Growth of thin films of functional oxides with the ALCVD method

by

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Dissertation presented for the degree of Doctor Scientiarium 2003

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Foreword

My personal interest in thin film growth was initiated already during my master study. During that period I visited the Technical University of Helsinki for three months and initiated growth of LaMnO₃ films in the research group of prof. Lauri Niinistö. This work gave rise to article VI presented in this dissertation. The novel research field of growing perovskite thin films with the ALCVD technique was started during the dr. study of Helene Seim as collaboration between the University of Oslo and the Technical University of Helsinki.

A major aim of the present work has been to set up an ALCVD thin film laboratory at the University of Oslo with necessary analysis equipment. This elaborate task is still going on, and two new ALCVD instrumentations, will be installed in the MRL-NMC building in Gaustabekkdalen in the late autumn of 2003.

In a wider aspect, this work represents a chemistry component in the research activities of the NMC (Norwegian Microtechnology Center), that were first planned in the middle of the 90s. In 1999 the Research Council of Norway granted a strategic university program for research related to microtechnology at University of Oslo (FIN; films interfaces and nanomaterials) to which the present research belongs. I started my dr. scient. study June 14th 1999, and the three year grant was extended by University of Oslo with 1.5 years owing to additional tasks in teaching at the Department of Chemistry.

The dr. scient. work has mainly focused on synthesis of thin films of materials with a large potential for microelectronics.

There are a number of persons that I am indebted to in relation to my dr. scient. work. Some of them have been noted in the acknowledgements of the separate articles, but there are still some that deserves special attention. I am grateful for the skilled guiding and for the almost unlimited freedom that my supervisors Helmer Fjellvåg and Arne Kjekshus have showed me. Ole Bjørn Karlsen has contributed with numerous almost non-ending discussions that have raised my awareness, taught me that everything
should be investigated, and led me into the world of crystal growth. Per Fostervoll has managed to provide solutions to problems and the things I missed or lost at the very time I missed/lost it. Special thanks go to the instrument-workshop, glass-blower and electronics department that has realized most of my ideas. I am also grateful for the contributions of our local thin film group: Martin Lie, Frode Tyholdt, Karina B. Klepper, and Anette Hauger, and to the rest of the persons at our department that make a good working environment.

Last but absolutely not least, I want to thank Elin Kalleson, my daughter Tina, and the rest of my family for never ending support and proving to me that there is more to life than just thin films.

Ola Nilsen

University of Oslo 13/10-2003
Abbreviations

AFM  Atomic force microscopy
AI   Antiferromagnetic insulator
ALCVD Atomic layer chemical vapour deposition
ALD  Atomic layer deposition
ALE  Atomic layer epitaxy
CI   Canted antiferromagnetic insulator
CMR  Colossal magnetoresistance
CVD  Chemical vapour deposition
DE   Double exchange
EDS  Energy dispersive spectroscopy
FI   Ferromagnetic insulator
FIN  Films Interfaces Nanomaterials
FM   Ferromagnetic metal
GMR  Giant magnetoresistance
ICT  Information communication technology
IR   Infrared
MBE  Molecular beam epitaxy
NMC  Norwegian Microtechnology Center
PI   Paramagnetic insulator
PVD  Physical vapour deposition
RBS  Rutherford backscattering
SAM  Self-assembled monolayers
SEM  Scanning electron microscope
TEM  Transmission electron microscopy
Hthd 2,2,6,6-tetramethylhepta-3,5-dione (see Fig. 3)
TMA  Trimethylaluminium
TMG  Trimethylgallium
XPS  X-ray photoelectron spectroscopy

Technicality

A double notation system has been applied for the references in this introduction. Arabic numerals refer to papers in the reference list, whereas Roman numerals refer to the papers contained in this dissertation.
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1. “Inexpensive set-up for determination of decomposition temperature for volatile compounds”

II. “Growth of manganese oxide thin films by atomic layer deposition”
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1. Introduction

This study is in brief about growth of thin oxide films with the atomic layer chemical vapour deposition technique (hereafter referred to as ALCVD). The aim has been to grow films of complex perovskites. Before presenting the results of this study, it might be beneficial to look at the field in a more general way.

1.1. Thin films

Research on thin films has in the recent years become a topic of an ever increasing interest. Synthesis of thin films is as such not a new process, sputtering was discovered around the middle of the nineteenth century, while vacuum evaporation was invented around the beginning of the twentieth. However the methods were not considered useful for manufacturing due to the lack of suitable pumps. It was first in the early 1930s that the work of C. R. Burch on diffusion pump oils made it possible to use these techniques satisfactory.

Effects originating from thin films and interference coatings were reported as early in the seventeenth century when Robert Hooke and Robert Boyle independently reported what is now known as “Newton rings”. The theory behind these observations was not satisfactory explained until 1801 when Thomas Young explained the principle of interference of light [1].

The first commercial application of a thin film (as a functional material) was in optical components. In the production of mirrors in Venice during the sixteenth century, an amalgam of tin was used on the back side of glass plates [2]. The first artificially produced anti reflection coating was probably made in 1817 by Joseph Fraunhofer by chemical etching of flint glass; however this was first exploited at the turnover to the twentieth century by Dennis Taylor [3]. Improved anti-reflection coatings produced by thin-film vapour deposition, became available in the 1930s. Shortly afterwards the optical components increased in complexity as one were able to deposit alternating layers of material with high and low index of refraction [1]. It was then possible to produce filters with more specific properties, mirrors, as well as broad-band anti-reflection coatings. These components are considered as the first
examples where thin films produce materials with properties being different from those of the constituents bulk form.

Today, the new properties that emerge by combination of different thin-film layers are utilized in components such as, e.g.: semiconductor lasers, quantum wells structures, giant magnetoresistant magnetic reading heads, and superhard films. This is one of the major reasons for a strong push on continued thin-film development; new properties may arise when materials are combined on nano- and microscale. Also for single-component materials, the properties may be dramatically altered when they are deposited as thin films as compared to the bulk state. This may be due to the limited size of the material in one dimension, e.g., the thickness of the film is less than the mean free path length of the electrons in the material. The latter effects have become major challenges in nanomaterial science.

The physical properties of compounds may be very dependant on the orientation and microstructure of the material. Growth of thin films represent today the most practical way to produce materials that are oriented and at the same time with some control of the microstructure. This is achieved by careful choice of substrate and deposition conditions, e.g., for colossal magnetoresistant La$_{0.7}$Ca$_{0.3}$MnO$_3$ films the properties are greatly influenced by the microstructure and thus the growth conditions [4,5].

A major economical driving force for enhanced research on thin film is the wide area of applications. Many of the commercial products today, at least in the electronics industry, rely on thin films. By knowledge of the growth process one may enhance these properties and/or increase the span of applications in an economically feasible way.

1.2. Perovskites

The aim of this study is controlled growth of complex oxides of the perovskite-type family. This family of materials have been chosen owing to its numerous interesting physical properties. The ideal ABX$_3$ perovskite-type structure is cubic and contains one large A-cation in a 12-fold position, one smaller B-cation in an octahedral position. The X-anion together with the large cation forms a ccp AX$_3$ structure. The idealized structure is shown in Fig. 1.
The perovskite family shows a large flexibility with respect to size and charge of A and B cations. There exists a large variety of structures, e.g., there exists 23 different schemes for tilting of the corner shared octahedra. In addition, the structures may have oxygen vacancies, cation ordering, non-centro-symmetry displacements, or may incorporate different building blocks, e.g., Ruddlesden Popper phases. Important in this context is the fact that both cations may be substituted with other cations and still keep the same principal structure, although undergoing structural displacements. In selected system, especially where the B cation is small, non-centro-symmetric displacements may occur and give rise to properties such as piezoelectricity, ferroelectricity, pyroelectricity, and/or ferroelasticity. Given the fact that the physical properties of a material is often strongly depending on its composition, one may imagine this structure type to offer numerous different properties, and also the possibility of individual tuning of each property. Some examples of physical properties among oxides of the perovskite family are presented in Table 1.
### Table 1. Examples of different properties found among the perovskites.

<table>
<thead>
<tr>
<th>Property</th>
<th>Compound examples</th>
</tr>
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<tbody>
<tr>
<td>Insulator</td>
<td>LaGaO₃, LaAlO₃, LaCrO₃, LaFeO₃</td>
</tr>
<tr>
<td>High-K dielectric</td>
<td>BaTiO₃, Ba₂EuZrO₅.₅, CaCu₃Ti₄O₁₂</td>
</tr>
<tr>
<td>Semiconductivity</td>
<td>LaMnO₃, PbCrO₃, RTiO₃ (R = La...Tm)</td>
</tr>
<tr>
<td>Half metallicity</td>
<td>LaBaMn₂O₅.₅, YBaMn₂O₅.₅, Sr₂FeMoO₆, Ba₂FeMoO₆, Ca₂FeMoO₆, Ca₂FeReO₆</td>
</tr>
<tr>
<td>Metallic conductivity</td>
<td>LaNiO₃</td>
</tr>
<tr>
<td>Superconductivity</td>
<td>YBa₂Cu₃O₇, HgBa₂CuO₄, La₁₋ₓNdₓ₂Cu₂O₄, Bi₂Sr₂Ca₃Cu₄O₁₀₋₆, HgBa₂Ca₂Cu₃O₈₊₅</td>
</tr>
<tr>
<td>Colossal magnetoresistance</td>
<td>A₀.₃La₀.₇MnO₃ (A = Ca, Sr, Pr, Pb)</td>
</tr>
<tr>
<td>Multi ferroics</td>
<td>BiMnO₃, BiFeO₃</td>
</tr>
<tr>
<td>Ferroelasticity</td>
<td>LaCoO₃</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td>SrRuO₃, LaMnO₃.₁₅, La₁₋ₓCaₓMnO₃, Sr₁₋ₓLaMnO₃</td>
</tr>
<tr>
<td>Anti ferro</td>
<td>BiMnO₃</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>PbZ₀.₄₇Ti₀.₅₃O₃</td>
</tr>
<tr>
<td>Spin glass</td>
<td>CaRuO₃</td>
</tr>
<tr>
<td>Multi valence materials</td>
<td>Ca₃Co₂O₆, Sr₄Fe₄O₁₁, YBaMn₂O₅.₅</td>
</tr>
</tbody>
</table>

It is almost unique to find a collection of such numerous properties among materials with similar structures. The structural similarities and the small variations of cell parameters are highly beneficial for growth of multilayers and superstructures.

