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DEVELOPMENT OF LOW-TEMPERATURE DEPOSITION PROCESSES BY ATOMIC LAYER EPITAXY FOR BINARY AND TERNARY OXIDE THIN FILMS

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Abstract

Atomic layer epitaxy (ALE) method was employed for the study of growth of binary and ternary metal oxide thin films. As background for the study, the basic principles of the ALE method are presented together with a review of existing ALE deposition processes and precursors for oxide thin films.

The suitability of β -diketonate type precursors ($M(\text{thd})_3$ $M=\text{Sc}, \text{Y}, \text{La}$; $\text{thd} = 2,2,6,6$ -tetramethylheptanedione) and ozone were studied for ALE depositions of Group 3 oxides, namely Sc_2O_3 , Y_2O_3 and La_2O_3 . All three oxides could be deposited by a self-limiting ALE process once a suitable deposition temperature was identified. The optimal deposition temperature was found to depend on the position of the self-limiting deposition region, but also on the impurity content, which increases at low deposition temperatures. Deposition rate of Sc_2O_3 was considerably higher from organometallic precursor, $(\text{C}_5\text{H}_5)_3\text{Sc}$, than from β -diketonate precursor ($0.75 \text{ \AA}(\text{cycle})^{-1}$ vs. $(0.125 \text{ \AA}(\text{cycle})^{-1})$).

In a second set of experiments, the suitability of the ALE processes developed was tested for the deposition of ternary thin films, namely yttria-stabilised zirconia (YSZ) and lanthanum aluminate. Before these processes were applied, study was made of the deposition of ZrO_2 from β -diketonate and organometallic precursors at 200-500 °C. Furthermore, ALE deposited MgO films were tested for their suitability as buffer layers between silicon substrate and LaAlO_3 film. Crystalline YSZ films were obtained regardless of the yttrium to zirconium ratio, whereas the LaAlO_3 films were crystalline only after annealing at 900 °C.

Preface

This thesis is based on experimental work carried out during the years 1997-2001 in the Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology.

I am very much indebted to my supervisor, Prof. Lauri Niinistö, for his expert help and advice over the years and for providing an interesting topic for my research. Dr. Suvi Haukka and Mr. Jarmo Skarp at ASM Microchemistry Ltd. are thanked for suggesting particular research problems.

Warm and sincere thanks are owed to many others. The input of my co-author Dr. Minna Nieminen was invaluable. Several co-workers are thanked for the assistance in the analysis of the precursors and thin films. Prof. Ari Koskinen from Laboratory of Organic Chemistry is thanked for providing facilities for the MS measurements and Mr. Kimmo Karinen performing the measurements. Dr. Eero Rauhala and Mr. Timo Sajavaara from the Laboratory of Physics, University of Helsinki, are thanked for their continuous effort in the impurity analyses by RBS and TOF-ERDA, respectively. Mr. Jaakko Niinistö is gratefully acknowledged for the AFM measurements, while Dr. Leena-Sisko Johansson and Dr. Joe Campbell at the Centre for Chemical Analysis at HUT are thanked for their skilful help with the XPS analyses. Not of least importance, the entire personnel of the Laboratory of Inorganic and Analytical Chemistry contributed to the creation of a pleasant environment in which to work.

Financial support was received from several sources including the Graduate School of Inorganic Material Chemistry, the Finnish Foundation of Technology, the Academy of Finland and the National Technology Agency of Finland (TEKES) is acknowledged.

My wife, Tiina, is deserving of very special thanks for her patience and understanding during the years it took to complete this work.

Helsinki, February 2002

Matti Putkonen

**'To most people solutions mean finding the answers.
But to chemists solutions are things that are still mixed up.'**

Anon. elementary school student

List of publications

The thesis consists of a summarising review and the following publications:

- I Putkonen, M., Nieminen, M., Niinistö, J., Sajavaara, T. and Niinistö, L., Surface-controlled deposition of Sc_2O_3 thin films by atomic layer epitaxy using β -diketonate and organometallic precursors, *Chem. Mater.* **13** (2001) 4701-4707.
- II Putkonen, M., Sajavaara, T., Johansson, L.-S. and Niinistö, L., Low temperature ALE deposition of Y_2O_3 thin films from β -diketonate precursors, *Chem. Vap. Deposition* **7** (2001) 44-50.
- III Nieminen, M., Putkonen, M. and Niinistö, L., Formation and stability of lanthanum oxide thin films grown by atomic layer epitaxy, *Appl. Surf. Sci.* **174** (2001) 155-165.
- IV Putkonen, M. and Niinistö, L., Zirconia thin films by atomic layer epitaxy. A comparative study on the use of novel precursors with ozone, *J. Mater. Chem.* **11** (2001) 3141-3147.
- V Putkonen, M., Sajavaara, T., Niinistö, J., Johansson, L.-S. and Niinistö, L., Deposition of yttria-stabilized zirconia thin films by atomic layer epitaxy from β -diketonate and organometallic precursors, *J. Mater. Chem.*, in press.
- VI Putkonen, M., Johansson, L.-S., Rauhala, E. and Niinistö, L., Surface-controlled growth of magnesium oxide thin films by atomic layer epitaxy, *J. Mater. Chem.* **9** (1999) 2449-2452.
- VII Putkonen, M., Sajavaara, T. and Niinistö, L., Enhanced growth rate in atomic layer epitaxy deposition of magnesium oxide thin films, *J. Mater. Chem.* **10** (2000) 1857-1861.
- VIII Nieminen, M., Sajavaara, T., Rauhala, E., Putkonen, M. and Niinistö, L., Surface-controlled growth of LaAlO_3 thin films by atomic layer epitaxy, *J. Mater. Chem.* **11** (2001) 2340-2345.

The papers I-VIII are referred to in the text by the Roman numerals given above.

The author's contribution

- Publication I The author planned the research and did the experimental work except for part of the Sc(thd)₃/O₃ depositions and the TOF-ERDA, AFM and XPS analyses. These were done by the co-authors. Interpretation of the results and writing of the article were carried out by the author.
- Publication II The author planned the research and did the experimental work except for the TOF-ERDA, AFM and XPS analyses. Interpretation of the results and writing of the article were carried out by the author.
- Publication III The research plan for the experimental work was made together with Dr. Minna Nieminen. The author was responsible for part of the ALE depositions, thickness determinations and XRD measurements and participated in the interpretation of the results. The author had a minor role in writing the article.
- Publications IV-VII The author made the research plans and did the experimental work except for the TOF-ERDA, RBS, AFM and XPS analyses. The author interpreted the results and wrote the articles.
- Publication VIII The author carried out the MgO buffer layer depositions and assisted in the interpretation of the results. The author had a minor role in writing the article.

List of abbreviations and acronyms

acac	2,4-Pentanedione, Acetylacetonate, $C_5H_7O_2$
AFM	Atomic Force Microscope / Microscopy
ALCVD	Atomic Layer Chemical Vapour Deposition
ALD	Atomic Layer Deposition
ALE	Atomic Layer Epitaxy
ATO	Aluminium Titanium Oxide, Al_2O_3 - TiO_2
bipy	2,2'-bipyridyl, $C_{10}H_8N_2$
Cp	Cyclopentadienyl, C_5H_5
CVD	Chemical Vapour Deposition
DTA	Differential Thermal Analysis
EL	Electroluminescence / Electroluminescent
EOT	Equivalent Oxide Thickness
HRTEM	High Resolution Transmission Electron Microscope / Microscopy
ITO	Indium Tin Oxide
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee of Powder Diffraction Standards
MEIS	Medium Energy Ion Scattering
MOCVD	Metal-Organic Chemical Vapour Deposition
MOSFET	Metal-Oxide-Semiconductor Field-Effect Transistor
MS	Mass Spectroscopy
NRB	Nuclear Resonance Broadening

O ⁱ Pr	isopropoxide
phen	1,10-phenanthroline, C ₁₂ H ₈ N ₂
QMS	Quadrupole Mass Spectrometer
RBS	Rutherford Backscattering
rms	root-mean-square
RT	Room Temperature
TCO	Transparent Conductive Oxide
TEM	Transmission Electron Microscope / Microscopy
tetraen	tetraethylene pentamine, C ₈ H ₂₃ N ₅
TFEL	Thin Film Electroluminescence
TG	Thermogravimetry
thd	2,2,6,6,-tetramethylheptane-3,5-dionate, C ₁₁ H ₂₀ O ₂
TMA	Trimethylaluminium, (CH ₃) ₃ Al
TOF-ERDA	Time-Of-Flight Elastic Recoil Detection Analysis
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
YSZ	Yttria-Stabilised Zirconia

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1. Introduction

The continually shrinking dimensions of advanced electronic and other devices set high demands on the materials to be used. Thin films, *i.e.* thin layers of a substance on a supporting material, are used in many applications in modern technology, in optics, optoelectronics and microelectronics as well as in devices based on magnetic, superconductive and thermal phenomena.¹ Other interesting applications include protective coatings – thermal, chemical and mechanical – although thick films have traditionally been employed in these applications.^{1,2}

Many thin film processing techniques have been developed in the search for the most suitable ones for specific applications. Typically thin films can be prepared from either liquid or gaseous phase. Vapour phase deposition processes, which are more popular, fall into the two main categories of physical and chemical vapour deposition techniques. Atomic layer epitaxy (ALE) technique applied in the present study is one variant of the chemical vapour deposition (CVD) method.

Some confusion surrounds the term atomic layer epitaxy, which is the name Suntola and Antson gave to this deposition method, when they introduced ALE in the mid 1970s.³ The term epitaxy comes from Greek and means ‘on arrangement’. Usually it refers to a single crystalline film on a crystalline substrate. In ALE, it describes the ordered monolayer of a precursor (or distinct fraction thereof) on a substrate after one saturated surface reaction,⁴ even if the deposited film may be amorphous or polycrystalline. Other terms, such as atomic layer deposition (ALD) and atomic layer chemical vapour deposition (ALCVD) have more recently been suggested to describe this deposition process and are widely used. However, mainly for historical reasons, the term atomic layer epitaxy is preferred in this work.

The numbering scheme for the groups in the periodic table approved by IUPAC is used,⁵ *i.e.* for the group consisting Sc, Y, La and Ac, the name Group 3 is used. Another point of terminology that requires clarification is the classification of lanthanum. The term lanthanoid means ‘like lanthanum’, and therefore IUPAC recommends that La should not be included into this group.⁵ In this work lanthanum is not included as lanthanoids, although in common use the term lanthanoid may cover the elements from La to Lu.⁶

The present study is focused on two different key areas. First, deposition processes for binary Group 3 oxides, namely Sc_2O_3 , Y_2O_3 and La_2O_3 (Figure 1), were systematically studied with a view to developing surface-controlled and reproducible ALE processes. Second, the new processes were tested for their applicability to the deposition of ternary thin films, where β -diketonates or organometallic compounds together with ozone were used as precursors. ALE has shown to be a practical tool for the deposition of complex oxide structures and ternary systems when halides and water are used as precursors. To demonstrate this approach with β -diketonates and ozone as precursors, two distinctly different ternary systems, namely yttria-stabilised zirconia (YSZ) and LaAlO_3 , were selected for closer study. Before the yttria-stabilised zirconia films could be deposited, study was required of processes for binary ZrO_2 . Similarly, ALE depositions for MgO thin films were investigated to allow use of MgO as a buffer layer between the silicon substrate and ALE-deposited LaAlO_3 films.

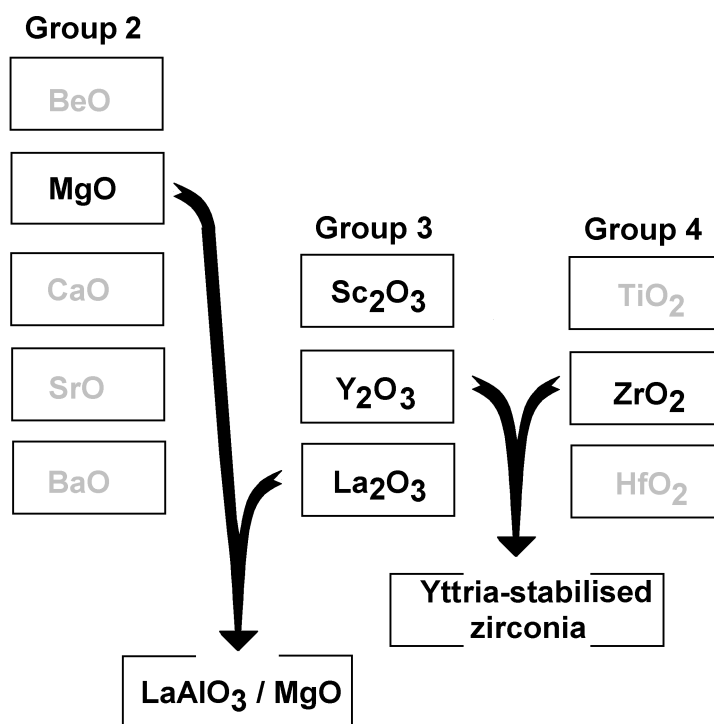


Figure 1. Schematic presentation of the oxides studied (bold face).

Besides the many present and potential applications of oxide materials,^{1,2} a driving force for this study was the lack of knowledge of the optimal conditions for the deposition of oxide films by ALE, when β -diketonates and ozone are used as precursors. Deposition processes have earlier been developed for NiO,⁷ Ga₂O₃,⁸ Y₂O₃,⁹ La₂O₃¹⁰ and CeO₂.¹¹⁻¹³ Only rarely, however, has the growth rate been independent of the deposition temperature. β -Diketonate-type precursors have been successfully used in other chemical vapour deposition methods, as well as in ALE depositions of metal sulphide films.^{14,15} Previously, studies on oxide films have also been carried out using β -diketonates and water as precursors.^{8,9,16} In view of the disadvantages of the β -diketonate-type ALE precursors, such as low growth rate and low reactivity, some other precursors were considered as well, in an attempt to increase the film growth rate.

1.1 Atomic layer epitaxy (ALE) method for thin film growth

Originally, the ALE method was developed for the deposition of thin films onto planar substrates. More recently, high-surface area powders have also been successfully employed as substrates in the preparation of heterogeneous catalysts.¹⁷ The ALE processes for oxides onto powder substrates are not reviewed here.

1.1.1 General principle of ALE

Atomic layer epitaxy can be considered as a variant of the well-established chemical vapour deposition (CVD) technique, based on separated surface-controlled reactions. In ALE, reactants are directed alternately over the substrate surface (Figure 2), separated by inert gas purging or by other method, such as by rotating of the substrates over different gaseous precursors.

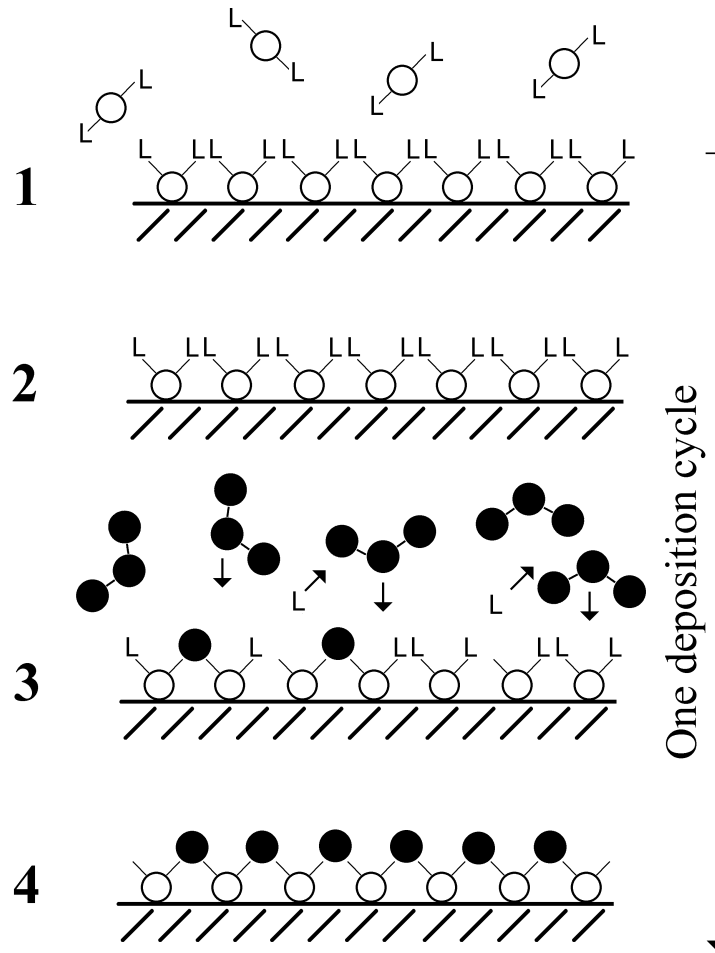


Figure 2. Schematic illustration of an ALE deposition cycle (1-4) leading to the formation of an imaginary binary oxide film of metal (○) and oxygen (●). L refers to the precursor ligand.

