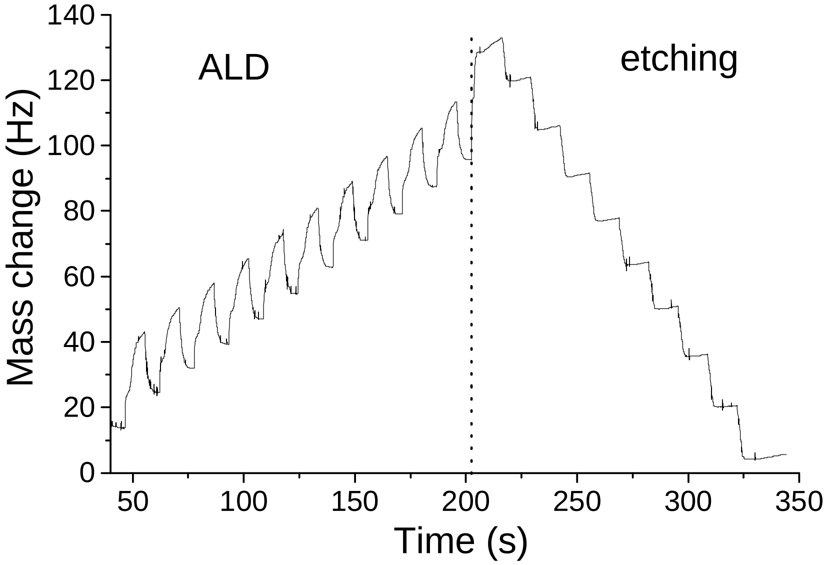

Figure 3. Etching of Nb_2O_5 measured with QCM. Ten cycles of the $Nb(OEt)_5$ – D_2O process were run first to deposit Nb_2O_5 and then ten $NbCl_5$ pulses were given to etch it.

The etching was clearly visible with QCM, Figure **3**. With QMS, $NbOCl_3$ was observed as the etching product. Therefore, the etching was concluded to take place according to reaction **13**. To my knowledge, this is the first time when in ALD interfering etching reactions have been thoroughly clarified with in situ experiments although a similar etching effect of $TaCl_5$ on Ta_2O_5 has been earlier witnessed with QCM.[9] In addition, conversion of ZnO to Al_2O_3 by $AlMe_3$ with release of $ZnMe_2$ has been verified.[10]

$$Nb_2O_5(s) + NbCl_5(g) \rightarrow 5\ NbOCl_3(g) \tag{13}$$

In spite of the etching effect, the $NbCl_5$ – D_2O process deposited film according to QCM that was located after the glass substrates. Also, DCl was evidenced as a byproduct with QMS. The deposition was concluded in reality to occur from the in situ generated $NbOCl_3$ according to process reaction **14**. Then, QCM and QMS agreed reasonably well on half-reactions **15-16**.

$$2\ NbOCl_3(g) + 3\ D_2O(g) \rightarrow Nb_2O_5(s) + 6\ DCl(g) \tag{14}$$

$$0.5\ –OD(s) + 2\ NbOCl_3(g) \rightarrow –Nb_2O_{2.5}Cl_{5.5}(s) + 0.5\ DCl(g) \tag{15}$$

$$–Nb_2O_{2.5}Cl_{5.5}(s) + 3\ D_2O(g) \rightarrow –Nb_2O_5(OD)_{0.5}(s) + 5.5\ DCl(g) \tag{16}$$

The specialty of the $Nb(OEt)_5$ – D_2O process[11] was that it did not constitute pure ligand exchange reactions. In addition to the expected EtOD, Et_2O was formed as a byproduct. Though the reaction that forms Et_2O in the ALD process resembles the decomposition reaction **17**, it is a different reaction that occurs below the onset temperature of the true precursor decomposition that also partially proceeds through reaction **17**. The difference between an ALD byproduct and a decomposition product was clearly seen in the Et_2O

signals at different temperatures: at low temperatures, the Et_2O signal during the ALD process saturates with the $Nb(OEt)_5$ pulse length and is greater than when $Nb(OEt)_5$ is pulsed several times successively. On the other hand at 400 °C, where precursor decomposition takes place, the Et_2O signal is independent of with which precursor the surface was saturated before the $Nb(OEt)_5$ pulse, and increases linearly with the pulse length. The reaction that produces Et_2O as an ALD byproduct is obviously catalyzed by the Nb_2O_5 surface and self-terminating whereas the true precursor decomposition reaction is unlimited.