### 1.3. The La-Ca-Mn-O system

The La-Ca-Mn-O system may form individuals of the La₁₋ₓCaₓMnO₃ family. These are manganites that adopt perovskite-related structures with a variation in the Mn³⁺ : Mn⁴⁺ ratio depending on the substitution level of Ca. The substituted manganites, \(A₁₋ₓA'ₓ\)MnO₃ (where \(A\) is trivalent and \(A'\) is divalent), have gained much attention after the discovery of colossal magnetoresistance (CMR; for \(x \approx 0.15–0.5\), with a maximum for \(x \approx 0.3\)) and charge ordering (CO; for \(x \approx 0.5\)). Electron hopping gives rise to double exchange (DE), thereby also high electronic conduction and ferromagnetic interactions. In addition superexchange is important for the magnetic properties. Both the electrical and the magnetic properties of the manganites are very susceptible to external effects such as magnetic fields and also stresses that may alter the angle of the corner sharing MnO₆ octahedras, viz. the Mn-O-Mn bonds. Any deviation from 180° will decrease the conduction. The physical properties of thin films of manganites are therefore very influenced by the microstructure and compositional
variations. Hence, numerous techniques have been applied for this type of synthesis. For a more thorough survey of this field see Refs. [4–6] and papers therein.

Fig 2. Magnetic phases in \((\text{La}_{1-x}\text{Ca}_x)\text{MnO}_3\). The shaded line represents the insulator-metal transition and is where CMR properties are found. The regions indicated are as follows: AI, antiferromagnetic insulator; CI, canted antiferromagnetic insulator; FI, ferromagnetic insulator; FM, ferromagnetic metal; PI, paramagnetic insulator. (Adapted from Ref. [6]).

1.4. ALCVD

There are several good reasons why to use ALCVD for growth of thin films of complex oxides. However, these do not necessarily exclude the use of other film-growth techniques. One of the major benefits of the ALCVD technique is the self-controlled surface growth. Thereby it becomes feasible to produce ultrathin, and pinhole-free films on intricate surfaces with a superb control of the thickness over large areas, and even at modest to low temperatures [7]. This is of most importance in production of insulating layers. Here ALCVD is superb; however, the disadvantage of slowness can be compensated by its ability to deposit large areas and on a large number of substrates simultaneously. Actually about 85 % of the research on thin-film growth by ALCVD is linked to growth of insulating layers. This does by no means imply that there is a lack of other interesting fields where ALCVD is beneficial.

One of the potential fields for ALCVD growth is in production of multilayers and superstructures. The ability to control the deposition at an atomic level and at modest to low temperatures renders this process very suitable for productions of sharp interfaces. It may therefore be an alternative to the more specific and expensive MBE (=molecular beam
epitaxy) technique. ALCVD is also very suitable for integration into processes where the thermal budget should be low.

1.5. The thd-type precursor

Hthd (2,2,6,6-tetramethylhepta-3,5-dione) (Fig. 3) is a β-diketonate where it is easy to form an acidic enolate. In this state, it will readily form complexes with almost all metallic elements of the periodic table. Fortunately these elements are relatively temperature stable and easily sublimable. With the β-diketonate group of precursors, it is possible to alter the vapour pressure and temperature stability by variation of the side chains (methyl, tert-butyl, fluor substituted tert-butyl). In this study we have constrained ourselves to side chains of tert-butyls, due to their acceptable thermal stability, availability, and cost.

![Fig. 3. Hthd = 2,2,6,6-tetramethylhepta-3,5-dione.](image)

This is a rather voluminous ligand and hence produces metal complexes of considerable size, even when they are adsorbed on a surface. They will there take up so much space that several active adsorption sites will be blocked for further reaction. The surface coverage of metal atoms will therefore be low even when there is full coverage of precursors. We have in this study experienced that it is necessary with 8-15 precursor cycles in order to produce one monolayer of oxide compound.

1.6. The abbreviations “ALCVD”, “ALD”, and “ALE”

In the articles of this dissertation, ALE (atomic layer epitaxy), ALD (atomic layer deposition) and ALCVD are all used as abbreviations. A good abbreviation is a collection of words that together give sufficient information so that the “topic” can easily be held apart
from others, and also indicate in which field of research it belongs. Names for techniques are usually made in the way that the most specific words form the beginning and the most general ones, the end. The abbreviation ALCVD is just such a collection of words that fulfils all these requirements:

Deposition  This informs the reader that the method deposit material in one form or another. Hence it is a synthesis method and probably one that forms thin films.

Vapour  The method utilizes the vapour phase to produce the deposit.

Chemical  The method belongs to the chemical discipline and thus involves breaking and formation of new bonds between different reagents. It is not to be regarded as a physical discipline.

Layer  The deposit is formed by deposition of individual layers.

Atomic  These layers are of atomic dimensions.

ASM Microchemistry has trademarked the ALCVD abbreviation as an acronym. The less specific but shorter ALD abbreviation has therefore been in many respects usual to apply.

One of the reasons for these numerous abbreviations for the same technique is that in the end of the 1990s there were disagreements in the scientific community concerning the original ALE abbreviation. It was stated that it could be misinterpreted as if the technique would give an epitaxial film in all cases, although the original interpretation of the word epitaxial in the ALE abbreviation had nothing to do with the texture of the formed film. It had rather to do with the idea that the process arranges one single layer of precursor on top of the substrate in an arranged manner. In the heat of the discussions one must have forgotten that the well known MBE abbreviation is in a similar situation to be misinterpreted into that the technique always gives an epitaxial texture, even this is not the case. The only reason why so many epitaxial textures are reported with this technique is the frequent use of lattice matched substrates. Still, the abbreviation has been kept as it is. The result of the disagreement was the formation of the ALD abbreviation and a requisition that “ALE” should be used only when epitaxial films are formed. The alternative abbreviation, “ALCVD”, formed at the same time by ASM Microchemistry, was used during our purchase of the F-120 Sat equipment (Fig. 4) in 1998, and was therefore adopted by us. More recently, ALD have gained so much recognition that editors of some journals from time to time only allow this abbreviation, and
thus we have been forced to use all three abbreviations in the articles of this study. In this introduction the more specific ALCVD abbreviation has been chosen to describe the process.

Fig. 4. Right, the F-120 Sat ALCVD reactor; left, inside; bottom, the reaction chamber.

1.7. Visions and perspective

ALCVD is a technique that is suitable for production of ultrathin layers, typically in the range 1–50 nm. This is also the reason why this technique has become so popular in fabrication of thin insulating layers of materials with a high dielectric constant. One of the major tasks today in the scale-down of microelectronics has been the production of ultrathin layers of an insulating material that will still be insulating when it is ultrathin. In order to achieve the present goals of an equivalent SiO₂ thickness of less than 1.5 nm, one has to use materials with larger dielectric constants than 3.9. Currently the industry has turned to thin films of amorphous aluminium oxide and produces such layers with the ALCVD technique by using TMA (trimethylaluminium) and water or ozone. This material and process have indeed made it possible for companies such as Samsung and Seagate to achieve their individual goals for 2004. However, there is still much to gain in changing from aluminium oxide to a material with even higher dielectric constant, such as hafnium oxides or mixtures of other oxides. This is currently ongoing research topic at major electronic industries such as Intel, IBM and Samsung. They are also looking into the possibilities of gaining even better electrical
insulation by usage of nanolaminates of different oxides. Also this is well within the major capabilities of the ALCVD technique [8].

Companies working with hard disk sensors, such as Seagate, have also shown interest in the ALCVD technique. They apply this technique today in the production of magnetic reading heads, since these also gain efficiency by reducing the insulating layers to even smaller dimensions. However, they are currently also looking into fields where ALCVD may help producing improved magnetic sensors. The sensors today are GMR (giant magnetoresistant) sensors that consist of thin alternating layers of metallic copper and cobalt. These metallic layers are still being produced by sputtering and suffer from roughness and interdiffusion effects. It is believed that these effects will diminish if one is able to produce the multilayered films by ALCVD. Unfortunately there is a shortage in knowledge on how to produce pure metallic films by ALCVD, but this has now become a main focus of attention for several research groups.

Neither copper nor cobalt can act as magnetic sensors separately, but when these are combined in thin (nanoscale) alternating layers, it is possible to produce a material that shows giant magnetoresistant properties ($\Delta R \approx 100\%$) (Fig. 5). This is an example where combination of materials with different properties and in a nanometre scale, gives rise to an additional property. This effect is one of the main benefits from nanotechnology. The ALCVD technique is a strong tool for synthesis of two dimensional nanomaterials over large substrates by controlled deposition of single monolayers at a time. Currently, as mentioned, this is utilized in production of insulating layers, and efforts are made in direction toward magnetic sensors. However, there are still a number of fields not yet explored, and many probably being unknown at the moment.

The chosen model compounds, perovskite-type oxides, exhibits an extraordinary number of magnetic and electrical properties for materials with virtually the same structure and unit-cell parameters. They are therefore especially good candidates for production of multilayers and superstructures. Several perovskites have interesting properties that can be exploited when the material is produced as thin and conformal layers. Examples are gas sensors, fuel cells and sealing of porous membranes. The bulk properties of perovskites are usually tuneable by substitution of cations or by variation in the oxygen stoichiometry.
Furthermore, by deposition of such oxides on near-lattice-matched substrates one may introduce stresses into the film, which in addition will be a parameter that tunes the physical properties. One ultimate goal would be to produce colossal magnetoresistant ($\Delta R > \approx 1000\%$) sensors that work in moderate magnetic fields and ambient temperature.