Deposition temperature is selected so that thermal decomposition of the precursor does not occur and only one monolayer or a distinct fraction thereof is adsorbed onto the substrate surface. Thus, self-limiting ALE deposition is not dependent on the precursor fluxes provided that a sufficient amount of each precursor is pulsed over the substrate. Film thickness is dependent only on the number of deposition cycles, making the thickness control facile.

The optimal ALE processing temperature range giving a constant growth rate is usually called as ALE window, which is limited at lower temperatures by reactant condensation or insufficient precursor reactivity (Figure 3).⁴ At higher temperatures, above the optimal deposition temperature, precursor decomposition or desorption destroys the self-limiting ALE growth mechanism.

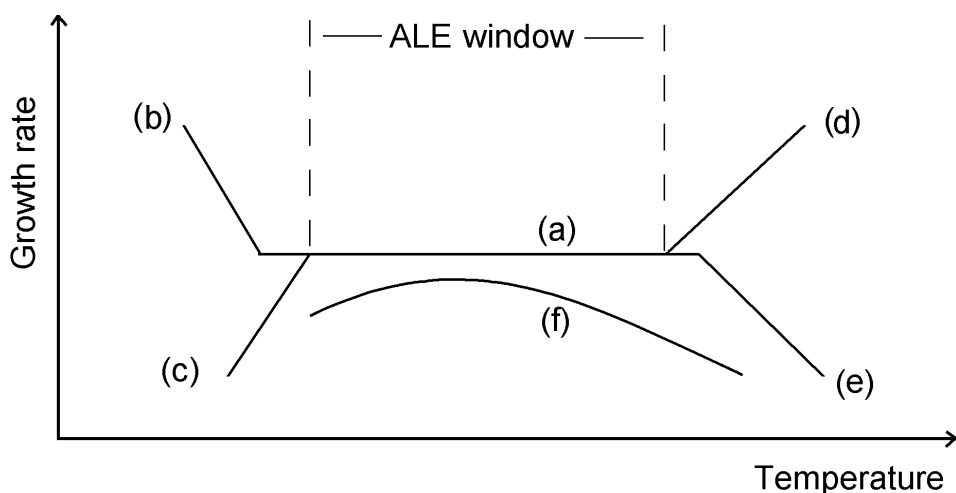


Figure 3. Scheme of (a) ALE processing window limited by (b) precursor condensation, (c) insufficient reactivity, (d) precursor decomposition and (e) precursor desorption. If deposition rate is dependent on the number of available reactive sites as in (f), no actual ALE window is observed.

Although in an ideal ALE process where deposition rate could be one monolayer per cycle, self-limiting deposition rate is usually lower when halides, β -diketonate or organometallic precursors are used. Possible reasons are steric hindrances in monolayer formation due to a large precursor ligand (Figure 2) or deficiency of favourable bonding sites. The number of bonding sites can also be dependent on the deposition temperature¹⁸ thus making growth rate dependent on the deposition temperature (Figure 3f).

1.1.2 ALE precursors for metal oxide films

Because ALE relies on surface reactions, a controlled process can only be obtained by quantitative chemisorption or by reaction between the gaseous precursor and the functional surface sites.¹⁹ Reactivity of the metal and oxygen precursors for ALE process can be higher than that for precursors used in CVD processes because the separate and sequential pulsing of the precursors makes gas phase reactions impossible.

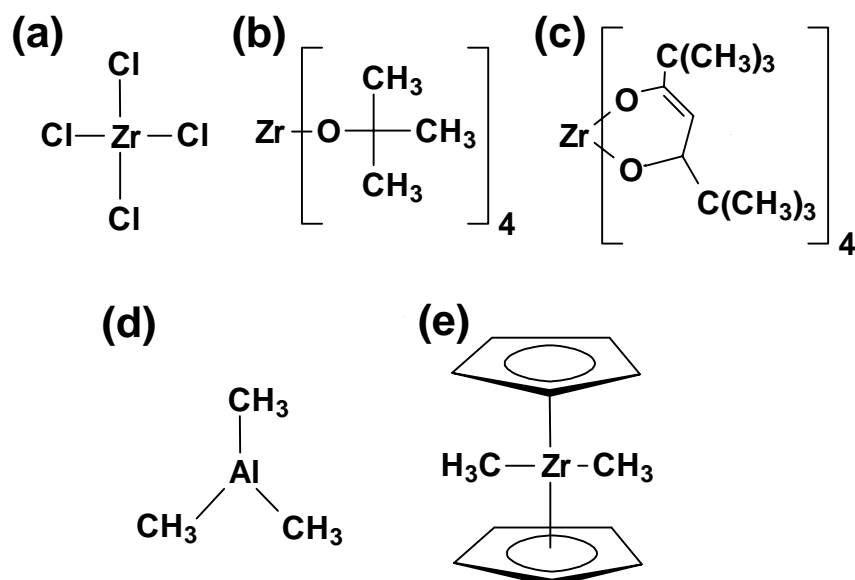
1.1.2.1 Metal precursors for oxide films

The metal precursors used in oxide CVD are also suitable for ALE processes provided that certain requirements are fulfilled.¹⁹⁻²¹ In the ALE method, in order to avoid uncontrolled reactions, sufficient thermal stability is needed in the gas phase as well as on the substrate surface within the deposition temperature range. In CVD methods, a constant flux of the precursor vapour is required to obtain a controlled process, but because ALE relies on self-limiting reactions, only a sufficient amount of the precursor is required during one pulse.

Solid and liquid precursors must be volatile under the operating temperature and pressure, and if heating is required to obtain sufficient vapour pressure, thermal stability over a prolonged time is necessary. Volatile halides and β -diketonate-type chelates, are used as ALE precursors (Scheme 1), but interest has recently increased in the deposition of oxide thin films from organometallic compounds.¹⁹ Other types of precursors, such as alkoxides, acetates and isocyanates, have also been used as ALE precursors for oxide films.^{19,22,23}

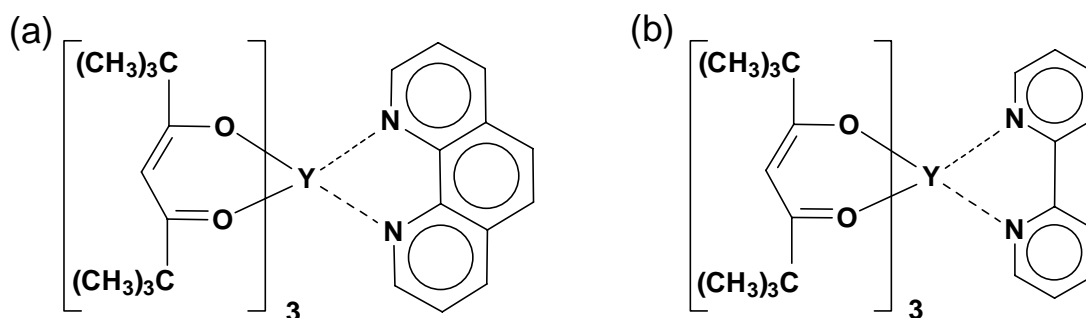
Several metal halide precursors have been applied in ALE processes, together with water as an oxygen source.¹⁹ The suitability of a particular metal halide for ALE depositions has been found to depend on the metal.¹⁹ Halide contamination of the film may cause problems at low deposition temperatures,²⁴⁻²⁶ although halides may be successfully used as ALE precursors. Liberation of HX (X = F, Cl, Br) during the deposition process may also cause problems, such as corrosion and etching.¹⁹

Oxyhalides are another type of inorganic precursor, which have been used in only a few studies, however. For instance, tungsten oxyfluoride (WO_xF_y) and H_2O have been used as precursors in the deposition of WO_3 ,²⁷ while CrO_2Cl_2 with CH_3OH as oxygen source have been used in the deposition of chromium oxide.²⁸



Scheme 1. Examples of precursors for ALE depositions of oxide films. Volatile (a) halides, (b) alkoxides, (c) β -diketonates, (d) organometallics and (e) organometallic cyclopentadienyl-type compounds have been exploited.

β -Diketonate-type metal chelates were originally synthesised for the separation of metals by fractional sublimation²⁹ and gas chromatography.³⁰⁻³³ In the 1970s they were utilised for the first time in CVD depositions of oxide materials.^{34,35} Good thermal stability and volatility of the β -diketonate-type metal chelates make them suitable for MOCVD depositions, and high deposition temperatures are required to enable gas phase reactions.³⁶⁻³⁹ β -diketonates in ALE processes were first utilised in the 1980s as dopant precursors for ZnS ⁴⁰ and other sulphide thin films.^{14,15} Somewhat later they were applied in metal oxide depositions by ALE,^{41,42} but quite high deposition temperatures are needed to obtain favourable reaction with water or hydrogen peroxide.¹⁹ Another approach is to use a strong oxidiser, such as ozone.

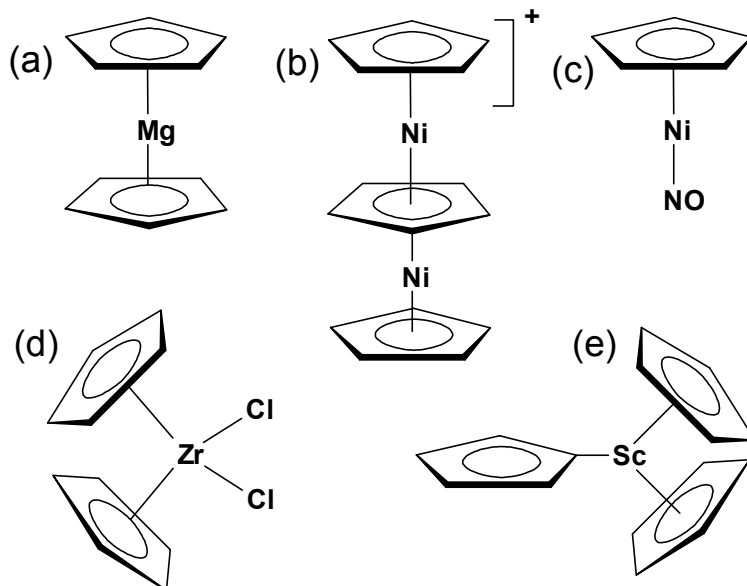


Scheme 2. $\text{Y}(\text{thd})_3$ adducts with (a) 1,10-phenanthroline and (b) 2,2'-bipyridyl.

It has been observed in CVD as well as in ALE depositions that coordinatively unsaturated β -diketonate type compounds may oligomerise and become less volatile.⁴³⁻⁴⁵ This is the cause for instability especially with larger central ions such as strontium and barium. β -Diketonate-type chelates can be protected against oligomerisation and room temperature reactions with moisture by adducting them with neutral molecule (Scheme 2).⁴⁶⁻⁴⁹ With adducted precursors, behaviour during heating depends on choices of metal, ligand and adduct and on the bond strengths between them. Adducted precursors may sublime in a single-step process, or alternatively may dissociate during heating, releasing the neutral adduct and leading to two-stage volatilisation where the second step corresponds to the sublimation of the original unadducted compound.⁴⁶ ALE depositions of sulphide films have been carried out with use of $\text{Ca}(\text{thd})_2(\text{tetraen})$ or $\text{Ce}(\text{thd})_3(\text{phen})$, where the growth process appears to be similar to that of the unadducted precursor.^{50,51} It seems that, even if one stage sublimation is observed, the adducted precursors dissociate at the deposition temperatures, producing unadducted precursor.⁵⁰

Another way to provide a constant supply of fresh precursor is to use *in situ* synthesis. This has been successfully applied to produce thd compounds of alkaline earth metals (Sr,Ba), by pulsing ligand vapour over heated metal or metal hydroxide.^{44,45}

True organometallic cyclopentadienyl compounds, or metallocenes (Scheme 3), *i.e.* compounds having at least one direct metal-carbon bond to the C_5H_5 ligand, were first synthesised in the 1950s.^{52,53} Since then, reactions of cyclopentadienyl reagents have been applied for almost every element.⁵⁴ The main application of metallocenes is their use as catalysts in the polymerisation of olefins (in Ziegler-Natta polymerisation processes). But many metallocene compounds are also suitable for use as MOCVD precursors for oxide thin films⁵⁵⁻⁵⁸ or as dopants for 13-15 (III-V) semiconductors.⁵⁹



Scheme 3. Examples of metallocene structures:⁵⁴ (a) parallel sandwich, (b) multi-decker sandwich, (c) half-sandwich, (d) bent/tilted sandwich and (e) compounds with differently bonded cyclopentadienyl ligands.

Cyclopentadienyl compounds have attracted considerable interest as precursors in CVD depositions, although they are sometimes too reactive.^{19,60} In general, they would seem to be suitable for ALE depositions, however, where the reactivity can be controlled by sequential pulsing of the precursors. Furthermore, cyclopentadienyl compounds often are of smaller physical size than β -diketonate-type compounds and higher ALE growth rate can be expected. Organometallic cyclopentadienyl-type precursors were first applied in ALE for the deposition of MgO,^{61,62} SrTiO₃^{63,64} and BaTiO₃⁶⁴ thin films. As well, cyclopentadienyl cerium compounds have been used for the doping of SrS thin films.^{65,66}

1.1.2.2 Oxygen sources

In the case of ALE-processed oxide films, precursors attached to the surface can be oxidised with H₂O, H₂O₂, N₂O₄,⁶⁷ NO₂,⁶⁸ O₂ or O₃, the choice depending on the metal precursor selected.¹⁹ Water has often been used as an oxygen source and it readily reacts with many metal halides, alkyls and alkoxides.¹⁹ Quite recently, water has also been applied to processes based on organometallic precursors.⁶¹⁻⁶⁴ H₂O₂ has been used as an oxygen source when the reactivity of water has not been sufficient.⁶⁹⁻⁷² Alcohols have been successfully applied in processes involving the inorganic and alkoxide-type precursors. For example, deposition of Al₂O₃ has been carried out with an AlCl₃ and ROH precursor combination, where R is H, CH₃, CH₂OHCH₂OH, *t*-C₄H₉OH or *n*-C₄H₉OH.⁷³

Sometimes metal alkoxides have been used as oxygen sources.⁷⁴⁻⁷⁶ No separate oxygen source is needed in this type of process because the metal alkoxide behaves as both metal and oxygen source. This method provides a convenient route to mixed oxides, when different metals are used in the precursor and the alkoxide.⁷⁴ For example, Zr-Si-O films have been deposited from $ZrCl_4$ and $Si(O(CH_2)_3CH_3)_4$ at 500 °C.⁷⁴

The use of H_2O , H_2O_2 , N_2O , CH_3COOH and O_2 as oxygen source has been explored for β -diketonate-type compounds,^{9,16} but the reactivities are usually too low, producing either no film growth or films with a high impurity content. For example, Ga_2O_3 thin films have been deposited from $Ga(acac)_3$ and H_2O , but the films contained 30 at% carbon as an impurity.⁸ Thermal stability of the β -diketonate-type chelates thus usually does not allow their usage in ALE with only mild oxidisers. In CVD, the thermal stability of β -diketonates is countered with the use of high deposition temperatures.^{19,42} For example, ZrO_2 films have been deposited by CVD from $Zr(thd)_4$ and O_2 at 540-570 °C.⁷⁷ β -Diketonate compounds can be employed as ALE precursors for oxide film depositions through use of a sufficiently strong oxidiser, such as a mixture of ozone and oxygen.⁸⁻¹¹ The use of a strong oxidiser guarantees that only a small amount of carbon residue is left in the film. Furthermore, better crystallinity and lower impurity content of films can be obtained with use of an O_2/O_3 mixture than with use of oxygen alone.⁹ Typically in ALE experiments ozone is generated with a continuous-flow electric-discharge-type generator.⁹ In this type of equipment the maximum ozone concentration at room temperature is 6-8 mol%.⁷⁸

Increase in film growth rate with processes based on halides, alkoxides, β -diketonate precursors or organometallics has been attempted by the use of mixtures of oxygen sources or increase in the oxidiser dosage. These methods increase the number of reactive surface sites on the substrate surface where metal precursors can be attached. These typical reactive sites in oxide deposition processes are OH groups.⁷⁹ An example of the use of mixtures of oxygen sources is the deposition of NiO film using water as an additional oxygen source together with O_3 . The growth rate increased by 15-20%.⁷ Secondly, larger dosage of the oxidiser is provided through increasing its flow rate or pulse time.⁸⁰ For example, the growth rate of Al_2O_3 films deposited from $(CH_3)_3Al$ and H_2O increased from 0.64 to 1.0 Å(cycle)⁻¹ when the amount of water was increased from 3×10^{-6} to 1×10^{-4} g/cycle.⁸⁰

1.2 Oxide materials deposited by ALE

The first ALE processes were reported for ZnS, GaP and SnO₂,³ while the first ALE-deposited dielectric oxide materials were Al₂O₃, Ta₂O₅ and Al₂O₃/TiO₂.⁸¹⁻⁸³ Several processes for oxide materials have been developed during the thirty-year history of ALE.⁸⁴ From the 1980s onwards until very recently, the main research and industrial interest in ALE studies has been the processing of materials for high quality thin film electroluminescent (TFEL) flat panel displays, both monochromatic and multicolour ones.⁸⁵⁻⁸⁷ The TFEL structure is a complex stack of thin films consisting of emissive, insulating and conducting materials (Figure 4).⁸⁸

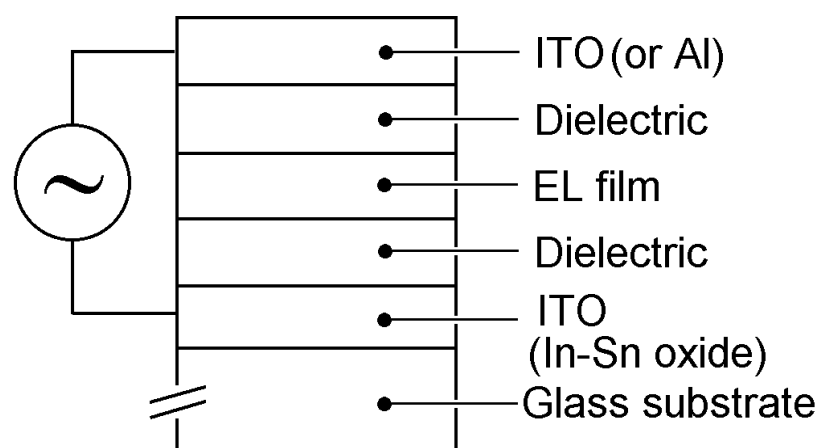


Figure 4. Scheme of typical film structure used in a thin film electroluminescent (TFEL) device.