$$2\ Nb(OEt)_5(g) \rightarrow Nb_2O_5(s) + 5\ Et_2O(g) \tag{17}$$

Because Et_2O is formed only during the $Nb(OEt)_5$ pulse, it upsets the match between the QCM and QMS results if just clean ligand exchange reactions are assumed. On the other hand, from these two results together also the amount of Et_2O can be deduced, if it is assumed to fully explain the difference. In this way, half-reactions **18-19** were obtained for the process.

$$0.4\ {-OD}(s) + Nb(OEt)_5(g) \rightarrow (-O)_{0.9}Nb(OEt)_{3.7}(s) + 0.4\ Et_2O(g) + 0.4\ EtOD(g) \tag{18}$$

$$(-O)_{0.9}Nb(OEt)_{3.7}(s) + 2.1\ D_2O(g) \rightarrow (-O)_{2.5}Nb(OD)_{0.4}(s) + 3.7\ EtOD(g) \tag{19}$$

3.3. Sb_2Te_3 and GeTe

The recently developed processes[12] that aim at deposition of the phase change memory material GST (germanium antimony telluride, $Ge_2Sb_2Te_5$) were studied.[V] These are the $SbCl_3$ – $(Et_3Si)_2Te$ process at 60 °C that deposits Sb_2Te_3 and the $GeCl_2{\cdot}C_4H_8O_2$ – $(Et_3Si)_2Te$ at 90 °C that deposits GeTe. These were concluded to be clean ligand exchange reaction processes with Et_3SiCl as the expected byproduct. However, this was not trivial to recognize, because the molecular peak of Et_3SiCl and also many of its expected fragments were weak. The strongest peak found was $HEtSiCl^+$ although Et_2SiCl^+ in reality apparently was not that much weaker. The inclusion of one silicon atom and one chlorine atom in $HEtSiCl^+$ was especially proven with the help of the isotope distributions of these elements. With the ligand exchange reaction byproduct recognized and another byproduct in the latter process being the trivial neutral adduct ligand $C_4H_8O_2$, that was released fully during the $GeCl_2{\cdot}C_4H_8O_2$ pulse, the half-reactions of the processes could be deduced. As results, reactions **20-21** and **22-23** were obtained with QMS and QCM agreeing perfectly.

$$4.6\ \text{–Te(SiEt}_3\text{)(s)} + 2\ \text{SbCl}_3\text{(g)} \rightarrow \text{–Te}_{4.6}\text{Sb}_2\text{Cl}_{1.4}\text{(s)} + 4.6\ \text{Et}_3\text{SiCl(g)} \quad (20)$$

$$\text{–Te}_{4.6}\text{Sb}_2\text{Cl}_{1.4}\text{(s)} + 3\ \text{(Et}_3\text{Si)}_2\text{Te(g)} \rightarrow \text{–Te}_3\text{Sb}_2\text{[Te(SiEt}_3\text{)]}_{4.6}\text{(s)} + 1.4\ \text{Et}_3\text{SiCl(g)} \quad (21)$$

$$0.7\ \text{–Te(SiEt}_3\text{)(s)} + \text{GeCl}_2{\cdot}\text{C}_4\text{H}_8\text{O}_2\text{(g)}$$
$$\rightarrow \text{–Te}_{0.7}\text{GeCl}_{1.3}\text{(s)} + 0.7\ \text{Et}_3\text{SiCl(g)} + \text{C}_4\text{H}_8\text{O}_2\text{(g)} \quad (22)$$

$$\text{–Te}_{0.7}\text{GeCl}_{1.3}\text{(s)} + \text{(Et}_3\text{Si)}_2\text{Te(g)} \rightarrow \text{–TeGe[Te(SiEt}_3\text{)]}_{0.7}\text{(s)} + 1.3\ \text{Et}_3\text{SiCl(g)} \quad (23)$$