**Fig. 5.** The response of a multilayered CMR material in magnetic field [9].

This study is the first contribution on ALCVD synthesis of cation substituted perovskites, here exemplified by $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. It is also the first example of controlled synthesis of oxides with three cations by ALCVD. Nevertheless, most of the articles in the present dissertation present growth of single oxide films that describe the required basis for the production of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ multi-component perovskite. They also describe effects that different substrates may have on the film texture. In the section about growth dynamics, the fact that different types of precursors may lead to different growth dynamics is also raised. Altogether, these are effects that may be vital to control in growth of complex oxides.

The ALCVD technique enables growth of materials at lower temperatures than most other gas phase deposition techniques. This will in turn enable integration of thin (oxide) films into several new fields where a low thermal budget is of importance. On the other hand, the low deposition temperature may be a complication in some cases, especially when multi-component films are deposited. This is due to low surface diffusion during growth, which may lead to a poor crystallinity or even amorphous films. Hence, temperature treatments may
be needed in order to enhance crystallinity. This complicating factor was indeed observed in the present work on La\(_{1-x}\)Ca\(_x\)MnO\(_3\) deposition on various substrates. Nevertheless, amorphous films may in some cases be an advantage since they may have properties that are otherwise unobtainable.

When the present results are compared with accomplishments of other techniques for the same compounds, some specific aspects stand out. We have been able to produce thin films at a lower temperature than otherwise seen; however, their degree of crystallinity is inferior unless the films have been post annealed. We have been able to produce materials that are partly amorphous, but with the desired composition. One may imagine that these would be ideal starting materials for study of growth and properties of nanocrystals in an amorphous matrix during annealing. We have furthermore been able to deposit the complex oxides over large substrates (10×5 cm\(^2\)) with only small variations in the composition.

This study provides a required, yet modest basis for growth of multicomponent perovskites. A natural continuation of this research would be to increase the skills on binary systems and subsequentially perovskites with interesting properties. It would be important and challenging to provide thin films of perovskites that are ferroelectrics, ferromagnetic, piezoelectric, isolating, metallic conducting, p- and n- type semiconducting, oxide conducting, or superconducting. In parallel one should commence studies on growth of multilayer oxides (Fig. 6) and study their properties as a function of thickness. The perovskites that have been grown by ALCVD up to now are presented in Table 2.

**Table 2.** Perovskites made by ALCVD.

<table>
<thead>
<tr>
<th>Compound</th>
<th>References</th>
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<tbody>
<tr>
<td>BaTiO(_3)</td>
<td>[10]</td>
</tr>
<tr>
<td>Bi-Ti-O</td>
<td>[11]</td>
</tr>
<tr>
<td>CaMnO(_3)</td>
<td>[VII]</td>
</tr>
<tr>
<td>La(_{1-x})Ca(_x)MnO(_3)</td>
<td>[VII]</td>
</tr>
<tr>
<td>LaAlO(_3)</td>
<td>[12]</td>
</tr>
<tr>
<td>LaCoO(_3)</td>
<td>[13]</td>
</tr>
<tr>
<td>LaGaO(_3)</td>
<td>[14]</td>
</tr>
<tr>
<td>LaMnO(_3)</td>
<td>[15]</td>
</tr>
<tr>
<td>LaNiO(_3)</td>
<td>[16]</td>
</tr>
<tr>
<td>SrTiO(_3)</td>
<td>[10,17,18]</td>
</tr>
</tbody>
</table>

**Fig. 6.** Schematic illustration of superlattice of two types of perovskite type oxides.
2. Thin film production

In the following some basic information about the synthesis and analysis techniques are presented.

2.1. The ALCVD method

The ALE (ALCVD) method was developed already in the 1970s by Tumo Suntola and co-workers [19–22]. However, it has up to now been a rather unknown method to most researchers. This is now about to change. During the last couple of years, huge international ICT companies such as IBM, Intel, Samsung, and Seagate have utilized ALCVD in order to be able to provide materials required by the next generation technology. One of the reasons for the late introduction of ALCVD is probably that the method is rather slow compared to other methods such as CVD, PVD and sputtering. However, this viewpoint may be false if one takes into consideration the capacity of this deposition technique.

The review paper by M. Ritala and M. Leskelä [7] explains most aspects about the technique. Nevertheless a short explanation is included here. The method is a chemical deposition technique where the reactants are transported to the substrate in the gas phase. The deposition is performed in a hot wall reactor, due to the reaction scheme. However, a patent has now also been taken out on a cold wall ALCVD technique [23]. The difference between this method and a regular CVD method is that the reactants (also called precursors) are only allowed to enter the reaction chamber one at a time, and is separated by an inert gas purging. In this way, gas phase reactions are eliminated, and the only reactions that can take place are those between the pulsed reactant and the surfaces in the reaction chamber. The temperature of the reaction chamber is chosen so that condensation of the pulsed reactants, as well as thermal decomposition, does not occur. When one reactant is pulsed into the reaction chamber, it will react chemically with the surfaces present and produce one monolayer of precursor fragments chemisorbed to the surface. The precursor may be voluminous so that even though the surface is saturated with precursor, only a fraction of the surface is covered with metal atoms. This is called steric hindrance. The following purge with inert gas will remove all unreacted precursors and by-products before a new reactant is admitted into the
chamber. The process is repeated for as many cycles that are needed in order to obtain the desired thickness of the thin film.

The first half of a cycle in the process for formation of Al$_2$O$_3$ by using TMA (=trimethylaluminium) and water, is illustrated in Fig. 7. The left part of the figure illustrates the reaction chamber. In (b-d) the TMA gas reactant is introduced and spread into the reaction chamber. The right part illustrates how the methyl groups of TMA reacts with the hydroxyl coated surface (a-b) and forms methane (b) and a monolayer of adsorbed aluminium precursor fragments (c). The excess TMA precursor in the gas phase is purged from the system by an inert N$_2$ gas (d). The continuation of this scheme would be to introduce water which would react with the remaining methyl groups to form methane and a hydroxylated surface. This would complete the cycle and return to case (a).

![Flow Diagram](image)

**Fig. 7.** The first half of the cycle for formation of Al$_2$O$_3$ from trimethylaluminium (TMA) and water. Left part show the reaction chamber (a) a hydroxylated precursor surface, (b) reaction of TMA and OH to form methane and adsorbed aluminium – precursor fragments, (c) after a complete reaction, (d) removal of excess TMA by purging with N$_2$, (e) the resulting monolayer of Al – precursor fragments.
Ideally this ALCVD thin film deposition technique is robust since minor changes in process parameters such as temperature, reaction dosage and purging, will not result in change of the produced film as long as the parameters have been chosen correctly.

Since the reaction is self limited to a monolayer of precursor at a time, ALCVD is highly suitable to provide uniform films with atomic roughness over large areas and on arbitrary shaped substrate. This is indeed true for, e.g., deposition of films of a material with an amorphous character [24]. These topics will be thoroughly discussed in the section on growth dynamics.

2.2. The substrates

Several different types of substrates have presently been used; from amorphous substrates such as soda-lime glass to single crystals of different types of materials. Most substrates were bought ready to be used for deposition (epi-poslished), but some (NaCl, KCl, KBr and KI) are more conveniently grown in-house by slow evaporation of a saturated water solution.

As with all thin film deposition techniques, the film will be no better than the quality and cleanliness of the substrates. All substrates were cleaned prior to the film growth. Most of the single crystal substrates were used as delivered since they were epi-polished by the manufacturer. The glass substrates were cleaned by boiling in trichloroethylene and then in acetone for 5 min before rinsing with methanol, then washed with a neutral soap and rubbed with cotton. They were thereafter rinsed with tap water over night before finally being rinsed with deionised water and quickly blown dry with nitrogen. This procedure should give substrates free from grease and without dust particles. The salt substrates were cleaned directly before use by a quick polishing on paper soaked in deionised water, or by cleaving. All substrates were, immediately prior to film growth, treated in the reaction chamber with a large dosage of ozone in order to remove any traces of organic material.
2.3. Analysis

There are some general differences in analysis of thin films as compared to bulk material. One of the major differences lies in the fact that the film is adhered to a substrate which easily also will contribute to the analysis. As the words “thin film” implies, the material under study is in the form of a thin layer, in the present cases usually 20–100 nm which corresponds to some 10–60 ng/cm². This minute amount of material limits the number of suitable analysis methods. They have shown to be too smooth to give any appreciable contrast in SEM (scanning electron microscope) analysis, and too thin for EDS (energy dispersive spectroscopy) analysis within a reasonable examination period. An effect which may be an advantage in some cases, whilst a disadvantage in others, is that the film may be highly textured. The film may be influenced by the substrate or simply the growth dynamics so that the texture may be all from amorphous to epitaxial crystalline. The texture may also change during the growth (viz. over the thickness) of the film and thus produce an inhomogeneous material with regards to microstructure. All in all analyses of thin films are complicated as compared to analysis of bulk materials. Nevertheless, there are numerous techniques that either are specific or have successfully been adapted for thin-film analysis. The following analysis techniques have been utilized in this work.

2.3.1. X-rays based methods

X-rays allow analysis of minute amount of materials and provide information on their crystal structures since the attenuation length is of the order of microns and the wavelength is close to the distances between crystal planes. In this study X-ray diffraction has been used for structure investigation both as regular Bragg-Brentano diffraction analysis, and as more detailed investigation of the microstructure by coplanar reciprocal space mapping of selected reflections. In addition, X-ray reflectometry has been used for thickness and density measurements. X-ray fluorescence has been adopted for elemental composition analysis.

2.3.1.1. Diffraction

Diffraction analysis of thin films can be performed in the same way as for bulk materials, here using regular Bragg-Brentano reflection geometry with 0-20 data acquisition.
With the thin film mounted in the $\omega$-plane, one will only record intensities from crystallographic planes that are parallel to the substrate plane. This will not be a problem if the film is polycrystalline and randomly orientated. If, however there is texture present, asymmetrical diffraction will have to be performed in order to scan further into the reciprocal space and fully characterize the sample. This can be performed on a diffractometer that has the possibility to control the angle of the tube, detector, and sample independently. In this way one may vary all three parameters in a pattern and thus perform reciprocal maps of selected peaks. This in turn can give information about the shapes and orientation of the crystallites.