More recently, the deposition of dielectric,⁸⁴ optical⁸⁹ and conducting^{90,91} oxide materials has been reported. Studies on oxide film depositions by ALE have mainly been focused on binary compounds, but studies on ternary oxides and oxide multilayers have also been published. Deposition processes for oxide materials of particular interest for the present study (Table 1) will be discussed in more detail below. Other ALE deposition processes and properties of the resulting oxide materials can be found in the published reviews.^{42,84,92,93}

Table 1. ALE deposition processes for selected binary oxides.

	Precursors	Dep. T / °C	Ref.
Group 3 oxides			
Y ₂ O ₃	Y(thd) ₃ / O ₃	425-600	9
La ₂ O ₃	La(thd) ₃ / O ₃	200-450	10
Lanthanoid oxide			
CeO ₂	Ce(thd) ₄ / O ₃	300-500	11
	Ce(thd) ₃ (phen) / O ₃	225-350	12,13
Other oxides			
MgO	Mg(thd) ₂ / H ₂ O	300-500	16
	(C ₅ H ₅) ₂ Mg / H ₂ O	360-900	61,62,94
Al ₂ O ₃	AlCl ₃ / H ₂ O	100-660	81,84,95
	AlCl ₃ / Al(OEt) ₃ or Al(O ⁱ Pr) ₃	300, 400	74
	AlCl ₃ , Al(OEt) ₃ , Al(OPr) ₃ / various alcohols	300-500	73
	(CH ₃) ₂ AlCl / H ₂ O	125-500	96
	(CH ₃) ₃ Al / H ₂ O	80-600	18,84,97-99
	(CH ₃) ₃ Al / H ₂ O ₂	RT-450	100,101
	(CH ₃ CH ₂) ₃ Al / H ₂ O	600-750	94
	(CH ₃) ₃ Al / Al(O ⁱ Pr) ₃	300	74
	(CH ₃) ₂ (C ₂ H ₅)N:AlH ₃ / O ₂ plasma	100-125	102
	ZrO ₂	ZrCl ₄ / H ₂ O	275,300,500
ZrI ₄ / H ₂ O		250-500	71
Zr[OC(CH ₃) ₃] ₄ / O ₂		300-400	108
Zr[OC(CH ₃) ₃] ₄ / H ₂ O		150-300	109

1.2.1 Group 3 and lanthanoid binary oxides

Previously only a few ALE processes have been developed for binary Group 3 and lanthanoid oxide thin films. Although these oxides can be prepared by ALE (Figure 5), it appears that the growth rate is dependent on the deposition temperature especially in the case of Y_2O_3 ⁹ and La_2O_3 .¹⁰ However, the number of Group 3 oxide depositions at lower temperatures is limited, especially in the case of Y_2O_3 , and these results are only preliminary. These studies will nevertheless be discussed in some detail as they provide a good basis for the present more systematic investigation.

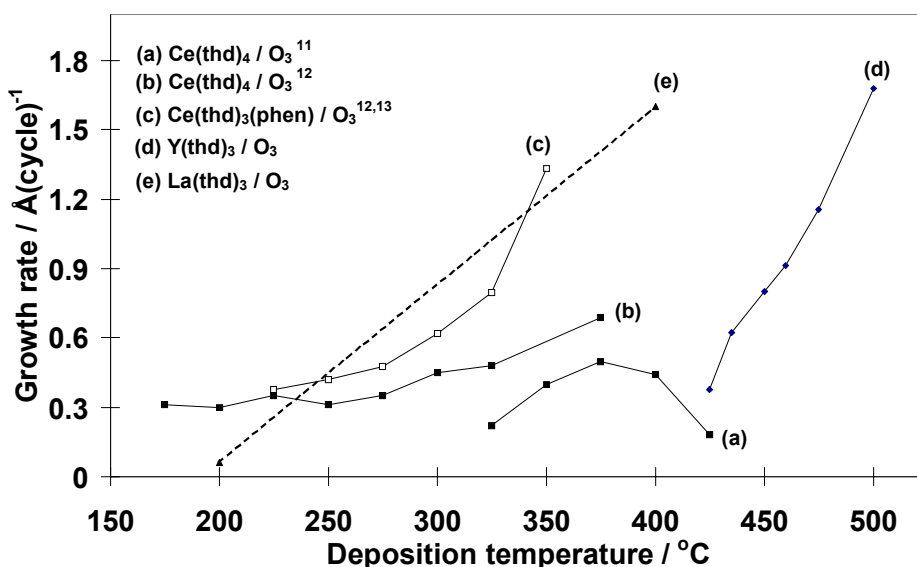


Figure 5. Growth rates of binary Y_2O_3 ,⁹ La_2O_3 ¹⁰ and CeO_2 ¹¹⁻¹³ oxides as reported in the literature with β -diketonates and ozone as precursors. In the case of La_2O_3 , only two numerical values were presented in the original article; the dashed line is thus only a guideline for the eye.

Y_2O_3 films have been deposited from $\text{Y}(\text{thd})_3$ and O_3 as precursors at 425-600 °C.⁹ Growth rate of $0.8 \text{ \AA}(\text{cycle})^{-1}$ was obtained at 450 °C on both soda lime glass and Si(100) substrates. Controlled growth was obtained at 425-500°C, *i.e.* growth rate was dependent on the number of deposition cycles and independent of the pulsing times of precursors if pulses were sufficiently long. However, growth rate increased with the deposition temperature. Y_2O_3 films were amorphous if the thickness was below 200 nm, while thicker films exhibited the (100) preferred orientation.

La₂O₃ thin films have been deposited using La(thd)₃ and ozone as precursors in connection with the development of an ALE process for LaCoO₃.¹⁰ No self-controlled growth region was observed in the deposition temperature range studied, *viz.* 200-450 °C. Films were not uniform above 400 °C, indicating decomposition of the La(thd)₃. Crystalline films containing cubic La₂O₃ were obtained when depositions were carried out at 300-350 °C. At higher deposition temperatures also hexagonal La₂O₃ was formed.

CeO₂ thin films have been deposited by ALE from Ce(thd)₄ and O₃ as precursors (Figure 5).^{11,12} Growth rate of about 0.32 Å(cycle)⁻¹ was obtained at 175-250 °C.¹² A small increase in growth rate was obtained when the pulsing time of Ce(thd)₄ was increased, indicating that the ALE process was not completely ideal. In previous studies,¹¹ deposition rate of 0.4-0.5 Å(cycle)⁻¹ was obtained at 300-400 °C on Si(100) substrates. However, no constant deposition rate was obtained, although differences in growth rate were relatively small. Furthermore, growth rate was dependent on the number of deposition cycles. The films were polycrystalline and (110) oriented when deposited at 375 °C but (111) oriented when deposited at 425 °C,¹¹ while in films deposited below 375 °C both (111) and (200) reflections were observed.¹²

Another CeO₂ process based on Ce(thd)₃(phen) and O₃ produced films with only a small variation in the growth rate at 225-275°C.^{12,13} Deposition rate of around 0.4-0.5 Å(cycle)⁻¹ was obtained in this temperature region by 0.5-1.0 s Ce(thd)₃(phen) pulsing time. However, growth rate increased with the pulsing time of the Ce-precursor. Similarly to the films deposited by unadducted cerium β-diketonate, (111) and (100) orientations were dominant.

1.2.2 Other binary oxides

Of the several binary oxide thin film materials that have been deposited by ALE,^{84,92,93} the preparation and properties of oxides only relevant to the present study, namely ZrO₂, MgO and Al₂O₃, will be discussed here.

1.2.2.1 Zirconium oxide

The first experiments to produce ZrO₂ thin films by ALE were carried out by using ZrCl₄ and H₂O as precursors.¹⁰³ Films deposited at 500 °C,¹⁰³ 300 °C^{104,105} and 275 °C¹⁰⁷ were nearly amorphous, showing the presence of only weakly crystalline monoclinic or tetragonal ZrO₂ phases. Growth rate of 0.53 Å(cycle)⁻¹ was obtained at 500 °C. The films were stoichiometric and chlorine contamination was below 0.5 at%.¹⁰³

Another zirconium halide, ZrI₄, was studied as an ALE precursor together with 30% hydrogen peroxide as oxygen source.⁷¹ ZrO₂ thin films were deposited at 250-500 °C. The maximum deposition rate of 1.25 Å(cycle)⁻¹ was obtained at 275 °C. The process was not completely ideal since decomposition of ZrI₄ was observed. Thinnest films were crystalline with the cubic ZrO₂ phase, whereas thicker films (>40-50 nm) also contained monoclinic ZrO₂. Films deposited at above 300 °C contained both cubic and tetragonal ZrO₂. According to XPS, 1.3-0.7 at% iodine were observed in films deposited at 250-350 °C. At higher deposition temperatures iodine concentration was below the detection limit.

Alkoxide-type volatile compounds have also been tested as precursors. ZrO₂ film deposition has been carried out using Zr[OC(CH₃)₃]₄ as a precursor with oxygen as an oxygen source.¹⁰⁸ Very high deposition rate of about 2 Å(cycle)⁻¹ were obtained at 300-400 °C measured from the 3-13 Å films. At higher temperatures (490-530 °C) decomposition of zirconium precursor occurred and films were nonuniform. Zr[OC(CH₃)₃]₄ has also been used together with H₂O as an oxygen source.¹⁰⁹ Growth rate decreased from 1.9 Å(cycle)⁻¹ to nil when the deposition temperature was increased from 200 °C to 325 °C when 0.4 s Zr[OC(CH₃)₃]₄ pulse was used. When precursor pulsing time was increased growth rate increased continually, indicating precursor decomposition.

Probably $Zr[OC(CH_3)_3]_4$ decomposes in this reactor setup completely before reaching the substrate at deposition temperatures above 300 °C. Films deposited at 150-300 °C were weakly crystalline and only very broad reflections of monoclinic or metastable tetragonal phases were detected in the XRD patterns. According to TOF-ERD analysis films deposited at 250 °C contained 8 at% hydrogen and 2 at% carbon. If the deposition temperature was decreased to below 250 °C, both H and C impurity levels significantly increased reaching 23 and 6 at%, respectively, at 175 °C.

1.2.2.2 Magnesium oxide

MgO thin films have been deposited by ALE from $Mg(thd)_2$ and H_2O_2 as precursors.¹⁶ However, this process suffers from the low reactivity of $Mg(thd)_2$ with H_2O_2 requiring the use of such a high deposition temperature that the Mg precursor partially decomposes. No film was obtained below 300 °C. At 300-450 °C, the growth rate was only 0.10-0.15 Å(cycle)⁻¹ and without self-limiting ALE mechanism. All deposited films were crystalline with the preferential cubic (200) orientation.

$(C_5H_5)_2Mg$ and H_2O have been studied as a precursor combination for depositing MgO thin films at 360-900 °C.^{61,62,94} No film was obtained when O_2 was used as an oxygen source. The results suggest that deposition probably takes place by a surface-controlled hydrolysis mechanism:



The growth rates obtained at 600-900 °C were 2.1-2.4 Å(cycle)⁻¹, which are close to the theoretical value for one monolayer/cycle, viz. 2.43 Å(cycle)⁻¹. It is interesting to note that at below 600 °C the growth rate increased with decreasing deposition temperature reaching a value of about 5 Å(cycle)⁻¹ at 360 °C.⁶² Deposited films were (111) oriented when deposited below 700 °C but the (200) reflection was the most intense at higher temperatures of 800-900 °C.

1.2.2.3 Aluminium oxide

Several types of volatile and sufficiently reactive compounds of aluminium exist, and consequently there are a large number of ALE processes for Al₂O₃. Only the main features of the processes are described here. References to original Al₂O₃ studies can be found in the reviews published by Leskelä *et al.*¹⁹ and Niinistö *et al.*⁸⁴ The first ALE deposition process for Al₂O₃ was developed using AlCl₃ and water as precursors at 250 °C.⁸¹ Later on, deposition temperatures of 100-660 °C were explored.⁸⁴ Various oxygen sources, including alcohols⁷³ and even aluminium alkoxides,⁷⁴ have been applied in the Al₂O₃ deposition from AlCl₃. Growth rate depends on the oxidiser and deposition temperature employed, but typically it has been about 0.5-0.9 Å(cycle)⁻¹.^{73,74,81,110}

Al(OEt)₃ and Al(OPr)₃ together with H₂O have been used as ALE precursors for Al₂O₃ at 250-500 °C.⁷³ The deposition rate was about 1.2 Å(cycle)⁻¹ when Al(OEt)₃ and H₂O were used as precursors at 350-450 °C.

Several organometallic compounds have successfully been applied as aluminium sources. Thus, (CH₃)₃Al has been used for ALE depositions together with H₂O^{18,111} or NO₂⁶⁸ as oxygen source. Owing to its volatility and reactivity towards surface hydroxyl groups, (CH₃)₃Al can be successfully deposited in a wide temperature range of 80-400 °C,^{18,95} with maximum deposition rate of 1.1 Å(cycle)⁻¹ obtained at about 180 °C.⁹⁷ Al₂O₃ deposition is suggested to proceed via the following surface exchange reactions (an asterisk refers to surface species):



A chlorine-containing metal alkyl, (CH₃)₂AlCl, together with H₂O, has been used as precursor at 125-500 °C.⁹⁶ Maximum growth rate of 0.8 Å(cycle)⁻¹ was obtained at 180-250 °C. Carbon, hydrogen and chlorine contents were high in films deposited at 100-200 °C, but they decreased to below 1 at% with increasing deposition temperature up to 400 °C. Furthermore, (CH₃CH₂)₃Al and H₂O have been studied for Al₂O₃ deposition at higher temperatures (600-750 °C).⁹⁴

Very low deposition temperatures of 100-125 °C have been obtained in plasma-assisted ALE with dimethylamine alane, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{N}:\text{AlH}_3$.¹⁰² This deposition method is not conventional ALE process since repetitive cycles consist of five metal pulses with H_2 plasma and one O_2 plasma pulse. The metal precursor was chemisorbed onto the surface using H_2 plasma after which oxidation was carried out with O_2 plasma.

1.2.3 Complex oxides and oxide structures

A controlled process for complex oxides is obtained only by depositing every constituent binary oxide in a self-limiting manner at the same temperature (Figure 6). Deposition inside the ALE window is not necessarily required if self-limiting growth is obtained over a wider temperature range. For example, Al_2O_3 thin films have been deposited using $(\text{CH}_3)_3\text{Al}$ and H_2O as precursors at 80-380 °C without the existence of a true ALE window.¹⁸ Unfortunately, the number of suitable precursors for complex oxides becomes fewer as the number of metal atoms in the target compound is increased.