3.4. Sb

The $SbCl_3$ – $(Et_3Si)_3Sb$ process that deposits Sb, among others a constituent of many phase-change materials, was studied at 90 °C.[VI] The process which was also first presented in the same paper, differs from all ALD processes previously known in that an elemental film is deposited so that this element is included in both precursors. In other words, the process involves comproportionation of the element. On basis of in situ results, the process was concluded to constitute clean ligand exchange reactions, similar to the processes discussed in the previous section. The process was concluded to consist, in average, of half-reactions **24-25**. There was however a certain trend in the data: the coefficient of $–SiEt_3(s)$ always diminished during a measurement session. This was suggested to be caused by a phase change in the growing film.

$$2.1\ –SiEt_3(s) + SbCl_3(g) \rightarrow –SbCl_{0.9}(s) + 2.1\ Et_3SiCl(g) \qquad (24)$$

$$–SbCl_{0.9}(s) + (Et_3Si)_3Sb(g) \rightarrow 2\ Sb(s) + 2.1\ –SiEt_3(s) + 0.9\ Et_3SiCl(g) \qquad (25)$$

3.5. Ir and IrO_2

Three processes that use $Ir(acac)_3$ as a precursor were studied.[VII] When used together with O_2, the noble metal Ir is deposited above 225 °C.[13] Below this temperature, nothing is deposited with O_2, but with O_3 the conductive oxide IrO_2 grows.[14] Furthermore, by giving an additional H_2 pulse after each O_3 pulse, Ir deposition is achieved at these lower temperatures.[15] The temperatures used in this study were 300 °C and 195 °C. In all the three processes, the only byproducts detected were CO_2 and H_2O. A lot of special effort was given to determine whether Hacac could have formed but gone undetected. Finally, this was concluded to be very unlikely but totally it could not be ruled out. If formed, Hacac would most likely be a protonated ligand, i.e. the H would have come from an oxygen atom, i.e. from a surface hydroxyl group. Very recently it was proposed that MeH released during the $MeCpPtMe_3$ pulse in the $MeCpPtMe_3$ – O_2 process could also be a hydrogenated ligand, i.e. the H would have come from a platinum atom and originated from a dehydrogenation reaction of another ligand catalyzed by the platinum surface.[16]

For the $Ir(acac)_3$ – O_2 process, QMS and QCM agreed perfectly on half-reactions **26-27**. Therein, the Ir surface that reacts with $Ir(acac)_3$ is covered with 80% of the saturation coverage of dissociatively chemisorbed O_2, that is known to be one monolayer, since the growth rate of the process is about 1/5.3 monolayer/cycle.

$$4.3\ –O(s) + Ir(acac)_3(g) \rightarrow –IrC_{12.9}H_{9.0}(s) + 2.1\ CO_2(g) + 6.0\ H_2O(g) \qquad (26)$$

$$–IrC_{12.9}H_{9.0}(s) + 17.25\ O_2(g) \rightarrow –IrO_{4.3}(s) + 12.9\ CO_2(g) + 4.5\ H_2O(g) \qquad (27)$$