Analysis of thin films by solely usage of regular 0-20 data acquisition may turn out to provide misleading results, especially if the film is deposited on a single crystalline substrate. There is always a risk that observed peaks in the diffractogram may result from the oriented substrate owing to minute traces of Cu K$\beta$ or W L$\alpha$ radiation – unless the X-ray source is highly monochromized. One should furthermore be aware of possible weak substrate reflections with intensities below those normally tabulated in the literature (1%) – again owing to the highly oriented substrate. These peaks may overlap with reflections from one or more of the possible polymorphic structures that the thin-film product may adopt, and hence lead to troublesome analyses. One way of distinguishing whether a given peak is due to the film or the substrate is to perform a full reciprocal space mapping of the peak. Due to the limited thickness of a thin film, the diffraction peaks will be broadened in the out-of-plane dimension ($q^\perp$). But if the film is thick, this broadening will be close to that of the substrate. It is, however, common for the crystalline film to have a limited size in the in-plane dimension ($q^\parallel$), due to columnar growth and dislocations. The peak will then be broadened in the $q^\parallel$ direction, which is only accessible through asymmetric scanning. The substrates usually have very sharp peaks in the $q^\parallel$ direction and thus a comparison of the reciprocal space maps of a known peak from the substrate and an unassigned peak, will easily distinguish whether such a peak belongs to the film or not. Fig. 8 illustrates these effects by both a regular diffractogram in 0-20 data acquisition mode and by a reciprocal space map.
Fig. 8. Left: Regular diffractogram of La$_{0.7}$Ca$_{0.3}$MnO$_3$ film on SrTiO$_3$(100) substrate in 0-2θ mode with impure X-ray source (Göbel mirror) showing additional diffraction peaks originating from Cu Kβ and W Lα radiation. (S denotes substrate and F film). Right: Reciprocal space map from the substrate and the film.

With properly acquired space maps of several peaks, it should in principle be possible to extract information about crystallite sizes in both in- and out-of-plane directions, as well as size distributions and mosaicity [25–27]. This has proved to be troublesome with the impure X-ray source applied in the present work.

2.3.1.2. Reflectivity

Thin films may affect the X-ray optical properties of a material in the same way as optical filters do for visible wavelengths. It will hence be possible to obtain information about physical properties such as thickness, density, X-ray refractivity, and roughness by probing with X-rays. In practice this is done by confined X-ray reflectometry in the vicinity of total reflection. In the present work this has been performed with a home-built X-ray profilometry set-up and a typical X-ray reflectometry profile is given in Fig 9. The density of a thin film may be found by calculations based on the angle where the total reflection disappears, and the thickness is derived from the periodicity of the ripples. The roughness is calculated on basis in the attenuation of the ripples.
2.3.1.3. X-ray photoelectron spectroscopy (XPS)

The surface sensitive X-ray photon spectroscopy (XPS) technique provides information on atomic composition of the surface layer as well as the electronic state of atoms in the material. The penetrated thickness of the surface depends on the escape depth of the low energetic photoelectrons, usually some 5–20 Å. Due to its surface sensitivity, XPS data will easily suffer from errors stemming from surface reactions with the polluted atmosphere, unless the XPS equipment is mounted on line with the synthesis equipment. This problem may be circumvented by removal of the surface layer by sputtering prior to analysis. However, present observations during the examination on manganese oxides show that sputtering may influence the electronic state of the constituents in the sample [II], this may be due to preferential sputtering of the lighter atoms during the sputtering process.

2.3.2. Atomic force microscopy (AFM)

The topography of a film may give information about growth mode and texture. Topography mapping can be performed with atomic force microscopy (AFM) which monitors the deflection of the tapping of a very small needle scanned in a grid across the surface (Fig. 10). The observed topography will always be convoluted by the shape of the needle, but still it is possible to resolve details on the level of a couple of interatomic distances. This
method has presently been utilized to measure the angle of different crystallite surfaces towards the substrate plane, and thus guide the indexing of these surfaces.

Fig. 10. Topography of La$_{0.7}$Ca$_{0.3}$MnO$_3$ film on (a,b) MgO(100) as-deposited and (c) annealed. From [VII].

2.3.3. Transmission electron microscopy (TEM)

Transmission electron microscope (TEM) is a very powerful analysis method for thin films since only very tiny amounts of sample is required. The method may give a visual picture of the structure on an atomic scale, as well as providing diffraction analyses and elemental analyses on the same scale. One drawback is a rather tedious sample preparation procedure for films to be analyzed on their substrates.

2.3.4. Rutherford backscattering (RBS)

Rutherford backscattering is a powerful tool to analyze thin films deposited on substrates with lighter atoms. It is an absolute technique, and hence does not rely on specific calibration procedures. It gives information on elemental composition and sample thickness. However, due to limited availability of such instrumentation only selected samples from the present study have been analyzed by RBS and always subjected to rather simple routines.
2.3.5. IR-Spectroscopy

Spectroscopy in the infrared region is used as a supplementary tool for phase identification. A prerequisite is that the phases possess characteristic absorption patterns. The technique is rather sensitive when strong absorption bands occur. Nevertheless it is an advantage to measure just the thickest films that conveniently can be grown with the ALCVD technique. Increased effective thickness was achieved by depositing film on both sides on a double-sided polished Si(100) substrate giving a typical total thickness of 200 – 500 nm. IR-spectroscopy turned furthermore important for proving the absence of materials with strong absorption bands, e.g., carbonates.

3. Growth dynamics

Most aspects of growth of thin films may be treated in the same way as a collection of crystals; hence regular crystal growth theories apply. In thin-film growth, the crystallization is heterogeneous since a substrate facilitating nucleation process is used. A relatively high nucleation density is expected in most cases which will lead to limitations in the lateral-directed growth of the individual crystallites. This is the same effect as seen in most directional crystallization processes, such as directional casting and continued growth of a dense precipitate.

There is, however, one major difference regarding the growth conditions in ALCVD compared with most other techniques, including bulk techniques. The growth rates for different facets by most techniques are dependent on effects such as nucleation rates, incorporation time, and the flux of reactants to the surface. The two first cases are again influenced by the surface free energy of the different facets. Ideally, and at low growth rates the morphology of the crystal can be determined by Wulff diagrams of the surface energies.

The situation for ALCVD growth is somewhat different. All surfaces are allowed to be saturated with precursor before the growth takes place for every growth cycle. Hence transport of material to the crystal will not be a growth-limiting process; neither will nucleation rate nor surface diffusion enforce limitations. The only rate limiting step for crystal
growth in ALCVD is the saturation density of precursors on the surfaces. Note that optimization of pulse/purge parameters are not considered as proper rate-limiting steps.

The morphology of a growing crystal is determined by the slowest growing crystallographic surfaces. The faster growing facets will leave edges of slower growing surfaces and themselves grow to extinction (Fig. 11). In normal crystal growth by low supersaturation, the rate-limiting step is usually the nucleation rate of a new layer. The nucleation energy is at its highest on surfaces where a nucleation implies large alterations of the surface. Hence, the nucleation energy is large on atomic smooth surfaces and small on rough surfaces. This means that rough surfaces rapidly grows to extinction and the resulting crystal will be a polyhedron with smooth crystal surfaces. Usually this involves crystal surfaces with low Miller indices, such as \{100\}, \{111\}, and \{110\}.

![Fig. 11. The resulting morphology of a quadratic crystal with two sets of surfaces growth rates and an indication of the fastest growth direction.](image)

As mentioned, for ALCVD growth, the surfaces with the lowest growth rate are those with a low saturation density of precursors. Then what determines the saturation density? The saturation density of a precursor on a surface is dependent on its size and shape as well as the size and shape of the surface lattice of active sites. When one estimates the size of a given precursor, one will also have to consider the possibility of limited rotational freedom of the adsorbent/chemisorbant precursor. The ideal case of a spherical precursor on a quadratic surface lattice has been treated earlier by Ylilammi in Ref. [28].

The most favourable saturation (with respect to growth rate) occurs when the area and shape of the adsorbed precursor fragment coincides with the surface lattice of the support, or
the size of the precursor is so small that all active sites may be filled without steric hindrance. The latter situation is achieved in growth of GaAs by using trimethylgallium and AsH₃ [29–31]. When steric hindrance occurs due to voluminous precursors, some active sites will be unattainable by other precursors and the saturation density will decrease.

The packing density may vary between different crystallographic surfaces depending on the efficiency of precursor packing. A high efficiency will follow when the density of active sites is large compared to the size of the precursor, or in the case of an amorphous film with densely packed active sites. In these cases the precursors may take on an arrangement of close packing of spheres which will give a maximum surface coating of 90.7 %.

The lowest efficiency of precursor packing are surfaces where the distances between neighbouring active sites are just below the diameter of a spherically shaped adsorbed precursor. Such an effect will be largest for a hexagonal lattice where the consequences will be observed in six directions (Fig. 12). Up to 2/3 of the precursor coverage will be absent due to steric hindrance, which leaves a packing density of 30.2 %. The effect will diminish as the ratio of the size of the precursor/size of lattice increases.

**Fig. 12.** Packing of spherical precursors on a hexagonal surface: (a) The precursor size coincides with the size of the lattice of active sites. (b) A mismatch situation in which the precursor size is increased by 10% compared to (a).
3.1. Growth modes

The film may grow with many different textures from amorphous to polycrystalline, columnar and single crystalline layers. The reason for these different growth modes will be outlined in the following:

3.1.1. Amorphous growth

When a material grows in an amorphous pattern, the deposited precursors react at specific active sites which are distributed randomly on the surface. The resulting monolayer will produce new active sites which again are distributed randomly on the surface, thus repeating the process. All imagined crystallographic directions of the amorphous material will grow with the same rate due to a high sticking coefficient, rather than a mechanism for a concentration of precursors on certain crystallographic surfaces. There will be no driving mechanism for a roughening of the surface. The process is actually self repairing, forming an as-smooth surface as possible. The film growth may be visualized by starting a nucleation of the film at several positions on a substrate and let the film grow as spheres from these positions, Fig 13. This will result in a growth that is self driven towards an atomic flat surface, such as observed on growth of Al₂O₃ from TMA and H₂O [32].