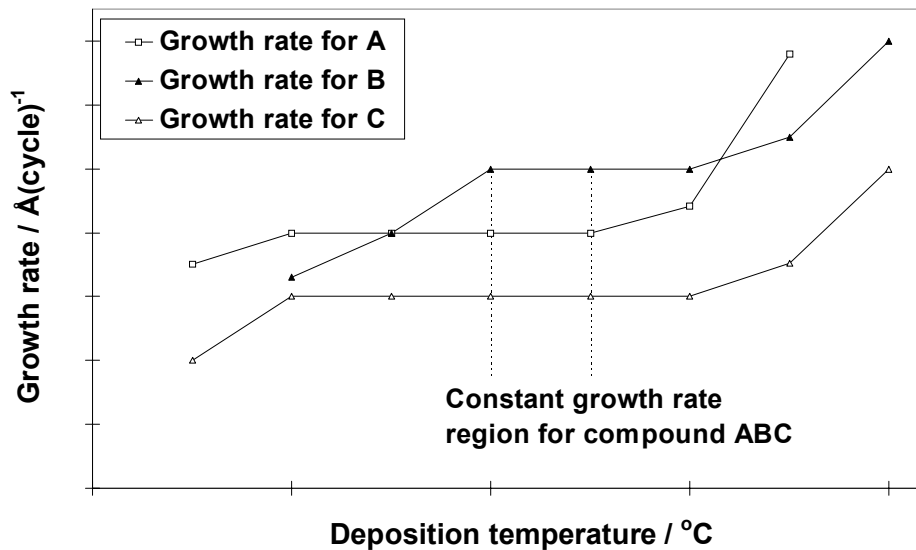


Figure 6. Possible constant growth ALE deposition temperature region, ‘ALE window’, for an imaginary compound ABC as a function of the deposition temperature of the binary compounds.

1.2.3.1 Oxide multilayers

Processes have been developed for various multilayer structures. Accurate thickness control by counting the ALE deposition cycles makes possible the preparation of nanolaminate structures of exact thickness. To obtain a controlled process for multilayer structures, deposition rates of constituent oxides on top of each other must be carefully studied, even though growth rates of the individual binary oxides are already known.⁸⁹

Optical multilayer coatings with a quarterwave structure for the 580 nm wavelength have been prepared using processes for low and high refractive index materials, Al₂O₃ and ZnS, respectively.⁸⁹ Deposition temperature was 500 °C. Aluminium oxide films were deposited with AlCl₃ and H₂O as precursors, while zinc sulphide films were deposited from ZnCl₂ and H₂S. According to NRB measurements the hydrogen content was below 0.1 at%. ALE-deposited Al₂O₃ and TiO₂ have been used to produce multilayer structures for soft-x-ray reflectors operating at 2.734 nm.⁹⁸ In this case, TiCl₄, (CH₃)₃Al and H₂O₂ were used as precursors at 140-700 °C. The temperature region for the controlled TiO₂ deposition was observed at 340-490 °C and multilayer structures were deposited at 400 °C.

Dielectric multilayers consist of a stack of several binary metal oxide films such as Ta₂O₅ films together with Nb₂O₅,¹¹² ZrO₂,^{113,115} HfO₂^{114,115} or Al₂O₃.¹¹³ Depositions of Ta₂O₅-containing nanolaminate films have been done with TaCl₅/H₂O¹¹² and Ta(OC₂H₅)₅/H₂O¹¹⁶ precursor combinations. Thickness uniformity and reproducibility of the films were better when the alkoxide-type precursor was applied. For the other metal oxides, halides such as ZrCl₄, HfCl₄ and AlCl₃ have been used as precursors. Films have usually been either amorphous or slightly crystalline. In ZrO₂-Ta₂O₅ structures, for example, tetragonal ZrO₂ begins to crystallise when its thickness increases above 5 nm.¹¹⁴

1.2.3.2 Mixed and ternary oxides

The difference between mixed and ternary oxides deposited by ALE is not clear-cut, as the compounds may be formed either during deposition or by solid state reactions upon annealing. Mixed oxides with a wide range of metal ratios have been obtained by varying the pulsing ratio of the precursors, but more precise control of the pulsing ratio is needed for stoichiometric ternary oxides. Ternary oxides with a clearly defined structure and stoichiometry have been obtained in only a few studies. Furthermore, in some cases as-deposited films have been amorphous, and crystalline films have been obtained by annealing.

ALE-deposited mixed oxides can be divided into two main categories, being either insulating dielectric oxides or transparent conductive oxides (TCOs) (Table 2).^{117,118} The first dielectric mixed oxide, $\text{Al}_2\text{O}_3\text{-TiO}_2$ (ATO), which was intended for the preparation of insulating films for TFEL devices (Figure 4) was prepared from $\text{AlCl}_3/\text{H}_2\text{O}$ and $\text{TiCl}_4/\text{H}_2\text{O}$.^{119,120} Leppänen *et al.*¹²¹ used 2-methyl-2-propanol instead of water as an oxygen source. In addition to the dielectric films listed in Table 2, mixed oxide films such as Al-Ti-O, Zr-Al-O, Hf-Al-O, Zr-Ti-O, Hf-Ti-O and Zr-Si-O have been deposited using metal alkoxides as oxygen sources.⁷⁴

Table 2. ALE-deposited dielectric and conductive oxide thin films with complex structure.

	Precursors	Dep. T / °C	Ref.
Dielectric oxides			
Al ₂ O ₃ - TiO ₂ (ATO)	AlCl ₃ /TiCl ₄ /H ₂ O	450-500	119,122
	(CH ₃) ₃ Al/TiCl ₄ /H ₂ O	250	123
Ta ₂ O ₅ - Al ₂ O ₃	TaCl ₅ /AlCl ₃ /H ₂ O	300	110
MgO-Al ₂ O ₃	(C ₅ H ₅) ₂ Mg/(CH ₃ CH ₂) ₃ Al/H ₂ O	600-750	94
ZrO ₂ - TiO ₂	ZrCl ₄ /Ti(OCH(CH ₃) ₂) ₄	200-300	76
Bi-Ti-O	(C ₆ H ₅) ₃ Bi/Ti(OCH(CH ₃) ₂) ₄ /H ₂ O ₂	200-325	124
Ta ₂ O ₅ - Nb ₂ O ₅	TaCl ₅ or Ta(OCH ₂ CH ₃) ₅ /	300,325	112
	Nb(OCH ₂ CH ₃) ₅ /H ₂ O		
Ba-Ti-O	Ba(thd) ₂ /Ti(O ⁱ Pr) ₄ /N ₂ O	400-500	125
Conductive oxides			
In ₂ O ₃ :Sn (ITO)	InCl ₃ /SnCl ₄ /H ₂ O or H ₂ O ₂	300-500	70,91,126
ZnO:B	(CH ₃ CH ₂) ₂ Zn/B ₂ H ₆ /H ₂ O	105-165	127,128
ZnO:Ga	(CH ₃ CH ₂) ₂ Zn/(CH ₃) ₃ Ga/H ₂ O	100-250	129
ZnO:Al	(CH ₃) ₂ Zn/(CH ₃) ₃ Al/H ₂ O	120-350	130,131
SnO ₂ :Sb	SnCl ₄ /SbCl ₄ /H ₂ O	500	132,133
SnO ₂ :F	(CH ₃ CH ₂) ₄ Sn/BF ₃ /N ₂ O ₄	250	67

Published studies concerning the ALE deposition of ternary oxides can be divided into two main groups. The first group consists of ternary compounds formed by lanthanum and the oxide of a transition metal (i.e. Co, Ni or Mn). These perovskite-type compounds have been deposited using the respective metal β -diketonate chelates together with ozone. In the case of LaNiO₃ and LaMnO₃ a narrow plateau in the growth rate was observed, indicating an ALE-window. Rather low growth rates of 0.08 Å(cycle)⁻¹ for LaNiO₃ and about 0.1-0.2 Å(cycle)⁻¹ for LaMnO₃ were obtained at 215-250 °C and 250-300 °C, respectively. In the case of LaMnO₃, the growth process was not completely ideal, as the film growth rate increased from about 0.1 to 0.4 Å(cycle)⁻¹ when the deposition temperature was raised from 200 to 400 °C. LaMnO₃ films also exhibited thickness nonuniformities.

Table 3. ALE deposition processes for ternary oxides

	Precursors	Dep. T/ °C	Ref.
LaCoO ₃	La(thd) ₃ /Co(thd) ₂ /O ₃	200-400	10
LaMnO ₃	La(thd) ₃ /Mn(thd) ₂ /O ₃	200-400	134
LaNiO ₃	La(thd) ₃ /Ni(thd) ₂ /O ₃	150-400	135
SrTiO ₃	Sr(C ₅ ⁱ Pr ₃ H ₂) ₂ /Ti(O ⁱ Pr) ₄ /H ₂ O	250-325	63,64
BaTiO ₃	Ba(C ₅ Me ₅) ₂ /Ti(O ⁱ Pr) ₄ /H ₂ O	275	64

The second group of ALE deposited ternary oxides consists of alkaline earth metal titanates deposited from organometallic precursors. SrTiO₃ thin films have been deposited from Sr(C₅ⁱPr₃H₂)₂, Ti(OⁱPr)₄ and H₂O at 250-325 °C.⁶³ At these temperatures, however, the strontium precursor decomposes, resulting in a slightly nonideal ALE process. The growth rate was 0.5-1.7 Å(cycle)⁻¹ depending on the deposition temperature, pulsing time of Sr(C₅ⁱPr₃H₂)₂ and pulsing ratio of the metal precursors. Stoichiometric films were obtained by varying the (Sr-O)/(Ti-O) pulsing ratio. (100) oriented films were obtained when the (Sr-O) to (Ti-O) precursor pulsing ratio was 2/3-1/1. Crystallinity increased with increasing film thickness and deposition temperature. Films deposited contained 0.4-1.2 at% hydrogen and 0.1-0.3 at% carbon.

BaTiO₃ thin films have been deposited from Ba(C₅Me₅)₂, Ti(OⁱPr)₄ and H₂O at 275 °C.⁶⁴ The growth rate was about 0.5 Å(cycle)⁻¹, but the deposition process suffered from problems in reproducibility due to the facile thermal decomposition of Ba(C₅Me₅)₂. As-deposited films were amorphous, and crystalline (101/110) oriented films were obtained by annealing at 500 °C.

1.3 Concluding remarks on ALE-deposited oxide thin films

Several processes for oxide films have been proposed ever since the introduction of the ALE method. Since TFEL displays were the first industrial application of the ALE technology⁸⁶ the main interest during the first decade was the production of high-quality electroluminescent sulphide films, although processes for certain dielectric films were also developed using metal halides and water as precursors.^{81,84,92} A turning point for oxide ALE studies occurred in the 1990s. At first there was an increase in the number of studies on ALE processes utilising halides and water. Later on, new precursor combinations such as alkoxides and water as well as β -diketonates and ozone were introduced. More recently, cyclopentadienyl type organometallics have been successfully employed in ALE processes.

A number of ALE processes for good-quality oxide films are now available. The unique feature of the ALE method, self-limiting growth, enables thin film deposition even onto large area, high aspect ratio or porous substrates.^{97,136-138} One promising application of ALE is in microelectronics where the current interest is in high permittivity gate dielectrics to replace SiO_2 ($\epsilon = 3.9$) in metal-oxide-semiconductor field-effect transistors (MOSFETs).¹³⁹ Here the ALE method would appear to be the method of choice to produce high-quality oxide films such as Al_2O_3 , ZrO_2 and HfO_2 .^{140,141} Recently other applications have been considered for the ALE deposited oxide materials in the field of optics¹⁴² and magnetic recording heads.⁹⁹

2. Experimental

This section presents the general methods for precursor analysis as well as depositions and analysis of films. More detailed descriptions can be found in the original publications (I-VIII).

2.1 Preparation and analysis of precursors

The precursors used in this study were either synthesised by previously reported methods or they were commercially available. All synthesised precursors were purified by sublimation under reduced pressure. The volatility of the precursors was routinely checked by simultaneous TG/DTA measurements (Seiko SSC 5200) in the temperature range from 20 to 400 °C. A small nitrogen (99.999%) flow and 1-3 mbar pressure were used to simulate the ALE deposition conditions.¹⁴³ All compounds except Mg(thd)₂ volatilised before melting.

Table 4. Origin and sublimation onset temperatures of the precursors.

Precursor	Melting point °C	Sublimation onset °C	Ref. for synthesis or manufacturer
Sc(thd) ₃		150-155	30
Y(thd) ₃		145-150	30
Y(thd) ₃ (bipy)		150-155	46
Y(thd) ₃ (phen)		210-215	46
La(thd) ₃		190-195	30
Zr(thd) ₄		200-205	144
Cp ₂ ZrCl ₂		155-160	Strem Chemicals Inc.,93-4002
Cp ₂ Zr(CH ₃) ₂		95-105	145
Al(acac) ₃		145-150	30
Mg(thd) ₂	128	170-175	30
(C ₅ H ₅) ₂ Mg		80-85	Morton Ltd or ref. 146

2.2 Film deposition

Thin films were deposited in a commercial (ASM Microchemistry F-120) or an experimental^{81,147} flow-type hot-wall atomic layer epitaxy reactor. Depositions were carried out at 1-3 mbar pressure using nitrogen (99.999%) as a purging and carrier gas. Precursors were alternately pulsed from the heated sources into the reactor chamber using inert gas valving. Solid β -diketonate-type precursors as well as organometallic zirconium and scandium precursors were evaporated from open glass or aluminium crucibles inside the reactor, while $(C_5H_5)_2Mg$ was evaporated in an external container and transported through heated lines to the reactor (Figure 7). Depending on the metal precursor selected, H_2O , H_2O_2 or O_3 was used as oxygen source. Water or hydrogen peroxide was evaporated in an external reservoir and transported to the reactor without additional bubbling. Ozone was generated from O_2 (99.999%) in an ozone generator (Fischer model 502) (Figure 7). The concentration of ozone in oxygen was about 3.5% and no additional carrier gas was used for the mixture, which had a flow rate of 50-75 sccm. Typically soda lime and Si(100) substrates were used, but sapphire and single crystalline $SrTiO_3$ were also employed in the $LaAlO_3$ film depositions. All substrates were ultrasonically cleaned in ethanol and water. Native oxide on Si(100) substrate was not removed. Total deposition area was 100-150 cm^2 depending on the reactor employed.

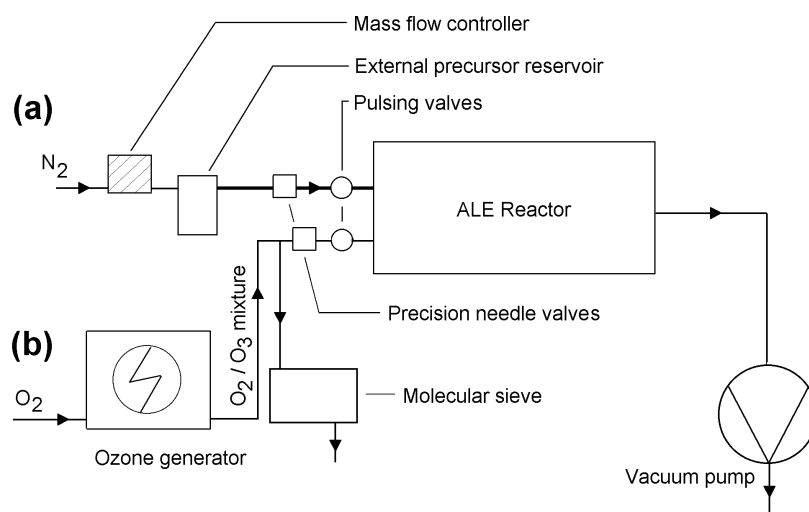


Figure 7. Schematic view of the external sources used for the transportation of (a) $(C_5H_5)_2Mg$ and (b) O_3 into the ALE reactor. For H_2O and H_2O_2 , a line similar to the (a) without N_2 carrier gas was utilised.

2.3 Characterisation of films

Thicknesses of the deposited thin films were measured by profilometry (Sloan Dektak 3030ST from Veeco Instruments) or by the optical fitting method for reflectance/transmittance spectra as described by Ylilammi and Ranta-aho.¹⁴⁸ The spectra were measured with a Hitachi U-2000 spectrophotometer. Steps for profilometric thickness determination were prepared by etching using a standard procedure with photoresist and dilute hydrochloric acid.

Crystalline phases and their orientations in the deposited films were determined by X-ray diffraction with Cu K α radiation in a Philips MPD 1880 diffractometer. AFM measurements were performed at the Laboratory of Physics of the Helsinki University of Technology. A Nanoscope III atomic force microscope (Digital Instruments) was operated in tapping mode with a scanning rate of 1-2 Hz. To check the uniformity of the samples, several 10-20 μm scans were performed from different parts of the samples. Final images were acquired with a scanning area of $2 \times 2 \mu\text{m}^2$. Roughness values were calculated as root mean square (rms) values.

Carbonate- and hydroxide-type impurities were analysed by FTIR using a Nicolet Magna-IR 750 instrument. Transmission spectra were collected for the samples deposited onto Si(100) substrates. Silicon substrate peaks were subtracted from the raw spectra.