In the $Ir(acac)_3$ – O_3 process, both the byproducts were released only during the O_3 pulse. Also QCM pointed to stoichiometric adsorption of $Ir(acac)_3$ and its complete combustion during the O_3 pulse. In the $Ir(acac)_3$ – O_3 – H_2 process, CO_2 was released only during the O_3 pulse and H_2O during both the O_3 and H_2 pulses. Also here, the adsorption of $Ir(acac)_3$ was thus stoichiometric, which conclusion QCM supported, and complete combustion occurred during the O_3 pulse. Furthermore, the O_3 pulse left on the surface oxygen, which was removed during the H_2 pulse. The amount of oxygen was deduced from the QCM data and concluded to be 20 oxygen atoms per each iridium atom deposited during the preceding $Ir(acac)_3$ pulse. However, because the growth rate of the process is only 1/11 ML/cycle, this result corresponds to a little less than one monolayer of IrO_2 on the surface. Thus, surface iridium atoms deposited before the current cycle were reoxidized during the O_3 pulse. This means that the process exhibits several times repeated oxidation and reduction of the same iridium atoms. As a conclusion, the two processes consisted of reactions **27-28** and **29-31**, respectively.

$Ir(acac)_3(g) \rightarrow Ir(acac)_3(ads)$ (27)

$Ir(acac)_3(ads) + 36.5\ O(g) \rightarrow –IrO_2(s) + 15\ CO_2(g) + 10.5\ H_2O(g)$ (28)

$Ir(acac)_3(g) \rightarrow Ir(acac)_3(ads)$ (29)

$Ir(acac)_3(ads) + 9\ –Ir(s) + 54.5\ O(g) \rightarrow 10\ –IrO_2(s) + 15\ CO_2(g) + 10.5\ H_2O(g)$ (30)

$10\ –IrO_2(s) + 20\ H_2(g) \rightarrow 10\ –Ir(s) + 20\ H_2O(g)$ (31)

4. Conclusions

In this thesis, reaction mechanisms of ten ALD processes were clarified with in situ QMS and QCM studies in a flow-type ALD reactor. The processes are summarized in Table **3**. As can be seen, substantially different kinds of metal precursors and indeed totally different other precursors have been used. Out of the latter, $(Et_3Si)_2Te$ and $(Et_3Si)_3Sb$ represent an entirely new ALD precursor family recently developed in our group. The materials aimed have been high-k oxides (ZrO_2, Nb_2O_5), phase-change materials (GST: Sb_2Te_3, GeTe and Sb), noble metals (Ir) and conductive oxides (IrO_2). The main reaction pathways in these processes, as in ALD processes in general, are ligand exchange and combustion mechanisms. The ligand exchange processes have been extensively studied in literature. Special cases (the $(CpMe)_2Zr(OMe)Me$ – D_2O, $NbCl_5$ – D_2O and $Nb(OEt)_5$ – D_2O processes) and recently introduced novel processes (the $SbCl_3$ – $(Et_3Si)_2Te$, $GeCl_2{\cdot}C_4H_8O_2$ – $(Et_3Si)_2Te$ and $SbCl_3$ – $(Et_3Si)_3Sb$) have been studied here. Research on combustion mechanisms, on the other hand, has emerged only in recent years. The processes studied here were found to differ significantly from each other, the $(CpMe)_2Zr(OMe)Me$ – O_3 process exhibiting chemisorbed active oxygen and the most diversified mechanism.

Table 3. Summary of processes studied in this thesis.

Metal precursor	Other precursor	Film material	Reaction mechanism
$(CpMe)_2Zr(OMe)Me$	D_2O	ZrO_2	Ligand exchange
$(CpMe)_2Zr(OMe)Me$	O_3	ZrO_2	Combustion with side-reactions
$NbCl_5$	D_2O	Nb_2O_5	Etching and ligand exchange
$Nb(OEt)_5$	D_2O	Nb_2O_5	Ligand exchange with side-reactions
$SbCl_3$	$(Et_3Si)_2Te$	Sb_2Te_3	Ligand exchange
$GeCl_2 \cdot C_4H_8O_2$	$(Et_3Si)_2Te$	GeTe	Ligand exchange
$SbCl_3$	$(Et_3Si)_3Sb$	Sb	Ligand exchange
$Ir(acac)_3$	O_2	Ir	Combustion
$Ir(acac)_3$	O_3	IrO_2	Combustion
$Ir(acac)_3$	$O_3 - H_2$	Ir	Combustion

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