Fig. 13. Schematic illustration of smooth surface resulting from an amorphous growth pattern on a rough substrate.
3.1.2. Epitaxial growth

The other extreme of film growth is epitaxial developed layers on a single crystal. When the film grows in this way, it is due to a rather good lattice match with the surface of the substrate. One may also imagine a form of oriented growth that resembles the epitaxial form if there are much stronger interactions between the adsorbed precursors than the exchanging interference with the surface beneath. In this way the precursors may be arranged in well defined crystalline domains. If there is a high nucleation barrier then (viz. large activation energy for the nucleation) there is a possibility that the size of such a domain will reach the physical size of the substrate and act as guide for subsequent growth. Such a mechanism has hitherto not been observed in ALCVD growth, even though self-assembled-monolayers (SAM) may show a similar behaviour.

Stress will develop in a film which grows in an epitaxial manner on substrates that are not fully lattice matched. The film will be stretched or compressed to match the size of the substrate when it is thin, but as the film grows thicker the potential elastic energy builds up and will eventually be released. This can be released by bending of the substrate, or more often, by introduction of a number of rather evenly spaced vertical lattice defects of the edge-dislocation type (Fig. 14). This is probably observed in article VII where La$_{0.7}$Ca$_{0.3}$MnO$_3$ was grown on SrTiO$_3$ at 300 °C.

![Fig. 14. Relaxation of a stressed epitaxial structure by introduction of dislocations.](image-url)
Even though a film may grow as one single crystal, there is no guarantee that the surface of such a film will become atomically smooth. An epitaxial film will only be properly smooth if the slowest growing crystal surface is parallel to the substrate surface. If this is not the case, there is a definite possibility that edges with other crystalline orientations can develop, because if a surface of a slow growing crystalline orientation has first developed, it will continue to spread further. The resulting film will be epitaxial, but with a roughened surface. This is observed in article III where ε-MnO₂ is grown highly epitaxial on α-Al₂O₃(001) but still produces a rough surface. This illustrates the importance of testing of new types of precursors in order to improve the growth control. Not only with respect to stability of the precursors itself, but also with respect to saturation density and hence, growth-rate control of different crystalline facets. It should also be possible to alter this effect by introduction of additional compounds that solely acts as surface rendering compounds.

3.1.3. Polycrystalline growth

If the deposited film crystallize in a polycrystalline way then some crystal facets will have surfaces that is more ideal for deposition of reactants than others. These surfaces will have a higher saturation density of precursors than others and normally obtain a larger growth rate. The result is that these surfaces will grow to extinction and leave surfaces with a low growth rate exposed. These will together produce hillocks on the surface which will be the source for a roughened surface. The typical film texture of polycrystalline growth is as follows: In the first stages of the growth the surface of the substrate will carry numerous tiny crystals with a random orientation. The next stage is a simple growth of all these tiny crystallites. Regular crystal growth theory will allow the crystallites to quickly become polyhedron with surfaces of low growth rates (viz. those with the lowest saturation density of precursor). The crystals will soon grow into each other and form a continuous film over the surface. This may in fact be accomplished during the first cycles of the process. As the crystals form a complete coverage of the substrate, the only possible direction for further growth is normal to the substrate surface. The crystals will still be randomly oriented with respect to the surface of the substrate and hence some will have a larger total growth rate normal to the substrate surface than others. These will protrude and eventually cover the crystals beneath. The surface will then consist of a larger fraction of crystals with a large growth rate normal to the surface. This will over time lead to a decrease in the number of...
crystallites protruding from the surface, and those protruding will be more equally oriented with a similar growth rate normal to the surface. The roughness of the film will increase as the growth proceeds and the number of protruding crystals decrease. This is called the columnar growth mechanism. It will give a film with a texture that consists of columns with virtually the same crystallographic orientation of the crystallites in the direction normal to the substrate plane. There will however be no in-plane orientation of the crystallites since there is no driving mechanism to ensure this.

A simulation of a thin-film cross-section of the process mentioned above is given in Fig 15. The simulation is based on a number of randomly deposited square crystallites that are in turn randomly rotated in the plane of the cross-section, but not tilted with respect to the plane of the cross-section.

![Simulation of columnar growth by random nucleation and in-plane rotation of square crystallites.](image)

Fig. 15. Simulation of columnar growth by random nucleation and in-plane rotation of square crystallites.

Fig. 16 shows another simulation of the three-dimensional topography of cubes that are randomly deposited and randomly oriented in all directions. The simulation work is based on a separate project and hence not reported in any of the articles in the present work.
The resulting surface of films grown in a polycrystalline way will have a roughness that depends on the nucleation density and the film thickness. The topography consists of polygons with facets that can be grouped into sets with similar slopes relative to the substrate surface. In a practical case these slopes may be measured by AFM and give indication to which crystallographic planes that has lowest growth rates. The present work has tried to apply this method to the growth of $\beta$-MnO$_2$ by Mn(thd)$_3$ and O$_3$ in paper II and III of this dissertation.

It should be noted that the just considered effect in polycrystalline growth is also present with other deposition techniques, and is actually minimized in the ALCVD growth regime. However, it is not possible to obtain uniform films of all types of materials on all types of substrates.

### 4. The present study

The main aim of the dr. scient. thesis “Growth of thin films of functional oxides with the ALCVD method” has been to explore the possibility to use ALCVD for growth of thin films of oxides (perovskites) with physical properties that eventually can be of interest for applied research. The La-Ca-Mn-O system was chosen due to its presence of colossal
magnetoresistant properties. This necessitated the investigation of Ca-O growth, which in this single metal component system rather led to growth of CaCO₃.

The articles in this dr. scient. thesis may be divided into two sections:

The foundation (precursors, single metal component films, effects of substrates and external fields):

I. Inexpensive set-up for determination of decomposition temperature for volatile compounds
II. Growth of manganese oxide thin films by atomic layer deposition
III. Effect of substrate on the characteristics of manganese(IV) oxide thin films prepared by atomic layer deposition
IV. Growth of calcium carbonate by the atomic layer chemical vapour deposition technique
V. Effect of magnetic field on the growth of α-Fe₂O₃ thin films by atomic layer deposition

Growth of perovskites:
VI. Thin film deposition of lanthanum manganite perovskite by the ALE process
VII. Preparation and characterization of La₁₋ₓCaₓMnO₃ thin films grown by atomic layer chemical vapour deposition

I. In order to produce thin films by ALCVD it is necessary to have some information about how the different precursors behave under the growth process. One of the parameters that are of interest is the decomposition temperature for the precursors which is not easily measured by standard methods. A simple and inexpensive method for gathering such data was therefore developed during this project, which despite its crudeness gives invaluable information about the upper limit of ALCVD growth for the different precursors.

II and III. The manganese oxides were studied in much more detail than the other compounds. Since they may adopt many different crystalline modifications, the growth could hence be susceptible to influences of external effects, such as the type of substrate. An additional reason why they were studied in more detail was an early observation of an
additional X-ray reflection that should be extinct for the $\beta$-MnO$_2$ phase, thus structural symmetry lowering by different phase formation or induced by stress.

**IV.** The study of thin films of calcium carbonate was a result of a more thorough investigation of the Ca(thd)$_2$ – O$_3$ system which was intended a precursor combination for Ca containing depositions in article VII. We suspected that carbonate would indeed be formed, but not to the systematic extent that we observed. The films were at first amorphous, but on introduction of a separate CO$_2$ pulse in the ALCVD sequence it proved possible to obtain crystalline films with orientated growth, and even epitaxial growth on $\alpha$-SiO$_2$(001).

**V.** Since ferro/anti-ferromagnetic properties are of interest for colossal magnetoresistant materials, an investigation of effects of magnetic fields on growth of magnetically ordered materials was considered of high interest. We have therefore studied the influence of an external effect such as a magnetic field on the growth process of $\alpha$-Fe$_2$O$_3$. This work was the result of an internal discussion on the possibility to alter the growth texture. The $\alpha$-Fe$_2$O$_3$ system was chosen because it has a Néel temperature above the growth temperature, and could hence be subjectable to effects imposed on the film by an external field. This subproject is carried out in collaboration with dr. scient. Student Martin Lie and article V will also be an integrated part of his doctoral thesis.

**VI.** This paper was already published in 1999 and gave confidence and background for the entire thesis work. LaMnO$_3$ was in fact grown successfully even though a full insight into the growth of the different components was not available beforehand. With such a successful attempt one became confident that a larger goal, growth of La$_{1-x}$Ca$_x$MnO$_3$, would be possible. However, a more thorough background investigation would clearly be required to reach the goal of controlled growth of multicomponent oxides.

The more systematic program was begun by looking into the growth of the different constituent’s one at a time. Growth of La$_2$O$_3$ was investigated with the new F-120 Sat system early in the project, however, we later learned that this compound had also been studied and submitted for publication by the group of Niinistö [33]. A brief account of the present findings on La$_2$O$_3$ is included in article VII and for the rest of our data we are content to note that these comply with Ref. [33].
VII. The main article of this study concerns probably the growth of the multicomponent films of \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \). The main aim of this sub project was to produce thin films of a compound with some practically interesting properties such as colossal magnetoresistance. This was done by depositing \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \) on different single crystalline substrates. This work also gives an indication about the reproducibility in the production of such complicated compositions over large surface areas and on different substrates.

5. Summarizing conclusion

The present project has exemplified some important aspects about controlled growth of thin films by the ALCVD technique. It has been shown that the microstructure/texture and crystal system of the films may be influenced by such effects as:

*Choice of substrate.* In the papers on the growth of \( \text{CaCO}_3 \) [IV], \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) [VII] and especially \( \text{MnO}_2 \) [II] it has been shown that the substrate may alter the texture as well as the crystalline phase of the thin film for otherwise equal growth conditions. The choice of substrate is shown also to have an effect on the physical properties of the films in growth of \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) [VII].

*Choice of precursor.* The paper on the growth of \( \text{CaCO}_3 \) [IV], reports that the texture of the films change from a (001) to a (104) columnar type as the temperature is increased from 250 °C to 350 °C. This is attributed to a structural change of the \( \text{Ca(thd)}_2 \) precursor molecule, which has previously been reported in Ref. [34]. This indicates that the state of the precursor will be able to affect the texture of ALCVD grown films.