Both elemental concentrations and their depth distributions were determined by time-of-flight elastic recoil detection analysis (TOF-ERDA) at the Accelerator Laboratory of the University of Helsinki. For the TOF-ERDA studies, a 53 MeV $^{127}\text{I}^{10+}$ ion beam was used, generated by a 5 MV tandem accelerator EGP-10-II. Both velocity and energy of the recoiled atoms are determined using timing gates and a charged particle detector, which enables the differentiation of masses. For heavy recoils, energy spectra were obtained from the TOF signal and for hydrogen from the charged particle detector.

3. Results and discussion

In this chapter the results of the ALE deposited binary Sc_2O_3 , Y_2O_3 and La_2O_3 thin films and the ternary oxide systems YSZ and LaAlO_3 are summarised. The main focus is on the deposition of binary Group 3 oxides reported in chapter 3.1 while the deposition of other binary oxides, namely ZrO_2 and MgO , are briefly reported in chapters 3.2.1.1 and 3.2.2.1, respectively.

3.1 Deposition of Group 3 oxide thin films

Although the ALE deposition of Y_2O_3 ⁹ and La_2O_3 ¹⁰ had been demonstrated before this work, no systematic study had been carried out on the deposition parameters and film properties. The deposition processes for binary Group 3 oxide thin films, namely Sc_2O_3 , Y_2O_3 and La_2O_3 , will be presented here, and general trends observed for the processes based on the β -diketonate chelates and ozone will be discussed. A more comprehensive discussion of the depositions can be found in publications I-III.

3.1.1 Sc_2O_3

ALE-type growth of Sc_2O_3 was achieved with two processes, employing the precursor combination $\text{Sc}(\text{thd})_3/\text{O}_3$ or $(\text{C}_5\text{H}_5)_3\text{Sc}/\text{H}_2\text{O}$. In the case of the β -diketonate-type precursor and ozone, self-controlled growth with a deposition rate of $0.125 \text{ \AA}(\text{cycle})^{-1}$ was obtained at 335-375 °C. The deposition rate of Sc_2O_3 from $\text{Sc}(\text{thd})_3/\text{O}_3$ was very low and, to increase it, an additional oxygen source was used after the O_3 pulse (Figure 8b). 1.0-3.0 s pulse of H_2O_2 after the O_3 pulse increased the growth rate to $0.14 \text{ \AA}(\text{cycle})^{-1}$. This represents a 12% increase in the deposition rate, which is a slightly smaller increase than that obtained in the NiO depositions (15-20%) where $\text{Ni}(\text{thd})_2/\text{O}_3$ was used together with H_2O as an additional oxygen source.⁷

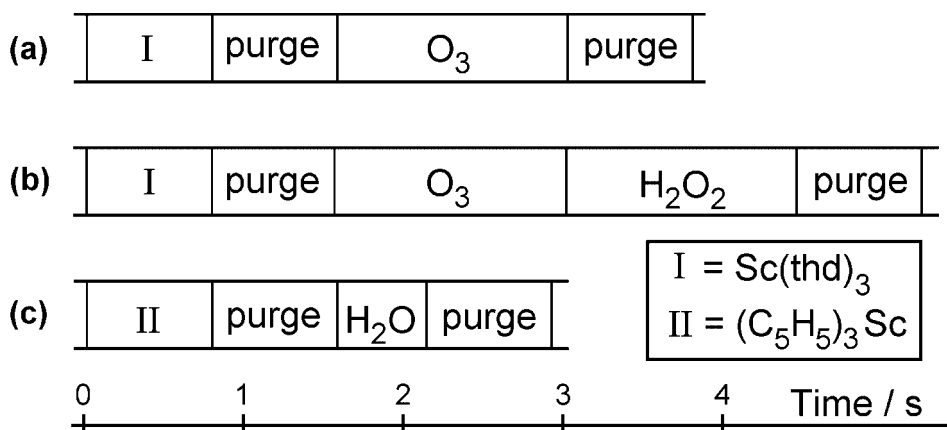


Figure 8. ALE pulsing sequences for Sc₂O₃ film depositions using (a) β-diketonate and ozone, (b) additional oxygen source in the β-diketonate process and (c) organometallic precursor of cyclopentadiene type together with water.¹

Sc₂O₃ films were also deposited from (C₅H₅)₃Sc and H₂O. A growth rate of 0.75 Å(cycle)⁻¹ was obtained at 250-350 °C. The growth rate decreased when the deposition temperature was increased above 350 °C. Films deposited at 450 °C and above were brownish-black indicating severe carbon contamination. Over 18 at% of carbon was measured by TOF-ERDA in the films deposited at 500 °C.¹ Crystallinity of the Sc₂O₃ thin films deposited from (C₅H₅)₃Sc/H₂O as precursors was lower than that of films deposited from Sc(thd)₃/O₃. The (222), (400) and (440) reflections were most intense when Sc₂O₃ films were deposited onto Si(100).

3.1.2 Y₂O₃

Y₂O₃ growth rate was 0.23 Å(cycle)⁻¹ at 250-350 °C when Y(thd)₃ and O₃ were used as precursors. The growth rate remained constant when at least a 0.8 s pulse for Y(thd)₃ and a 1.0 s pulse for O₃ were used, indicating self-controlled growth. The growth rate increased at higher deposition temperatures and at 425 °C it was almost same (0.38 Å(cycle)⁻¹) as that observed by Mölsä *et al.*⁹ (0.40 Å(cycle)⁻¹). Use of adducted Y(thd)₃ precursors (Scheme 2) employed earlier in CVD resulted in a similar growth rate. In the case of Y(thd)₃(bipy)/O₃, the ALE growth rate was equal to that of Y(thd)₃/O₃, but for Y(thd)₃(phen)/O₃ it was slightly lower, *i.e.* 0.22 Å(cycle)⁻¹.

3.1.3 La₂O₃

With the La(thd)₃/O₃ precursor combination, constant growth rate of 0.36 Å(cycle)⁻¹ was obtained at 225-275 °C.^{III} According to impurity analyses, these films were La₂O₂CO₃, evidently because of the low deposition temperature together with the tendency of La₂O₃ to react with carbon dioxide.¹⁴⁹ When the temperature was raised above 275 °C the growth rate increased and crystalline cubic La₂O₃ phase was observed (Figure 9). An additional annealing of as-deposited films at 600-900 °C was required to obtain crystalline hexagonal La₂O₃ films.

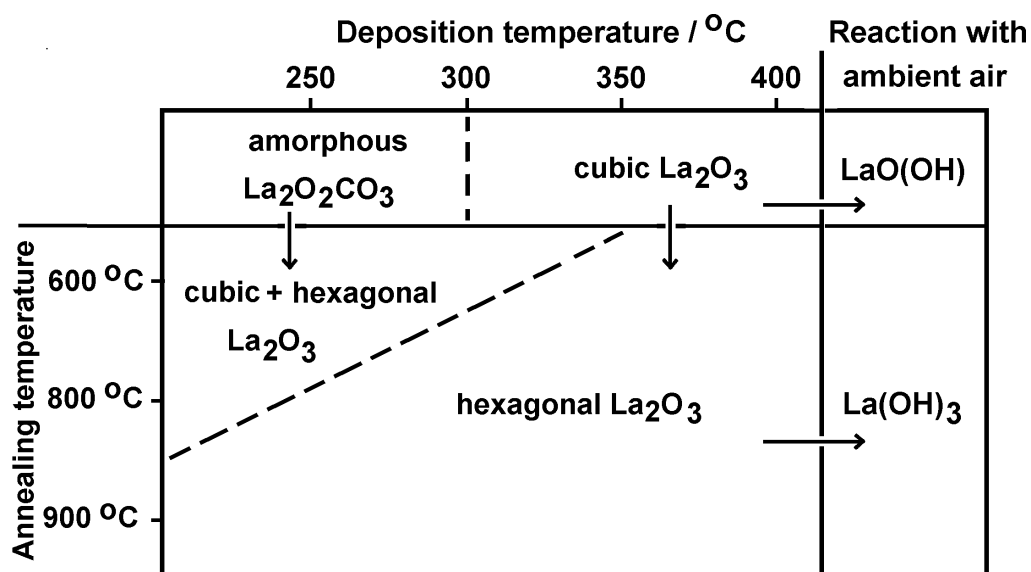


Figure 9. Summary of the effects of deposition and annealing temperatures on La₂O₃ thin film composition.^{III}

Although growth rate increased with deposition temperature, films were uniform without a notable thickness profile when depositions were carried out at 425 °C or below. When the deposition temperature was raised above 425 °C, uncontrolled precursor decomposition resulted in nonuniform films. Film thickness was linearly dependent on the number of reaction cycles at 250, 350 and 375 °C regardless of the pulsing time of the precursors, indicating controlled growth at higher temperatures as well as at the ALE window temperatures.

3.1.4 General trends in ALE deposition processes for Group 3 oxides

ALE deposition rates for the Group 3 oxides obtained with metal β -diketonates as precursors decrease in order of diminishing ionic size, *viz.* $\text{La} > \text{Y} > \text{Sc}$.^{I-III} Deposition rates inside ALE windows were $0.125 \text{ \AA}(\text{cycle})^{-1}$ for $\text{Sc}(\text{thd})_3/\text{O}_3$, $0.23 \text{ \AA}(\text{cycle})^{-1}$ for $\text{Y}(\text{thd})_3/\text{O}_3$ and $0.36 \text{ \AA}(\text{cycle})^{-1}$ for $\text{La}(\text{thd})_3/\text{O}_3$ (Figure 10).

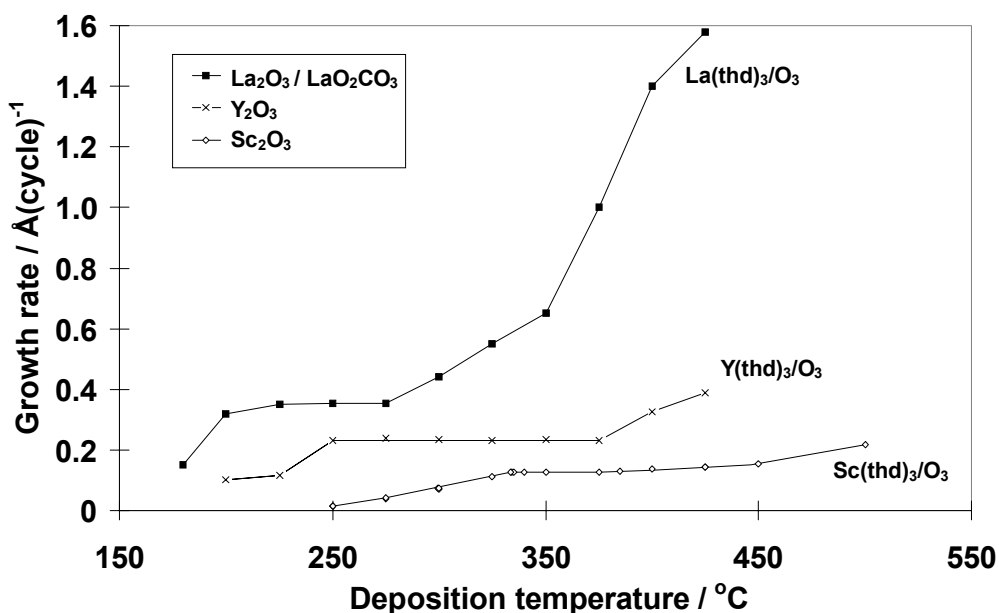


Figure 10. Growth rates of Group 3 binary oxides using $\text{M}(\text{thd})_3$ and O_3 as precursors. ($\text{M}=\text{Sc}, \text{Y}, \text{La}$).^{I-III} In the $\text{La}(\text{thd})_3/\text{O}_3$ process, $\text{La}_2\text{O}_2\text{CO}_3$ was formed below $300 \text{ }^\circ\text{C}$ and La_2O_3 only at higher temperatures.

The temperature range of the constant growth rate for Group 3 oxides, shifted towards lower temperatures when heavier compounds were deposited, being lowest for La_2O_3 (Figure 10). Increase in the deposition rate above the ALE window also depended on the precursor used. A possible explanation for the different behaviour in the growth rates and ALE window positions is the enhanced thermal stability of the β -diketonate complexes with decreasing ionic radius of the metal ion.¹⁵⁰

It should be noted that smooth Sc_2O_3 films were obtained only when deposited at 375 °C or below, whereas ALE depositions of other Group 3 oxides produced smooth films also above the ALE window up to 425 °C. This may be due to a partially decomposed precursor in the gas phase, possibly $\text{M}(\text{thd})_2$ ($\text{M}=\text{Sc}, \text{Y}, \text{La}$), which may still be chemisorbed in a self-limiting manner.^{II,III} Another possibility is that $\text{M}(\text{thd})_3$ loses at least one ligand at the substrate surface. In the case of $\text{Y}(\text{thd})_3$, high temperature mass spectrometric and FTIR analyses showed that the amount of $\text{Y}(\text{thd})_2$ increased when temperature was raised above 300 °C and $\text{Y}(\text{thd})_2$ was the main component in the gas phase above 400 °C.^{151,152} Unfortunately, to the best of our knowledge, no similar gas phase studies have been carried out for $\text{Sc}(\text{thd})_3$ and $\text{La}(\text{thd})_3$. However, $\text{Sc}(\text{thd})_3$ has recently been studied at 20-350 °C by coupled TG-QMS.¹⁵³ Similarly as in the case of MS studies of $\text{Y}(\text{thd})_3$,^{II,151} $\text{Sc}(\text{thd})_2^+$ was major Sc-containing species observed.^{I,153}

In an ALE process, the growth rate partly depends on the size of the precursor adsorbed on the surface. It has been proposed that steric hindrances due to the bulky β -diketonate-type precursors lower the growth rate.¹⁵⁴ Thus, when the ligand for the same centre ion was changed to a smaller one, *i.e.* thd to acac, the ALE growth rate increased. If growth rates of ALE-deposited oxide materials are evaluated against the effective ionic size, it can be concluded that the ALE growth rate depends both on the ionic size of the metal and the size of the precursor ligand (Figure 11). It is interesting to note that although the larger members of Group 2 and 3 metals, *e.g.* Sr, Ba and La, have a tendency to produce carbonate-containing films,^{III,155} the growth rate appears to be comparable to the other deposition processes.

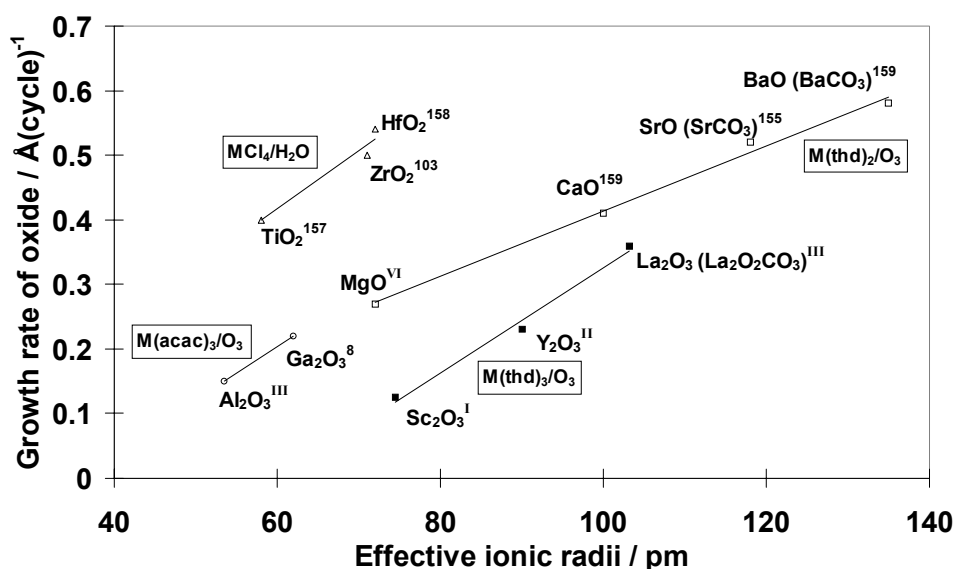


Figure 11. ALE growth rates of oxides and selected carbonates as a function of the effective ionic radius¹⁵⁶ of the corresponding metal ion.

As noted, although O₃ is a strong oxidiser, M-O-C (M = Sr, Ba, La) bonds still remain in the film, especially when depositions are carried out at low temperatures. The increase in the carbonate contamination level is at least partially due to the instability and the basicity of these oxides.^{III} This problem mostly concerns depositions from β-diketonate type precursors, because direct ALE deposition of SrO appears to be possible from organometallic precursors.⁶³

All Group 3 oxides are basic and tend to absorb CO₂. Basicity decreases in the order La > Y > Sc.¹⁶⁰ This is a possible explanation for the observed increase in carbonate-type contamination, which originates from the β-diketonate ligand during the deposition process, leading to the formation of LaO₂CO₃.^{III} According to TOF-ERDA, carbon contamination in the Sc₂O₃ films was below 0.1 at% regardless of the deposition temperature (Figure 12). Y₂O₃ thin films deposited within the ALE window (250-375 °C) contained 5.0-1.0 at% carbon depending on the deposition temperature. La(thd)₃ together with O₃ yielded in the ALE window (225-275°C) La₂O₂CO₃ films corresponding to 11.5 at% carbon.