*Combination of elements.* Growth of \( \text{MnO}_2 \) has been shown to be surface controlled only up to a temperature of ca. 240 °C where the \( \text{Mn(thd)}_3 \) precursor decomposes, [I,II]. However, this decomposition temperature may be increased to ca. 320 °C when \( \text{Mn(thd)}_3 \) is used on surfaces that also contain terminated Ca or La atoms. Another demonstrated effect is that by
combination of elements, new phases may be formed with a different stability toward product
gasses such as CO₂. It has been demonstrated that the usage of Ca(thd)₂ and ozone as
precursors will form a carbonate [IV], whereas it will form an oxide when grown together
with manganese [VII]. This study has also demonstrated some of the difficulties by using
ozone in growth of manganese oxides [II], since Mn-O will act as a catalyst for ozone
decomposition with the result of films with relatively large gradients. These gradients are
almost removed when La and/or Ca are introduced [VII].

Magnetic field. Paper V demonstrates that presence of magnetic fields in the 0.14 T range,
may influence the texture of α-Fe₂O₃ growth, when deposited on amorphous substrates. Note
that these findings are compound specific. We have shown that there is no effect on growth of
CaCO₃ and MnO₂.
References

Heating zone no. 1
Plug Test ampoule Alumina tube Test ampoule

(a) 

(b) 
![Graph showing temperature variation along the longitudinal coordinate.]

(c) 
![Diagram showing a cross-section of the heating zone with temperature distribution.]

(d) 
![Diagram showing a longitudinal view of the heating zone with temperature profile.]

Temperature (°C)
Longitudinal co-ordinate (cm)

0 10 20 30 40 50 60 70 80 90
100 200 300 400 500 600
Inexpensive set-up for determination of decomposition temperature for volatile compounds

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Received 12 December 2002; accepted 17 February 2003

Abstract

The utility of precursors for atomic layer chemical vapour deposition (ALCVD) growth is limited by the sublimation and decomposition temperatures. Sublimation temperatures are conveniently obtained by thermogravimetry (TG) under vacuum. We present here a relatively inexpensive method to obtain information about the decomposition temperature for a precursor candidate for ALCVD. This approach requires an oven with a controlled temperature gradient and a long ampoule for each precursor. The precursors tested in this work comprise the thd complexes (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, La, and Ca.

Keywords: Thermal decomposition; ALCVD; ALD; ALE; CVD; β-Diketonate; VO(thd)2; Cr(thd)3; Mn(thd)3; Fe(thd)3; Co(thd)2; Ni(thd)2; Cu(thd)2; Zn(thd)2; La(thd)3; Ca(thd)2

1. Introduction

Atomic layer chemical vapour deposition (ALCVD, also named atomic layer epitaxy (ALE) or atomic layer deposition (ALD)) [1] is a thin-film growth process where the film is systematically manufactured by sequential gas pulses of two or more precursors, each pulse being followed by a purge of an inert gas. The precursor will for each pulse react with all surfaces in the reaction chamber and produce a chemically adsorbed layer. This layer will, in turn, function as a reactant for the following pulse in the precursor sequence. The growth will be limited to one monolayer of precursor per pulse, and is a self-limited growth process. Thermal decomposition of the precursors is highly unwanted since this will produce uncontrolled growth, and reliable information about decomposition temperatures for precursors is accordingly of great importance.

There are other criteria that apply for precursors used in ALCVD processes than for those in ordinary CVD growth. These have been surveyed thoroughly in [1,2], and among the many factors involved special attention has been focused on: volatility, stability, reactivity, etching, and purity. The most critical factors in this respect are that the precursors have to be volatile and thermally stable during the entire growth step they are involved in. The concern for the latter factors usually limits the lower and upper temperature windows for ALCVD growth. To select a precursor for ALCVD growth one therefore needs information about the sublimation as well as decomposition temperature.

The main criterion for precursors used in ordinary CVD growth is that they should be easily volatilised and that the precursor mixtures should not be too...
reactive so that undesirable gas-phase reactions are limited. Thermal decomposition of a precursor is not a problem here as long as the unwanted decomposition products are volatile and chemically stable under the conditions in the reaction chamber. Many CVD growth processes are based on thermal surface decomposition of one or more precursors.

In ALCVD growth, the precursors are used in a different way. The precursors are brought into the gas phase in more or less the same way as with normal CVD, but they should be reactive enough to react with all surfaces in the reaction chamber. In fact the precursors used for ALCVD may just as well be highly reactive since gas-phase reactions and associated problems are eliminated, but they should not decompose on any surface or in the gas phase. Decomposition hampers self-limiting growth and hence the control with, and quality of, the film diminishes. However, films may be formed with a tolerable thickness inhomogeneity even though a small part of a precursor is decomposing, but it should be recalled that the decomposition rate increases exponentially with temperature.

Information about sublimation temperature may conveniently be obtained by thermogravimetric (TG) analysis under vacuum. Vacuum should be used to mimic the conditions during the growth process, viz. in order to ensure comparable sublimation kinetics during the TG testing and the actual film growth. A simple method for determination of the decomposition temperature for a compound in the gas phase is apparently not described in the literature. Differential thermal analysis (DTA) or differential scanning calorimetry (DSC) can not be used since the precursors per definition are volatile. Attempts have been made to use mass spectrometry to determine the decomposition temperature for different precursors [3–5], but this method is cumbersome. Moreover, although mass spectrometry may give invaluable information about decomposition paths and products, it is an expensive technique and not even vaguely accurate enough when it comes to temperature control and determination unless precautions as mentioned in [3–5] are taken. A part of the problem stems from the fact that it is difficult to establish whether the precursor decomposes in the gas phase before it enters the mass spectrometer, or decomposes by the bombardment of electrons in the ion chamber. It would, of course, be possible to use softer ionisation, e.g., chemical ionisation with CH$_3^+$, but such an approach is not often used for the purpose. Mass spectrometric analyses may, with rather large rebuilding of the units concerned, be integrated into the ALCVD growth chamber [6–8] and in this way give instant information about whether decomposition of a given precursor takes place during the deposition step. Another approach is to use IR analysis in different geometries [9], but this still requires rather sophisticated equipment and analyses.

This report concerns an inexpensive method that may be used to obtain information about the decomposition temperature of volatile compounds.

2. Equipment and procedures

A furnace with a well defined and controllable temperature gradient is needed. The present furnace (Fig. 1(a)) has an overall length of 1 m and includes eight separate zones. However, this turned out to be more zones than actually necessary. In the present equipment, the temperature was set by applying a constant voltage to each zone. This was supplied from one common voltage source that in turn was subjected to the variations in the current flow from the in-house outlet. This gave some variation in power to the eight-zone oven, and a resulting temperature fluctuation of ca. ±1% on the Celsius scale over a period of 1 day. It is of course possible to increase the temperature precision by applying separate temperature controllers for each zone, but this increases the cost of the system appreciably without improving the results noticeably.

A central design criterion for the equipment has been that the precursors should be exposed to the same type of environment as in the ALCVD reactor. This has been accomplished by making an ampoule of silica glass and loading it with a small amount of precursor, conveniently placed in an open container. The loaded ampoule is sealed under a pressure resembling that in the reactor during film growth, and inserted into the gradient oven with the precursor at a position where the temperature is close to the sublimation temperature. The precursor will then sublime and diffuse into the warmer parts of the ampoule where it decomposes at an appropriate temperature.

The thermal gradient in the oven is set so that the temperature profile give high resolution (low temper-
Fig. 1. (a) Gradient oven with decomposition test ampoule inserted. Separate power supplies for individual zones are indicated. (b) Typical temperature profile. (c) Schematic illustration of detection of decomposition deposits for complexes with coloured products. (d) Means to detect decomposition deposits for complexes with transparent or non-coloured products.

A convenient experimental procedure is: the gradient oven is preheated to establish a gradient with a desired temperature profile. The loaded ampoule is, after evacuation and sealing, inserted into the gradient oven with the precursor located in the colder zone at a temperature close to the sublimation temperature established by TG. The ampoule is left in the oven until most of the precursor has sublimed and diffused lengthwise along the ampoule (usually 1–2 days). The heat treatment is concluded by removing the ampoule from the furnace and leaving it to cool in air. The ampoule is then subjected to visual inspection, which in the successful case will show that most of the precursor has been sublimed from the cold end and decomposed in the warmer parts (Fig. 1(c)). Data are extracted by noting the positions of the deposits on the ampoule wall and comparing these positions with the temperature profile of the gradient oven.
The estimated precision in thus determined decomposition temperatures depends on the temperature gradient at the location of the deposit and the fluctuations of the supplied voltage. In the set-up used, the temperature precision is estimated to be some ±4°C for up to 300°C, ±6°C in the range of 300–400°C, and ±8°C above 400°C.

The procedure works best for precursors who produce coloured deposition products. The present test series was performed on thd (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) complexes of the 3d metals. The decomposition products of most of these precursors are usually the corresponding metal or metal oxide(s) with distinct colours. In cases where one expects colourless decomposition products it may turn out to be difficult or impossible to detect decomposition products on the ampoule wall by visual inspection. A remedy in such cases is to insert pieces of a non-transparent material with a polished surface in the ampoule (Fig. 1(d)). Changes in the reflectivity of the polished pieces can then be used to establish that deposition has taken place. Care must be taken to ensure that heat transport along the inserted material is minimised in order not to alter the temperature profile along the ampoule. One venture is to cut the insert material in small irregular chips so that heat conduction from chip to chip becomes limited. Small spheres may also be used. The use of longer pieces of metal wires may change the temperature profile in the ampoule significantly and should accordingly be avoided. Pieces of polished single crystals of silicon were used in the present case.

The described procedure is intended for solid precursors that do not melt during the sublimation process. However, liquid and gaseous precursors may be used in the same set-up after minor modifications. A liquid precursor may simply be inserted into the ampoule in a suitable container to avoid that the precursor floats along the entire ampoule. Alternatively, small floating barriers may be made during the forming of the ampoule. The gradient oven may also be given an inclined position when liquid precursors are involved. For a gaseous precursor the ampoule may be replaced by an open tube, where a slow stream of precursor gas is fed in at a cool end of the tube. Reduced pressures may be achieved by connecting a pump at the other end of the tube.

3. Experimental

We have studied the decomposition of VO(thd)₂, Cr(thd)₃, Mn(thd)₃, Fe(thd)₃, Co(thd)₂, Ni(thd)₂, Cu(thd)₂, Zn(thd)₂, La(thd)₃ (La₂(thd)₆ [10]), and Ca(thd)₂ (Ca₃(thd)₆ [11]) according to the above procedure. The precursors have been made in-house according to a modified procedure of the one described in [12].

TG analysis under ca. 1 mbar of flowing N₂ and with a heating rate of 1°C/min was performed with a Perkin-Elmer TGA 7 system to establish the sublimation temperature for these precursors. The onset temperature for a detectable TG mass loss was chosen as the sublimation temperature (Table 1). The ampoules used for the decomposition experiments were made of silica glass and had an inner diameter of 5 mm and a length of ca. 1 m. A small silica-glass container (volume: ca. 0.06 ml) charged with the precursor to be tested was inserted into the ampoule prior to evacuation. The Zn(thd)₂, La(thd)₃, and Ca(thd)₂ complexes produce colourless decomposition products, and chips of the polished silicon were in these cases accordingly inserted lengthwise along the ampoule prior to evacuation. The experiments and their evaluations followed the procedure described earlier.

4. Results and discussion

The TG analyses show that all tested complexes undergo a simple one-step sublimation process. The degradation experiments show that the decomposition mainly occurs in two steps. The first step occurs in the lower-temperature region where the deposition product has the same colour as the metal or metal oxide under study, the next at higher temperatures where black coloured products are seen. Fe(thd)₃ shows in addition also deposition in an intermediate temperature range where the product has the same colour as in the first range. For Ca(thd)₂ and Ni(thd)₂, it seems that the two decomposition stages overlap.

The estimated decomposition temperatures for the tested complexes (Table 1) appear to show some correlation with the electron count (EC) for the central metal atom of the complex (all counts referring to mononuclear species). The complexes with EC = 18 (Cr and Ni) have the highest thermal stability. The
Table 1

Temperatures (°C) for onset ($t_{\text{ons}}$) of sublimation of complex (uncertainty ± 3 °C), onset and end ($t_{\text{end}}$) of decomposition of complex (uncertainty in parentheses), onset and end of degradation of organic fragment (uncertainty ± 8 °C), and electron count (EC) for the central metal atom of the complex (assuming mononuclear species)

| Complex | Sublimation $t_{\text{ons}}$ | Decomposition
<table>
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<tr>
<td></td>
<td></td>
<td>$t_{\text{ons}}$</td>
</tr>
<tr>
<td>VO(thd)$_2$</td>
<td>129</td>
<td>368 (6)</td>
</tr>
<tr>
<td>Cr(thd)$_3$</td>
<td>127</td>
<td>435 (8)</td>
</tr>
<tr>
<td>Mn(thd)$_3$</td>
<td>124</td>
<td>240 (4)</td>
</tr>
<tr>
<td>Fe(thd)$_3$</td>
<td>124</td>
<td>210 (4)</td>
</tr>
<tr>
<td>Co(thd)$_2$</td>
<td>118</td>
<td>311 (6)</td>
</tr>
<tr>
<td>Ni(thd)$_2$</td>
<td>138</td>
<td>330 (20)</td>
</tr>
<tr>
<td>Cu(thd)$_2$</td>
<td>127</td>
<td>173 (4)</td>
</tr>
<tr>
<td>Zn(thd)$_2$</td>
<td>121</td>
<td>349 (6)</td>
</tr>
<tr>
<td>La(thd)$_3$</td>
<td>184</td>
<td>451 (8)</td>
</tr>
<tr>
<td>Ca(thd)$_2$</td>
<td>190</td>
<td>Not detected</td>
</tr>
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Temperatures refer to measurements at an estimated pressure of ca. 1 mbar.

thermal stability decreases with both larger and smaller EC, but the decrease in decomposition temperature is more pronounced for the complexes with the higher ECs. VO(thd)$_2$ (and possibly La$_2$(thd)$_6$ and Ca$_3$(thd)$_6$) should perhaps be neglected from such comparisons because of the special composition and structure, and the possibility that some of the complexes are subjected to dimerisation or de-polymerisation should be kept open.

Decomposition of complexes like these may be homogeneous (viz. occur in the gas phase) and/or heterogeneous (viz. take place on a surface). The present type of experiment is not able to differentiate between the two types of decomposition courses. However, both types of decomposition incidents are unwanted in AL-CVD growth.

When metalorganic complexes decompose at low temperatures, the products will most likely be the metal or its oxide and volatile organic fragments. The organic fragment(s) will in turn diffuse further into the warmer parts of the apparatus and in the end decompose to a carbon-like residue. Bykov et al. [5] have studied the decomposition of the residues that form when thd complexes decompose, and found that these decompose at ca. 600 °C, which is consistent with our findings of black deposits in the same temperature region (Table 1). The decomposition of Ni(thd)$_2$ represents an exception to this pattern in that the dark deposit at around 600 °C was absent, whereas the lower-temperature deposition region was extended. Our working hypothesis is that the first decomposition product of Ni(thd)$_2$ here acts as a catalyst for the decomposition of the organic fragments. In this way, the latter species never reach the higher-temperature region. When Ni(thd)$_2$ decomposition experiments were run for 3 days it was indeed also possible to observe a grey area stretching all the way from 185 °C and into the organic-fragment degradation zone specified in Table 1. Throughout the entire deposition region there were also seen randomly distributed darker spots signalising regions with more extensive decomposition. A satisfactory explanation is not found, but in close association with this behaviour it is recorded that the reproducibility of the decomposition temperatures for Ni(thd)$_2$ (some ±20 °C between repeated runs) are somewhat poorer than for the other precursors (ca. ±5 °C) studied.

The decomposition of Ni(thd)$_2$ and Cu(thd)$_2$ have also been studied by MS which gave decomposition temperatures of 362 [3] and 330 °C [5], respectively. This is consistent with our findings for Ni(thd)$_2$ (330–465 °C), but significantly higher than our decomposition temperature for Cu(thd)$_2$ (173–225 °C; repeatedly obtained in several runs).

Even though thermal decomposition of one precursor may give uncontrolled growth in mono-component ALCVD growth, the same will not necessarily be true for multi-component growth. For example, Mn(thd)$_3$
decomposes already at 240°C and the depositions of MnO$_2$ above this temperature reflects uncontrolled ALCVD growth [13]. Nevertheless, it is possible to use Mn(thd)$_3$ as precursor in combination with La(thd)$_3$ at higher temperatures to obtain controlled growth of lanthanum manganite [13,14]. The reason for this important distinction is most probably that when Mn(thd)$_3$ decomposes on a MnO$_2$ surface, the thd ligands simply desorb, whereas when Mn(thd)$_3$ breaks down on a surface where La is present, the thd ligands are swapped from Mn to La. A surface-controlled growth is, therefore, still possible since the thd ligands now adsorbed at the La atoms block further Mn(thd)$_3$ ligands from being adsorbed and subsequently decomposed. Such an effect works only if the decomposition of the precursor is surface activated. The ALCVD growth will in such a case again become uncontrollable above the decomposition temperature for La(thd)$_3$.

Acknowledgements

This work has received financial support from the Research Council of Norway. The authors also thank Dr. M.A.K. Ahmed for the synthesis of the precursors and performing the TG measurements.

References

Mn$_3$O$_4$ (hausmanite)
Growth of manganese oxide thin films by atomic layer deposition
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Received 13 March 2003; received in revised form 3 July 2003; accepted 3 July 2003

Abstract
Thin films of manganese oxide are made by the ALD (atomic layer deposition) technique using Mn(thd)₃ (Hthd=2,2,6,6-tetramethylheptan-3,5-dione) and ozone as precursors. Pulse parameters for ALD-type growth are established and such growth can be achieved at deposition temperatures between 138 and 210 °C. Films have been deposited on both soda-lime glass and Si(100) single crystals. The electrical resistivities of as-deposited films grown on soda-lime glass are measured to be 0.3–3.2 V cm (linear four-point-probe measurements).

Keywords: Manganese oxide; Atomic layer deposition (ALD)

1. Introduction
Manganese can hold a number of oxidation states, +2, +3, and +4 being the most common for the oxides. Nominal compositions of such phases are MnO, Mn₂O₄, Mn₃O₄ and MnO₂, but non-stoichiometry has been observed for some of these phases. Moreover, except for MnO, two or more crystalline modifications are known for each composition. The MnO₂ composition has proved to be the most stable in the ALD-growth regime subject to this study. (ALD, atomic layer deposition; also known as ALE, atomic layer epitaxy and ALCVD, atomic layer chemical vapour deposition.)

The MnO₂ composition is attributed to at least six crystalline modifications (designated as α, β, γ, δ, ε, and λ) where β-MnO₂ and (possibly) λ-MnO₂ appear to be stoichiometric variants. Several of the MnO₂ phases need the presence of foreign components such as hydroxide, water or an alkali constituent in order to be formed. All manganese oxides are semiconductors, the lowest resistivity being found at the MnO₂ composition. The bulk resistivity of β-MnO₂ is as low as 0.0028 Ω cm at room temperature [1], more generally resistivities of manganese dioxides fall in the range 1000 to 0.1 Ω cm [2–4].

Manganese dioxide is successfully used as a layer material in tantalum thin-film capacitors [5,4]. It is furthermore used as catalyst for oxidation of hydrocarbons [6,7], oxidation and reduction of nitric oxide [8,9], and decomposition of ozone [10]. Moreover, it has interesting electrochromic properties [11–16], but most commonly manganese dioxide is used in batteries [17,18].

Thin films of manganese oxides have hitherto been synthesised mainly by wet chemical processes (such as anodic oxidation [13,19], electrodeposition [12,14,15,20], electroless deposition [21], and spray pyrolysis [5]), but also by electron beam evaporation [16], chemical vapour deposition [11,22,23], reactive sputtering [3,4], molecular beam epitaxy [24,25], pulsed layer deposition [26], and now by ALD. The latter technique allows growth of ultra-thin and uniform films with conformal coating [27]. The process is robust in the so-called ALD regime where the growth rate is little affected by variations in the process parameters [28].