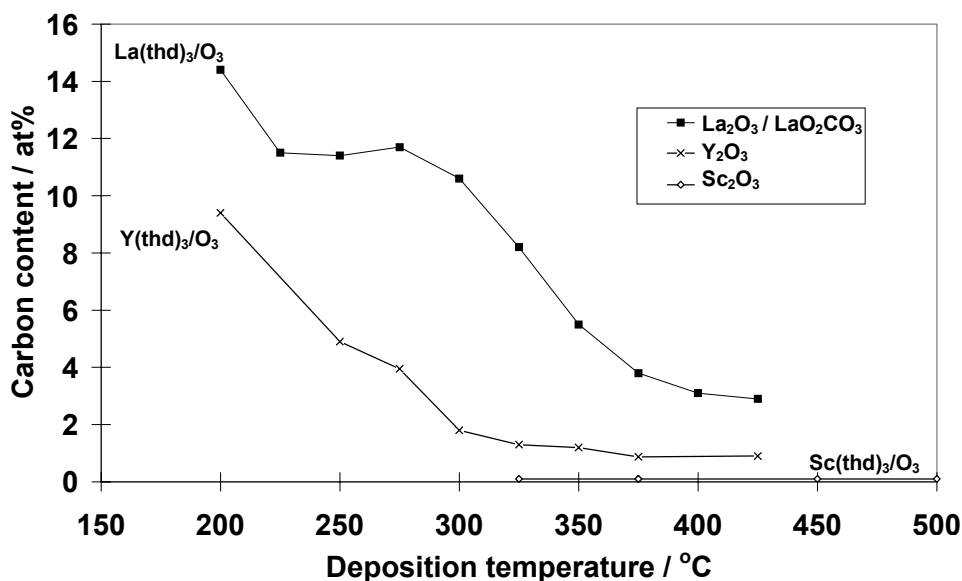


Figure 12. Carbon content of Group 3 binary oxides deposited by ALE from $M(\text{thd})_3/\text{O}_3$ ($M = \text{Sc}, \text{Y}, \text{La}$).

3.1.5 Properties of binary films

The main interest of the present investigation was the development of deposition processes for binary oxide thin films. Thus, analysis and characterisation of the obtained films were mostly focused on materials properties such as crystallinity and surface morphology. In addition, in collaboration with other groups, a detailed analysis of the impurities was carried out by advanced analytical techniques such as TOF-ERDA and XPS.

3.1.5.1 Film crystallinity

Binary films deposited at low temperatures from β -diketonate and O_3 were only slightly crystalline and the crystallinity increased with deposition temperature when β -diketonates and O_3 were used as precursors.

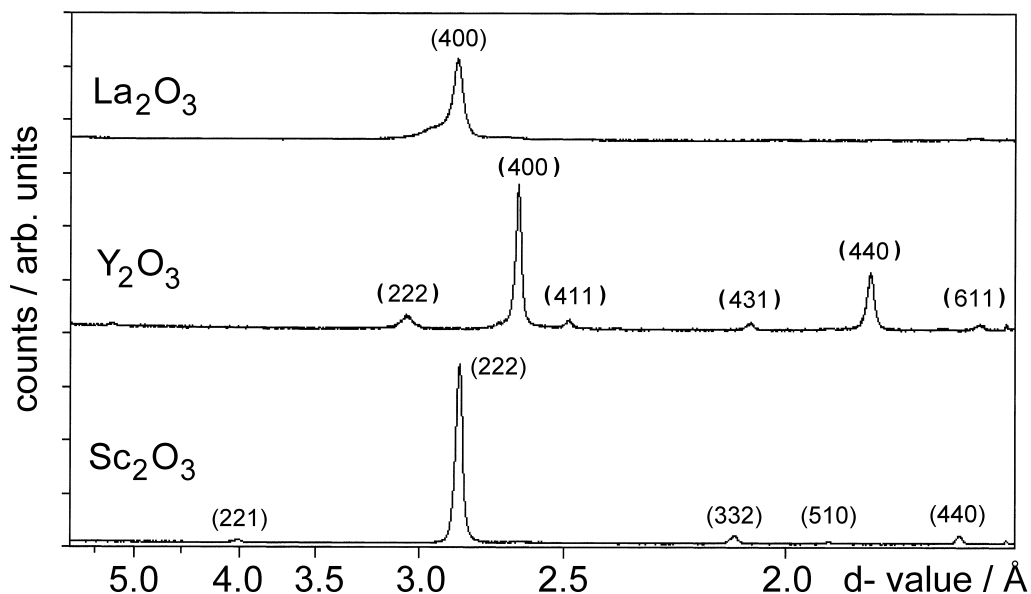


Figure 13. XRD patterns of 150 nm thick binary Group 3 oxides. Deposition temperatures were 375, 350 and 350 °C for Sc_2O_3 , Y_2O_3 and La_2O_3 , respectively.

Sc_2O_3 thin films were crystalline with (111) as preferred orientation when depositions were carried out at 300 °C by using $\text{Sc}(\text{thd})_3$ and O_3 as precursors.^I (211), (332), (510) and (440) reflections were also observable (Figure 13).

Y_2O_3 films were only slightly crystalline when deposited on Si(100) substrate below 275 °C, but they were amorphous when deposited on soda lime substrates below 350 °C.^{II} Intensities of the (400) and (440) reflections were highest in the films deposited inside the ALE window at 275-375 °C. At higher temperatures the intensity of the (222) reflection increased, and films had a preferential (111) orientation when deposited at 425 °C.

The use of $\text{La}(\text{thd})_3$ and O_3 as precursors resulted in amorphous $\text{La}_2\text{O}_2\text{CO}_3$ films when deposited below 300 °C.^{III} At higher temperatures, carbon content decreased (Figure 12) and polycrystalline cubic La_2O_3 was observed. Films deposited above 350 °C were (100) oriented.

3.1.5.2 Surface morphology

Surface morphology of the films was studied by AFM. Although films were deposited onto both soda lime glass and Si(100), only the latter substrate was used for systematic study. Y_2O_3 films on soda lime glass substrates were relatively smooth when deposited at 350 °C or below (Figure 14),^{II} because the Y_2O_3 was then amorphous. It has been noted earlier that when the deposition temperature is increased above the temperature where phase transition from amorphous to crystalline occurs, film roughness increases.²⁴

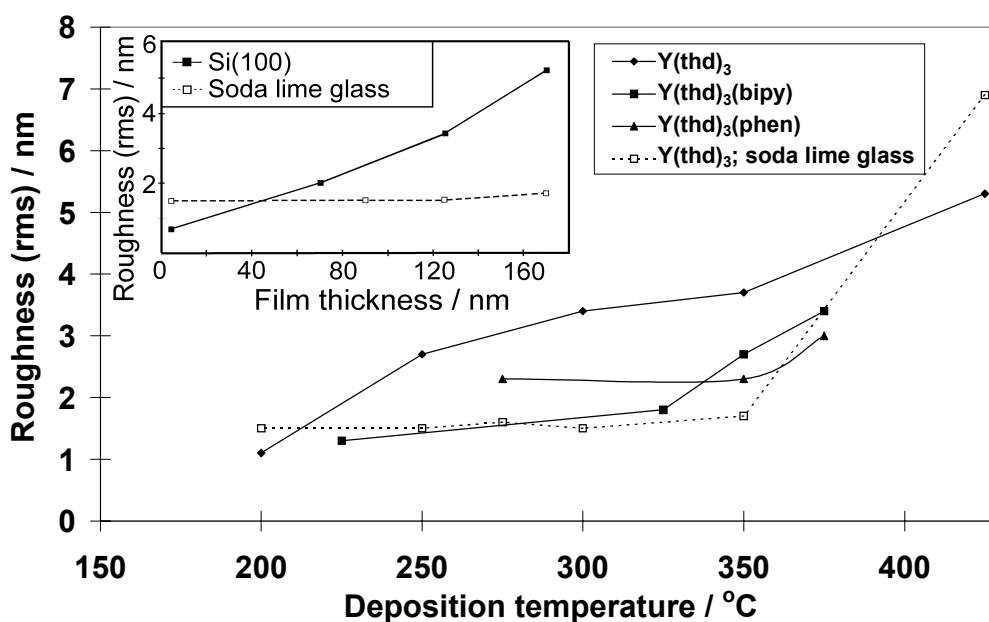


Figure 14. Roughness of 120-140 nm thick Y_2O_3 films deposited at various temperatures from β -diketonate-type precursors and ozone. The inset illustrates the roughness as a function of film thickness when depositions were carried out at 350 °C with soda lime or Si(100) as substrate.^{II}

The film roughness on Si(100) substrate were dependent on the film thickness (Figure 14, inset). Samples for AFM measurements were therefore selected to have equal thickness. Thicknesses of investigated films were 70-80 nm for Sc_2O_3 ,^I 120-140 nm for Y_2O_3 ^{II} and 70-75 nm for La_2O_3 .^{III} Characteristic of all the deposited films was that they were uniform. Grain sizes were estimated from the AFM images. As can be seen in Figure 15, grain size was smaller for the Y_2O_3 and La_2O_3 films than for the Sc_2O_3 film. When films with a thickness of about 70 nm were deposited at 350 °C, grain sizes were about 140-160 nm for Sc_2O_3 , 100-120 nm for Y_2O_3 and 80-100 nm for La_2O_3 .

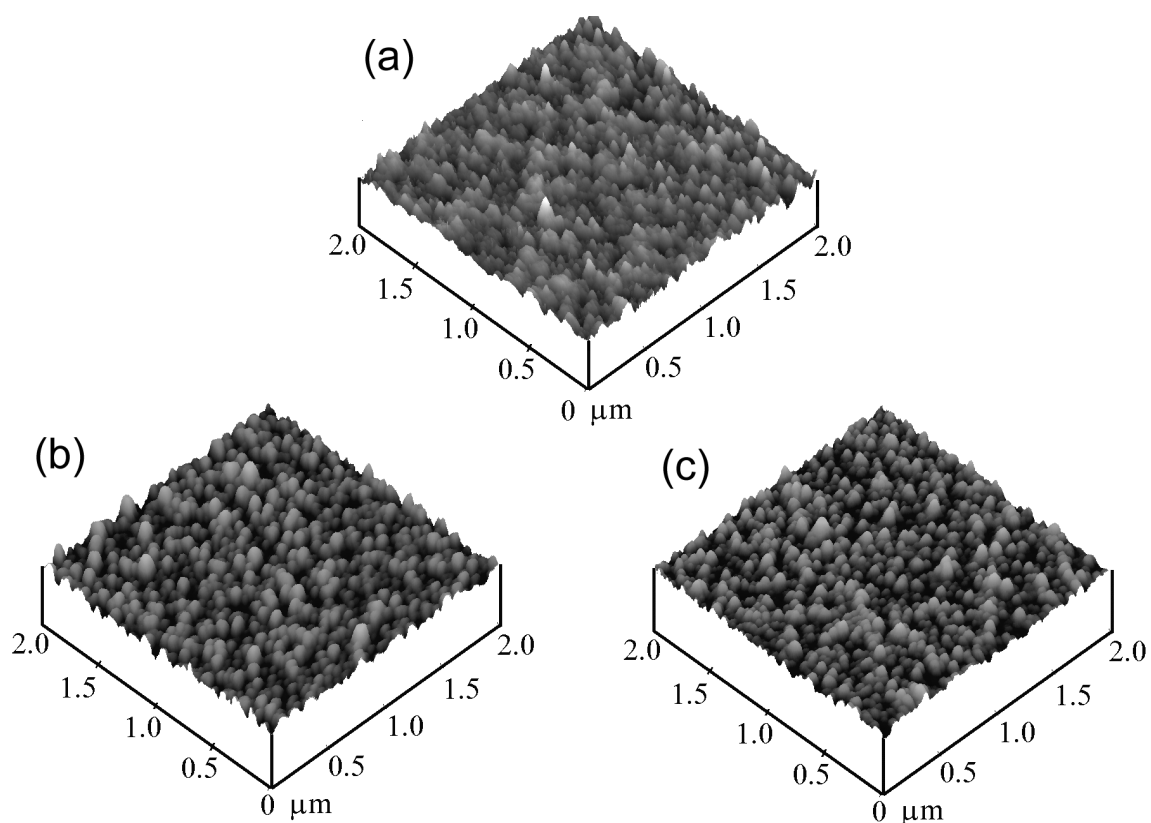


Figure 15. AFM images of the (a) Sc_2O_3 , (b) Y_2O_3 and (c) La_2O_3 films. Deposition temperature was $350\text{ }^\circ\text{C}$ and film thickness about 70 nm .

For Sc_2O_3 thin films, roughness remained more or less constant: about $1.3\text{--}1.7\text{ nm}$ when films were deposited below $375\text{ }^\circ\text{C}$, *i.e.* at the ALE window or below (Figure 16). Roughness increased rapidly when deposition was carried out at higher temperatures, being at $500\text{ }^\circ\text{C}$ about 9 nm .

Roughness of Y_2O_3 films increased from 1.1 to 3.7 nm as the deposition temperature was raised from 200 to $350\text{ }^\circ\text{C}$. It should be noted that these systematically studied films were thicker than Sc_2O_3 and La_2O_3 films, so roughness values are not directly comparable. However, Y_2O_3 films with a thickness of 70 nm (Figure 15b) had a roughness value of 1.7 nm , which is in the same range as for the other Group 3 oxide films of thickness of about 70 nm deposited at $350\text{ }^\circ\text{C}$. Adducted yttrium precursors produced films with a slightly lower roughness, perhaps due to the somewhat lower crystallinity.^{II} Regardless of the precursor or substrate, roughness increased when the deposition temperature was increased above $350\text{ }^\circ\text{C}$.

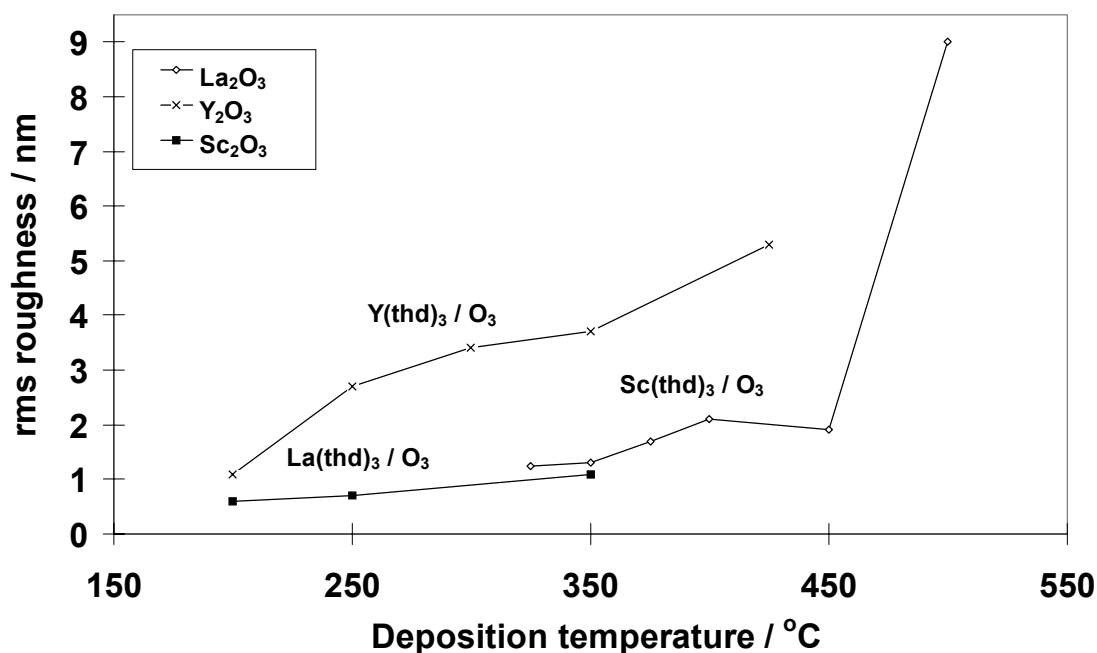


Figure 16. Roughness of the deposited Group 3 oxides where $M(\text{thd})_3$ and ozone were used as precursors ($M = \text{Sc}, \text{Y}, \text{La}$). Film thicknesses were 70-80 nm for Sc_2O_3 , 120-140 nm for Y_2O_3 and 70-75 nm for La_2O_3 .

When the La_2O_3 deposition temperature was increased from 200 to 250 °C, film roughness remained constant at 0.6-0.7 nm. When the deposition temperature was increased further, the film roughness increased slightly, reaching a value of 1.1 nm at 350 °C. It is interesting to note that, unlike that of other ALE-deposited Group 3 oxides, La_2O_3 film roughness remained relatively constant as film thickness was increased. Even films with a thickness of ~300 nm had a low roughness of 1.2 nm on Si(100) substrates.^{III}

3.2 Deposition of ternary thin films containing Y_2O_3 or La_2O_3 .

Several ternary and more complex compounds containing Sc_2O_3 , Y_2O_3 and La_2O_3 have been processed as thin films by other deposition methods than ALE (see references in publications I-III). Although ternary oxide thin films have also been deposited by ALE, Group 3 oxides have mostly been deposited by ALE as binary compounds. It is interesting to note that ALE deposition of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been attempted at 450 °C.¹⁶¹ Difficulties in the reproducibility due to the decomposition of β -diketonate-type precursors, mainly $\text{Cu}(\text{thd})_2$, have prevented use of this ALE process.

An important part of the present investigation was study of the ALE deposition of the ternary films containing Y_2O_3 and La_2O_3 , namely yttria-stabilised zirconia^V and lanthanum aluminate.^{VIII}

3.2.1 Yttria-stabilised zirconia

As noted above, ZrO_2 thin films have successfully been deposited at 275, 300 and 500 °C from ZrCl_4 and water.¹⁰³⁻¹⁰⁷ However, before the present work, no comprehensive study had been made of the ALE deposition of ZrO_2 in a wider temperature range using different precursors. In this work ZrO_2 processes were studied with the aim of developing a well-documented process for the deposition of yttria-stabilised zirconia thin films.

3.2.1.1 ZrO₂

A relatively low deposition rate of 0.24 Å(cycle)⁻¹ was obtained for the Zr(thd)₄/O₃ process, compared with a deposition rate of about 0.5 Å(cycle)⁻¹ for processes based on organometallic precursors (Table 5).^{IV} The temperature region for surface-controlled deposition was also dependent on the zirconium precursor.

Table 5. ALE-window positions and deposition rates of ZrO₂ as a function of precursor combination.^{IV}

Process	ALE window / °C	Growth rate / Å(cycle) ⁻¹
Zr(thd) ₄ /O ₃	375-400	0.24
Cp ₂ ZrCl ₂ /O ₃	310-365	0.53
Cp ₂ Zr(CH ₃) ₂ /O ₃	275-350	0.55

Crystallinity of the ZrO₂ films was dependent on the precursor and deposition temperature. The Zr(thd)₄/O₃ process produced films that were only slightly crystalline. Both monoclinic (M) and orthorhombic (O) phases were observed regardless of the deposition temperature (Figure 17). ZrO₂ films deposited from Cp₂Zr(CH₃)₂/O₃ or Cp₂ZrCl₂/O₃ were weakly crystalline when deposited below 300 °C. With increasing deposition temperature, however, monoclinic M(-111) became the most intense reflection, exhibiting a maximum value in the films deposited at 350 °C from Cp₂Zr(CH₃)₂/O₃ and at 425-450 °C from Cp₂ZrCl₂/O₃. The O(111) reflection was observed over the whole temperature range of 250-500 °C. Metastable orthorhombic phase of ZrO₂ has been reported in thin films,¹⁶² and in bulk material only when the grain size is very fine (below 30 nm).¹⁶³

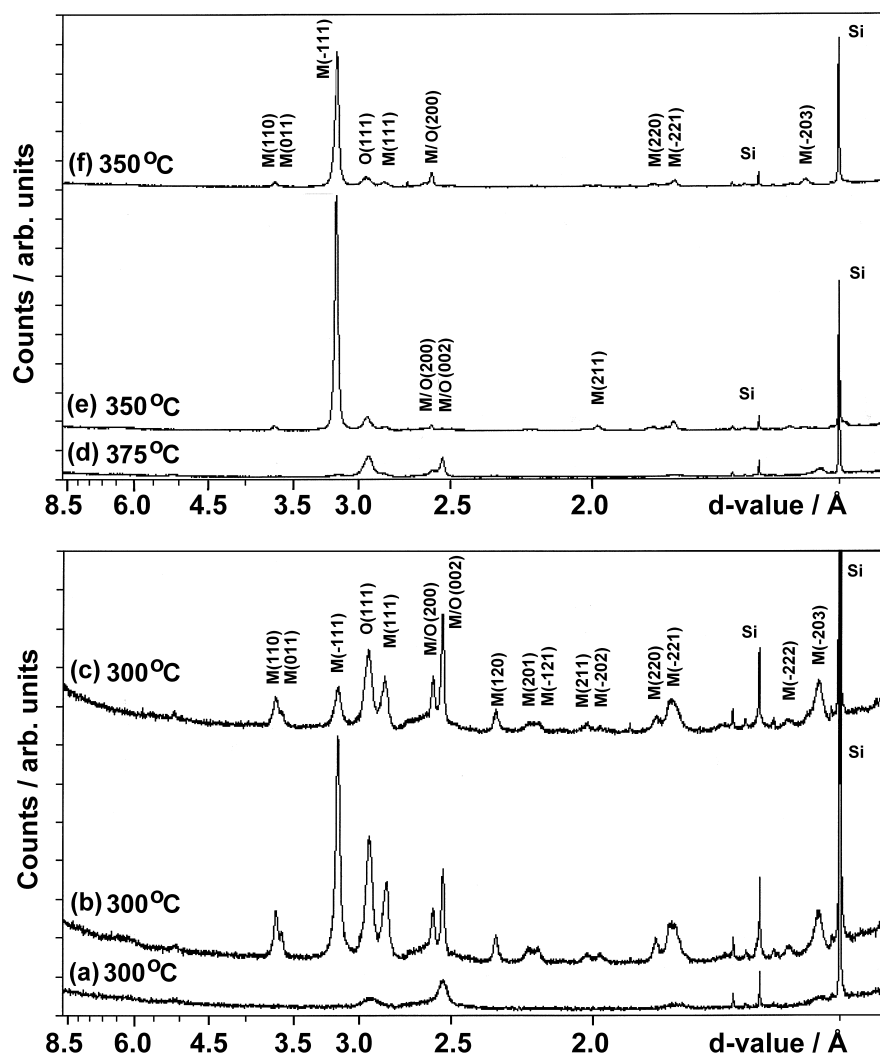


Figure 17. XRD patterns of ZrO_2 films deposited from (a, d) $\text{Zr}(\text{thd})_4/\text{O}_3$, from (b, e) $\text{Cp}_2\text{Zr}(\text{CH}_3)_2/\text{O}_3$ and from (c, f) $\text{Cp}_2\text{ZrCl}_2/\text{O}_3$ at selected temperatures.^{IV} Diffraction peaks were identified according to JCPDS cards 37-1484 for monoclinic phase and 37-1413 for orthorhombic phase.

The deposited films were nearly stoichiometric, but regardless of the process there was a slight excess of oxygen. Hydrogen and carbon impurity levels were low in all cases, *i.e.* in the range of 0.1-0.5 at% for hydrogen and 0.2-0.5 at% for carbon depending on the precursor. The presence of chlorine impurities in the ZrO_2 films originating from $\text{Cp}_2\text{ZrCl}_2/\text{O}_3$ was studied by XRF. Earlier it has been found that, at lower temperatures, ALE deposition of oxide materials from metal chlorides may lead

into the incorporation of Cl impurities.^{24,25} For example, chlorine contamination in Group 4 oxide films was observed when deposition was made from TiCl₄/H₂O,²⁴ ZrCl₄/H₂O¹⁰⁷ and HfCl₄/H₂O.²⁵ According to XRF measurements, chlorine from Cp₂ZrCl₂/O₃ was not incorporated into the ZrO₂ films when depositions were carried out above 275 °C.^{IV} However, below 275 °C, 0.3-1.0 at% Cl was found. According to TOF-ERDA results, chlorine content was below the detection limit (0.07 at%) when ZrO₂ films were deposited at 300 °C or above.

3.2.1.2 Yttria-stabilised zirconia film deposition by ALE

Yttria-stabilised zirconia films were deposited using Zr(thd)₄, Cp₂Zr(CH₃)₂ and Cp₂ZrCl₂ as zirconium precursors and Y(thd)₃ as yttrium source. Films were deposited at 275-375 °C depending on the precursor (Table 6). Extensive studies with Y(thd)₃/O₃ : Cp₂Zr(CH₃)₂/O₃ and Y(thd)₃/O₃ : Cp₂ZrCl₂/O₃ precursor combinations were carried out at only one deposition temperature, at 350 °C and 300 °C, respectively. The YSZ film deposition rate was higher than the value calculated from the binary oxides would indicate.^{II,IV} the maximum growth rate was 10-23% higher depending on the precursor and pulsing ratio employed. One reason for this may be differences in the surface chemistry during ALE depositions.

Table 6. YSZ film deposition temperatures and yttrium oxide content and lattice parameter of YSZ films as a function of precursor pulsing ratio.^V

Precursors	Dep. T / °C	Pulsing ratio	Mol% Y ₂ O ₃	Lattice spacing / Å
Y(thd) ₃ Zr(thd) ₄	375	1:10 - 30:1	5.8 – 89	5.10 - 5.28
Y(thd) ₃ Cp ₂ Zr(CH ₃) ₂	310-365	1:2 - 30:1	8.3 - 82	5.12 - 5.26
Y(thd) ₃ Cp ₂ ZrCl ₂	275-350	1:5 - 60:1	5.5 - 88	5.09 - 5.28

Regardless of the deposition temperature and precursor, YSZ films had the crystalline cubic structure when the pulsing ratios listed in Table 6 were used. (100) orientation was preferred except in the thinner films (<60 nm) deposited from the $Zr(thd)_4/O_3 : Y(thd)_3/O_3$ precursor combination, which were (111) oriented. Regardless of the precursor combination and deposition temperature, minor intensity (111), (211) and (311) reflections were also observed (Figure 18).

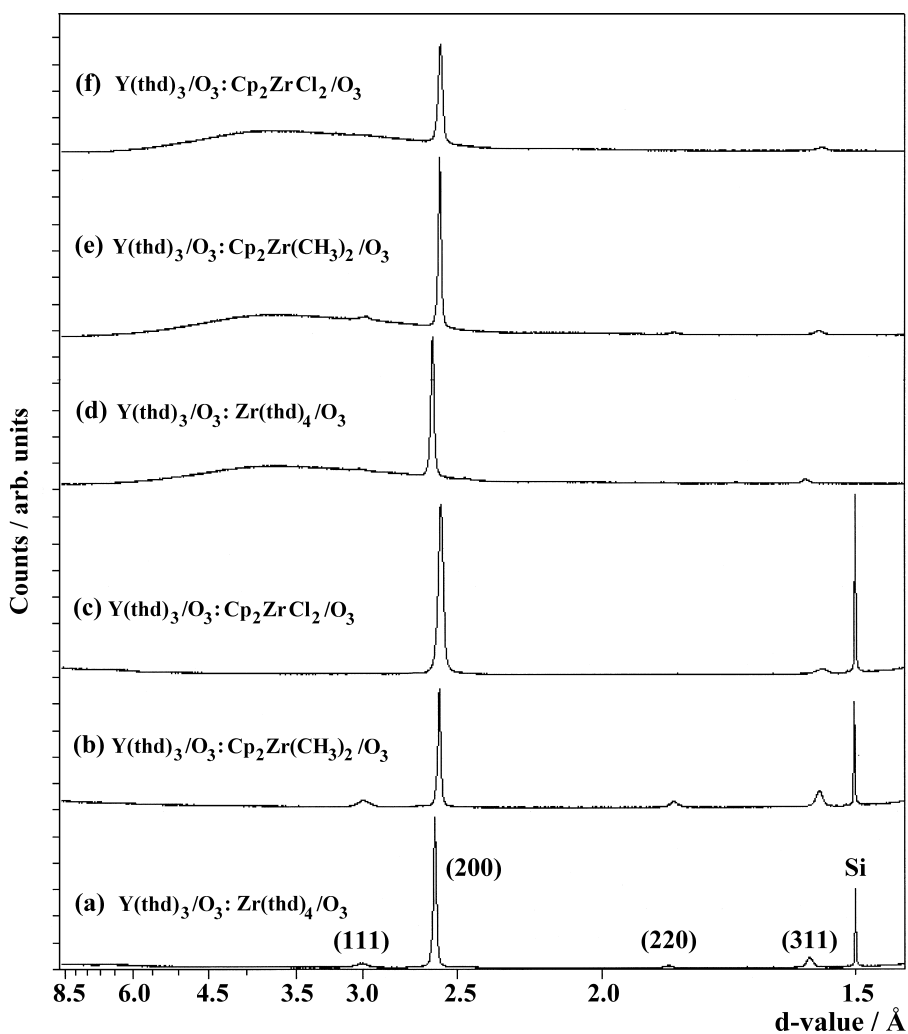


Figure 18. XRD patterns of YSZ film deposited from selected precursor combinations onto (a-c) Si(100) and (d-f) soda lime glass at 1:1 pulsing ratio.^V Deposition temperatures were (a, d) 375, (b, e) 350 and (c, f) 300 °C. Diffraction peaks of the cubic phase were identified according to JCPDS card 30-1468.

Roughness of the deposited films was also dependent on the pulsing ratio of the precursors. Films 100-150 nm thick had a roughness value of 1-4 nm depending on the precursor and pulsing ratio (Figure 19). It is interesting to note that YSZ film roughness was less than the roughness of the constituent binary oxide thin films.

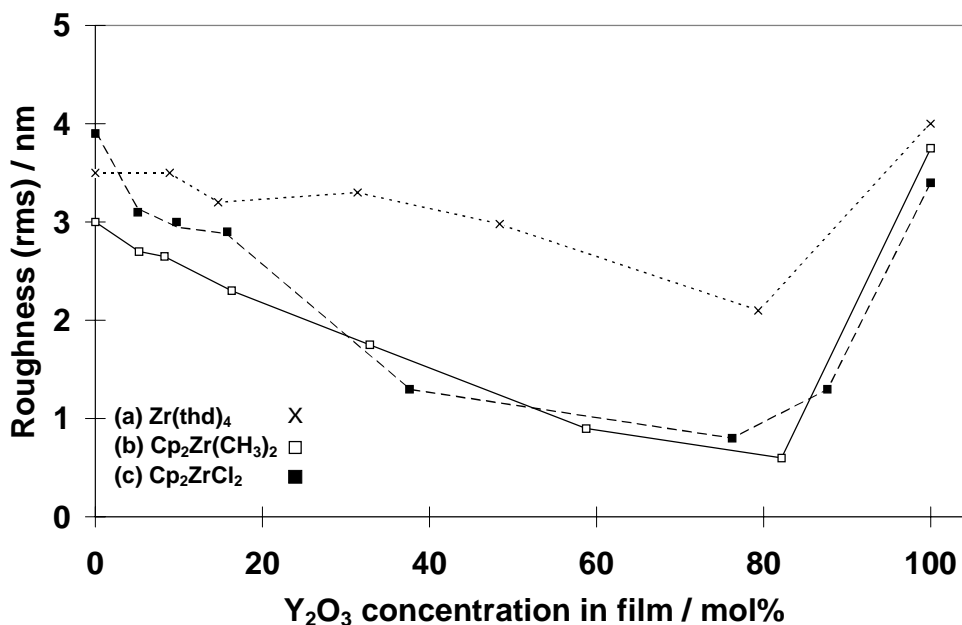


Figure 19. Roughness of YSZ films as a function of precursor pulsing ratio as measured by AFM. Film thickness was in the range of 100-150 nm.

YSZ film grain sizes were estimated from the AFM images.^v Grains were slightly larger for films deposited from the Y(thd)₃/O₃ : Zr(thd)₄/O₃ precursor combination than from the organometallic zirconium precursors (70-90 nm vs. 50-70 nm).

3.2.2 Lanthanum aluminate

Lanthanum aluminate thin films were deposited onto Si(100), SrTiO₃ and sapphire substrates. It has been observed that LaAlO₃ films react with silicon substrate at high temperatures¹⁶⁴⁻¹⁶⁶ and buffer layers must be applied between the silicon substrate and LaAlO₃ film if deposition or post-annealing is carried out at high temperatures. One candidate material for the buffer layer is MgO, and ALE deposition processes for MgO were accordingly developed.

3.2.2.1 MgO buffer layers

ALE depositions of MgO thin films were studied using $\text{Mg}(\text{thd})_2$ and O_3 as precursors.^{VI} A growth rate of $0.22 \text{ \AA}(\text{cycle})^{-1}$ was obtained on Si(100) in a narrow temperature region of 225-250 °C. It is interesting to note that the deposition rate on soda lime glass substrates was higher, namely $0.27 \text{ \AA}(\text{cycle})^{-1}$. Previously TiO_2 growth rate has been observed to be dependent on the substrate used.¹⁵⁷ Above 250 °C the deposition rate decreased, probably due to the decomposition of the $\text{Mg}(\text{thd})_2$ precursor before reaching the substrate area. Similar decomposition has been observed for ZrO_2 deposited from the $\text{Zr}[\text{OC}(\text{CH}_3)_3]_4/\text{H}_2\text{O}$.¹⁰⁹

The MgO films were (100) oriented when the film thickness on Si(100) was below 66 nm. For thicker films, also the (220) reflection was observed (Figure 20). According to RBS analysis, the deposited films were nearly stoichiometric with Mg to O ratio of 1.05 ± 0.10 when deposited at 250 °C. Furthermore, XPS analysis suggests that if the signal originating from OH groups at the surface is disregarded the MgO deposited at 250 °C had a metal to oxygen ratio close to 1:1.

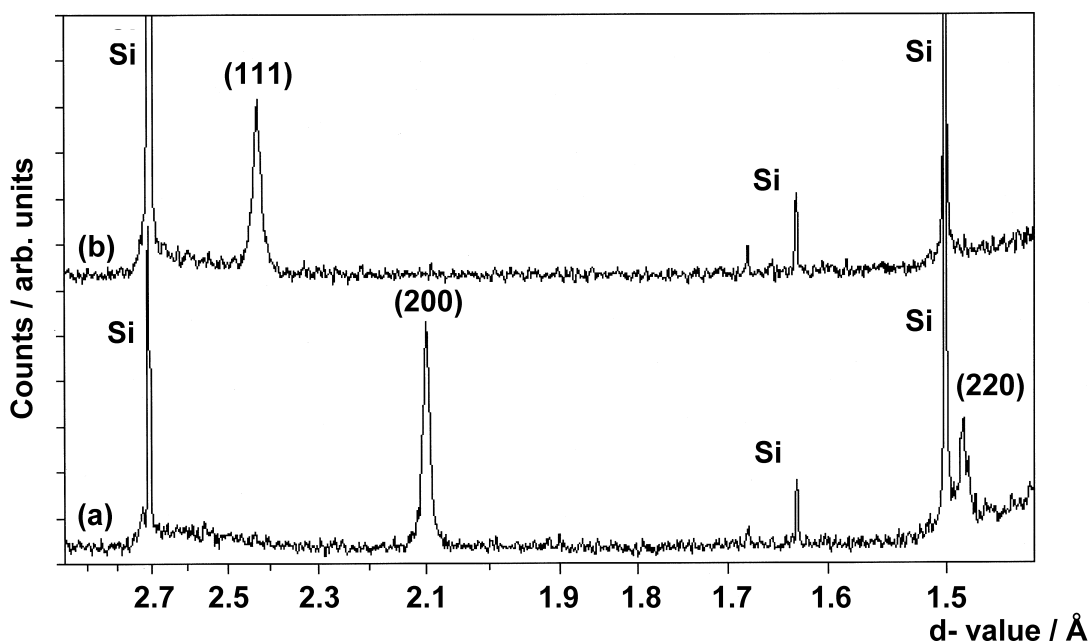


Figure 20. XRD patterns of MgO films deposited from (a) $\text{Mg}(\text{thd})_2/\text{O}_3$ at 250 °C^{VI} and from (b) $(\text{C}_5\text{H}_5)_2\text{Mg}/\text{H}_2\text{O}$ at 300 °C.^{VII} The thickness of films was (a) 110 nm and (b) 160 nm. Diffraction peaks were identified according to JCPDS card 4-829.

MgO films were also deposited from $(C_5H_5)_2Mg$ using H_2O as an oxygen source.^{VII} A constant growth rate was observed at 200-300 °C where the deposition rate of $1.16 \text{ \AA}(\text{cycle})^{-1}$ was obtained. Growth rate decreased when the deposition temperature was outside of this range. A growth rate of $0.76 \text{ \AA}(\text{cycle})^{-1}$ was obtained even at 100 °C. Films deposited above 200 °C were slightly crystalline with (111) preferred orientation (Figure 20). According to TOF-ERDA analysis, stoichiometric films were obtained at 200-400 °C. Furthermore, both carbon and hydrogen content were dependent on the deposition temperature. Lowest impurity levels were obtained at 300 °C, being 0.1 at% of carbon and 0.5 at% of hydrogen. The films deposited at lower temperatures contained more impurities, especially hydrogen, which was assigned by FT-IR to $Mg(OH)_2$.

3.2.2.2 Lanthanum aluminate film deposition by ALE

Lanthanum aluminate deposition was studied with use of $La(thd)_3$, $Al(acac)_3$ and ozone as precursors.^{VIII} Films were grown on soda lime glass, Si(100), MgO-buffered Si(100), sapphire and $SrTiO_3(100)$ substrates. Both (100)^{VI} and (111)^{VII} oriented MgO were used as buffer layer. Although an ALE window was observed for Al_2O_3 at 350-380 °C, uniform films were obtained over a wider range of 300-400 °C. In contrast to the YSZ depositions,^V the growth rate of the ternary compound was lower than the calculated value from the constituent binary oxides suggests. The explanation may lie in the surface chemistry. It seems that an Al-O layer diminishes the growth rate of the following La-O layer, possibly because the reactive surface sites, such as OH groups,⁷⁹ on the Al-O surface are not favourable for the adsorption of $La(thd)_3$.

According to TOF-ERDA measurements, nearly stoichiometric $LaAlO_3$ films were obtained with the $La(thd)_3/O_3 : Al(thd)_3/O_3$ pulsing ratio of 2:1. Impurity levels at this pulsing ratio were 0.8-1.9 at% carbon and about 0.3 at% hydrogen. Carbon content decreased from 2.4 to 0.8 at% and hydrogen content from 0.5 to 0.1 at% when the deposition temperature was increased from 325 to 400 °C.

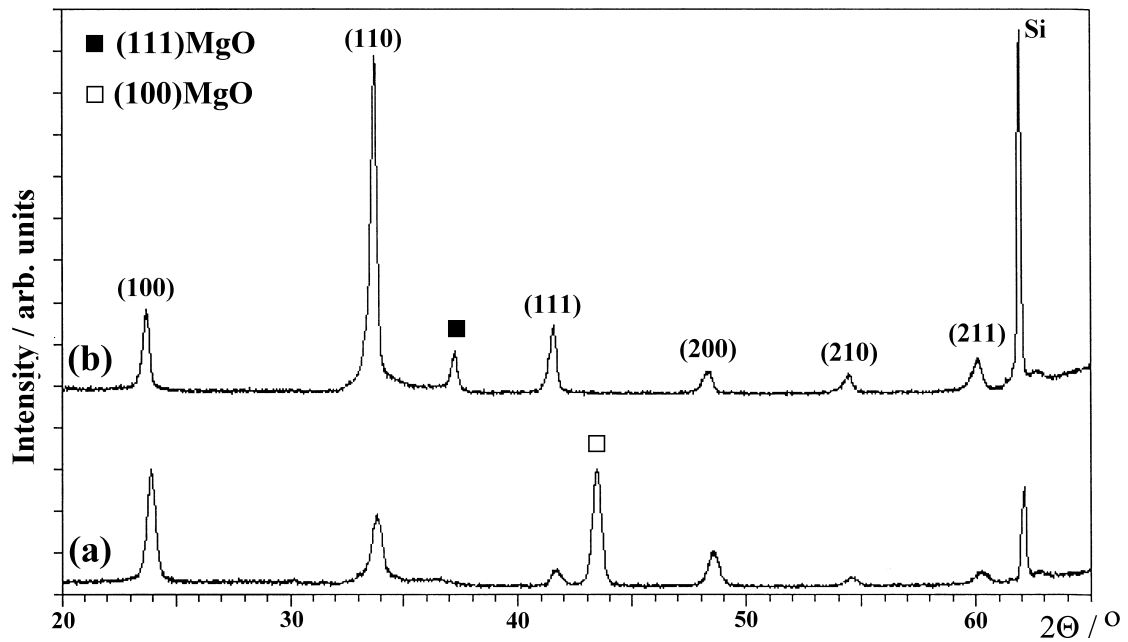


Figure 21. XRD patterns of LaAlO_3 films obtained by annealing films deposited onto silicon substrates buffered with (a) (100) or (b) (111) oriented MgO .^{VIII}

The LaAlO_3 films deposited at 325–400 °C were amorphous regardless of the pulsing ratio. Crystalline (110) oriented films were obtained when stoichiometric films deposited onto Si(100) or $\text{MgO}(111)$ -buffered Si(100) substrates were annealed at 900 °C. However, interdiffusion of aluminium and silicon was obtained when annealing was carried out at 950 °C. Only thinner films (<100 nm) deposited onto $\text{MgO}(100)$ -buffered Si(100) substrates and annealed at 900 °C had preferential (100) orientation (Figure 21); thicker films were randomly oriented. Furthermore, epitaxial LaAlO_3 was obtained on $\text{SrTiO}_3(100)$ by annealing films at 900 °C. Slower heating and cooling rates as well as longer heating times increased the film crystallinity.

4. Summary of the oxide processes studied

4.1 Precursor selection

Often the same oxide material can be deposited by an ALE process from a wide range of volatile compounds and oxygen sources. For example, ZrO₂ thin films can be deposited from halides,^{71,103-107} alkoxides,^{108,109} β-diketonates^{IV} and organometallics.^{IV}

Selection of an optimal precursor combination is not straightforward, as it depends on the film properties desired and the processing conditions. When an ALE process is developed for the deposition of ternary or more complex structures, deposition temperature may be the most critical parameter. Several other parameters, such as deposition rate, contamination levels, precursor handling and stability, may affect the usefulness of the process as well. The stability of precursors is critical parameter to obtain self-limiting ALE growth, depending considerably on the fundamental properties of the metal ion used, such as electronegativity, physical size and preferred coordination number.

On the other hand, the oxidising agent used should be carefully selected. Despite the obvious merits of ozone as an oxidiser for the deposition of the metal oxide films, a number of aspects remain to be clarified before ozone processes are employed to deposit films for specific applications, such as the very thin films to be used as gate oxides in microelectronics.^{139,140} The quality of the silicon substrate-oxide film interface as well as the extent of oxidation of the silicon are still requiring further study.^{167,168} To investigate these features would require the use of highly sophisticated techniques such as HRTEM and MEIS. Characterisation of the electrical properties of the deposited films must also be carried out. Very recently, interface quality and electric properties of ALE-deposited Al₂O₃, ZrO₂ and Y₂O₃ have been studied.^{169,170} Gusev *et al.*^{170,171} observed that when O₃ was used as an oxidiser the thickness of interfacial SiO₂ increased substantially up to ~11-14 Å, which may limit the scalability of Y₂O₃ to 10 Å (EOT).

4.2 General trends of the deposition processes

Increasing hydrogen and carbon contents restricted the use of ALE processes at very low deposition temperatures. Impurity levels were dependent on both the basicity of the film and the deposition temperature. Increasing amount of carbonate-type impurities was observed especially in the Y_2O_3 and La_2O_3 films at low deposition temperatures.^{II,III} Impurity levels in processes based on cyclopentadienyl-type precursors and water were also dependent on deposition temperature: a low deposition temperature produced hydroxide-type impurities.^{I,VII} Traces of other impurities were sometimes present, originating from the precursor synthesis,^{I,IV} adducted ligands^{II} or reactor set-up.^{II,III}

Regardless of the particular β -diketonate precursor, there was an upper limit to the reproducible deposition, where thermal decomposition of the precursor destroyed the self-limiting ALE growth. The same has been observed in ALE depositions from β -diketonates onto porous high-area substrates, although there the decomposition starts at lower temperatures.^{17,172} It should be noted that different deposition pressure and exposure time may also affect the decomposition.

For processes based on the cyclopentadienyl-type organometallic precursors two types of deposition behaviour above the ALE window were observed. Thermal decomposition of the precursor increased the deposition rate.^{IV} On the other hand, in some cases, deposition rate decreased with increasing deposition temperature when more stable precursor was used.^{VII} Decrease in growth rate is related to decrease in the number of reactive sites at the surface as a function of increasing deposition temperature.¹⁸

4.3 Film properties

Both orientation and crystallinity of the oxide films were dependent on the precursors and deposition temperature. For example, (100) oriented MgO films were obtained from $Mg(thd)_2/O_3$ process while (111) oriented films were favored when deposited from $(C_5H_5)_2Mg/H_2O$.^{VI,VII} The films deposited at low deposition temperatures had low crystallinity. An increase in the deposition temperature typically increased film crystallinity, although in some cases the increment was small.^V

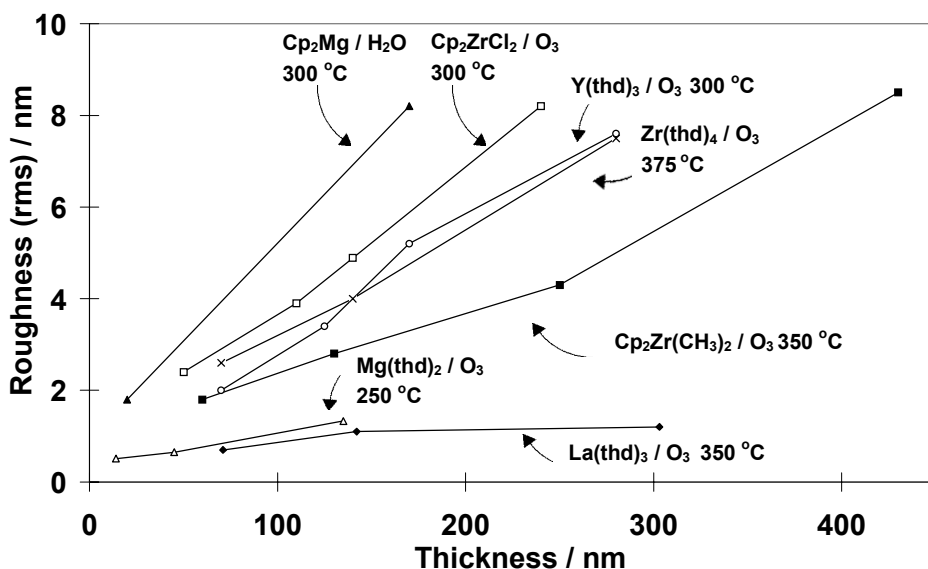


Figure 22. Roughness as a function of film thickness in ALE-deposited binary oxide thin films.

Surface roughness of the binary oxides was dependent on the film thickness as well as the process used (Figure 22). Choosing a deposition temperature within the ALE window allows some control of the roughness to a certain extent. Regardless of the oxide material deposited, the deposition seemed to proceed without as marked agglomeration as observed in some ALE processes based on metal halides and water.^{158,173,174} The agglomeration of film deposited from MCl_4/H_2O ($M = Ti, Zr$) has been suggested to originate from surface migration.¹⁷³ Even though substantial agglomeration of Group 3 oxides as well as MgO and ZrO_2 was not observed, roughness was dependent on the film thickness. For example, MgO films deposited at 300 °C from $(C_5H_5)_2Mg$ and H_2O ,^{VII} showed a largest increase in roughness with film thickness.

5. Conclusions

In the present investigation, ALE deposition processes for several metal oxide films were systematically studied. The following conclusions about oxide thin film processing by atomic layer epitaxy can be drawn on the basis of the results.

Many kinds of binary oxide film depositions by ALE can be successfully carried out with β -diketonates and ozone as precursors, provided that the deposition temperature is carefully selected. These binary oxides include MgO, Sc_2O_3 , Y_2O_3 and ZrO_2 . Lower limit for a successful deposition is due either to lack of reactivity at low temperature or to greatly enhanced impurity content. Interestingly when the attempt was made to deposit La_2O_3 films at ALE window temperatures, the films contained carbon impurity in the form LaO_2CO_3 , originating probably from the carbon-containing precursor. At higher temperatures (above 300 °C), however, crystalline La_2O_3 phase was observed.

Regardless of the process based on the β -diketonates, the upper limit of the temperature range for self-limiting deposition is set by the thermal decomposition of the precursors, which for the β -diketonate compounds typically occurs at about 350-425 °C, and sometimes at even lower temperatures, such as at 250 °C for $\text{Mg}(\text{thd})_2/\text{O}_3$ process.^{VI}

In general, the deposition rate of β -diketonate processes for oxide films is quite low due to the bulky size of the precursors. This was clearly seen in a comparison of the deposition rates with those where halides and organometallic compounds were the metal precursors. A slight increase in the deposition rate can be obtained by using additional oxygen sources, but the increment has typically been only 12-20%.^{I,7} A much greater increase in the growth rate can be obtained by using organometallic precursors.^{I,VI,VII}

Ternary oxides can be deposited by ALE with β -diketonate or organometallic type precursors if the deposition conditions are selected so that self-limiting growth is achieved for each of the constituent oxides. Both for stoichiometric ternary compounds and for solid solutions, the pulsing ratio must be carefully selected in order to obtain the desired stoichiometry. Representative examples for the ternary oxides, with exact composition or solid solutions are LaAlO_3 and yttria stabilised zirconia, respectively, both successfully deposited in the present study.

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