2. Experimental details
Thin films were deposited in a commercial F-120 Sat reactor (ASM Microchemistry) using ozone and Mn(thd)₃ (Hthd=2,2,6,6-tetramethylheptan-3,5-dione) as precursors. The Mn(thd)₃ precursor was partly made in house as described in Ref. [29] and partly purchased.
from Strem Chemicals (claimed purity 99%). The adapted sublimation temperature was 133 °C. The ozone was made by feeding 99.999% O₂ into an OT-020 ozone generator from Ozone Technology, giving an ozone concentration of 15 vol.% according to specifications. An ozone flow of ca. 500 cm³ min⁻¹ was used during the ozone pulses. Tests proved that regular CVD growth does not occur for the chosen sublimation temperature of Mn(thd)₃ and the used ozone flow. When powdered Mn(thd)₃, as a test, was reacted with ozone at 200 °C under atmospheric pressure, poorly crystalline Mn₃O₄ (hausmanite) was formed.

During all depositions a background pressure of 1.8 mbar was obtained by applying a carrier gas flow of 300 cm³ min⁻¹ N₂. The carrier gas was made in a Schmidlin UHBN3001 N₂ purifier with a claimed purity of 99.999% with regards to N₂ + Ar content.

Most films were deposited with a total of 1000 pulses. This resulted in film thickness between 5 and 35 nm. The films were deposited on 5 × 5 cm² substrates of soda-lime glass and Si(100) single crystals. Normally one soda-lime glass and one Si(100) substrate were used in a back-to-back configuration for each run. The size of the reaction chamber is ca. 0.2 dm³. The Si(100) substrates were used as obtained from the manufacturer. The soda-lime glass substrates were cleaned by first boiling them in trichloroethylene for 5 min, then in acetone for 5 min, immersed in ethanol, washed with neutral soap, and rubbed with cotton. Thereafter, they were rinsed in running water over night, then rinsed with deionised water, and finally quickly blown dry with N₂.

The films formed were examined with a Siemens D5000 diffractometer equipped with a Göbel-mirror to obtain a parallel beam with Cu Kα radiation. This setup was used to measure the X-ray reflectivity as well as for conventional X-ray diffraction (XRD) in reflection mode. X-Ray fluorescence (XRF) measurements, using a Philips PW2400 unit, gave an alternative assessment of the film thickness. The UniQuant analysis software [30] was used with basis in just fundamental parameters for the intensity interpretation. A selected substrate was also measured on an Itrax XRF microscope in order to reveal thickness gradients in the direction normal to the gas flow.

X-Ray photoelectron spectroscopy (XPS) was recorded on a Vacuum Generator Microlab III spectrometer, a conventional Al Kα anode was used at 15 kV and 20 mA as the source for the X-ray radiation. The normal take-off angle of the photoelectrons was 90°. The detail spectra were collected with a 20 eV pass energy, providing an instrumental resolution better than 0.85 eV. The background pressure during the analyses was ca. 10⁻⁹ mbar. The poorly conducting manganese oxides give rise to distinct charge shifts. The fixing of the energy scale was established by adjusting the C(1s) binding energy for the omnipresent air-borne hydrocarbons at 284.6 eV. The mean oxidation state of Mn is mirrored in the multiplet splitting [31] of the Mn(3s) peak and the Mn oxidation state in the films was established by relating the as-measured splittings to reference compounds. Since the manganese oxides may exhibit significant ranges of homogeneity, care was taken (by limiting the amount of ion etching to a minimum) not to change the oxidation state of Mn in the films.

The resistivity of the films was measured by a linear four-point probe set-up with 1-mm spacing between the pins, and probe tips with a curvature of 500 μm. The typical current used for these measurements was 20 nA, which ensures a voltage drop of less than 1 V over the two outermost pins. No correction was made for the finite size of the substrates since these were considered large relative to the probe size (estimated correction less than 5%).

Selected films were studied with atomic force microscopy (AFM; Nanoscope E, Digital Instruments in contact mode) in order to determine topography and roughness. Selected films were also analysed with transmission FT-IR spectroscopy on a Perkin-Elmer System 2000 FT-IR spectrometer. Films for the latter analyses were deposited on both sides (both sides polished) of Si(100) substrates. An uncoated substrate was used as reference. Powdered samples were pressed and measured in KBr pellets using a blank pellet as reference.

3. Results

The effect of pulse and purge parameters on the growth was investigated by changing one parameter at a time, and keeping all others at values that were believed to be well within the ALD-growth regime. Results are presented in Fig. 1 for a reaction-chamber temperature of 186 °C.

Fig. 1 shows that a 1.5 s Mn(thd)₃ pulse is sufficient at a precursor sublimation temperature of 133 °C. The subsequent purging can safely be limited to just 0.1 s and still prevent CVD growth. The ozone pulse provides a modest increase in growth rate with the pulse time. On this basis a pulse time of 6 s was chosen. Due to the large ozone flow chosen, the reactor pressure increased to 3.5 mbar during the ozone pulse. Although the subsequent purge time can be chosen as short as 0.5 s without indication of CVD growth, a longer purge time of 3 s was chosen in order to sufficiently lower the reactor pressure.

The growth rate as measured with X-ray profilometry and XRF as function of the temperature in the deposition chamber is shown in Fig. 2. The rate varies only little with the temperature in the range 140–230 °C. The XRF data suggest that possibly there may be seen two growth regimes, one in the range 140–190 °C and
the above maximum thickness on both kinds of films, and applying Si of the valleys between the extremes will be smaller for on Si. However, since the column density is larger for films columns on both types of substrates should be equal. Nature of ALD growth, the extreme length of the columnar manner. This implies that, because of the oriented and accordingly believed to have grown in a Z-range (Z = 3.0 nm, Z-range = 3.0 nm, Z-range = 12 nm). Both kinds of films are oriented and accordingly believed to have grown in a columnar manner. This implies that, because of the nature of ALD growth, the extreme length of the columns on both types of substrates should be equal. However, since the column density is larger for films on Si(100) than on soda-lime glass substrates, the depth of the valleys between the extremes will be smaller for Si(100)-based films. Therefore, on postulating the same maximum thickness on both kinds of films, and applying the above Z-ranges, there necessarily appears a difference in the mean thickness of (12 – 5)/2 = 3.5 nm; viz. identical with the above-mentioned apparent thickness difference.

In an ALD-growth mode, the thickness ought to vary strictly linearly with the number of pulses. This anticipates that there is no hindrance for the deposition of the first layer. As seen from the inset into Fig. 2, this condition is satisfied for the MnO_2 films grown at 186 °C.

The θ–2θ XRD data (Fig. 4), show that the films contain one and the same phase up to ca. 230 °C. Above this temperature Mn_3O_4 (hausmanite) is formed. At deposition temperatures below ca. 230 °C an oriented growth is seen on both soda-lime glass and Si(100) substrates, the orientation corresponds to (h00) for a tetragonal phase, except for the presence of a weak (110) reflection at 162 °C. The diffraction pattern of the oriented phase shows close resemblance to β-MnO_2 (pyrolusite), but contains an additional peak at 4.39 Å (2θ = 20.23°) that can be indexed as (100) for a phase with the same unit-cell dimensions as β-MnO_2. However, since β-MnO_2 crystallizes in space group P4_2/mnm, (100) should be extinguished. The presence of this additional peak may signal a new distinct phase closely related to β-MnO_2, or originate from induced stress in the films, which could cancel the extinction of this reflection. Regardless of the correct interpretation, the phase, which exhibits this reflection, will be designated hereafter as β'-MnO_2. The difference between Mn_3O_4 films grown at 283 and 331 °C in Fig. 4 indicates that the films become more (103) oriented as the surface decomposition proceeds.
In one of the 5000-cycle runs at 186 °C, the sublimation temperature for the Mn(thd)$_3$ precursor was set higher than the 133 °C used in the rest of the series. The XRD data in Fig. 5 reveal that such an enhanced Mn(thd)$_3$ flux results in unoriented growth of β’-MnO$_2$.

The mapping of (h00) peaks of the oriented β’-MnO$_2$ phase, on soda-lime glass as well as Si(100) substrates, in reciprocal space shows that the films are not fully oriented normal to the substrate, but exhibit a random tilting of the crystallites with a FWHM of ca. 7°. A ϕ-scan of the asymmetric reflection (310) confirmed that the films were polycrystalline with a random crystallite orientation within the substrate plane, typical for columnar growth.

The oxidation state of Mn was probed by XPS on the as-deposited films, and the observed splitting of the Mn(3s) peak was compared with reference spectra for powdered MnO, Mn$_2$O$_3$, and MnO$_2$. Fig. 6 shows that films deposited at temperatures up to ca. 230 °C contain mainly manganese in oxidation state +4. At higher deposition temperatures the oxidation state decreases, viz. consistent with the thermodynamic stability of the solid phases in the Mn–O system. One of the depositions made at 200 °C was also checked by RBS (Rutherford back scattering), which gave the composition MnO$_{2.0±0.1}$, in full consistency with the XPS results.

The resistivities at room temperature for as-deposited films at different reactor temperatures are shown in Fig. 7. The resistivity decreases from 3.2 to 0.3 Ω cm as the deposition temperature is increased from 138 to ca. 230 °C. At still higher temperatures the resistivity increases again due to changes in composition from MnO$_2$ to Mn$_3$O$_4$. A resistivity of 0.3 Ω cm is close to the reported value [2] for bulk MnO$_2$. 

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Fig. 3. AFM topography measurements of MnO films on Si(100) grown at: (a) 186 °C, 1000 cycles; (b) 186 °C, 5000 cycles; (c) 283 °C, 1000 cycles; (d) on soda-lime glass substrate at 186 °C, 1000 cycles.
Fig. 4. XRD diffractograms for as-grown films on soda-lime glass substrates of ca. 100-nm thickness (5000 cycles) at different deposition temperatures. Miller indices on the upper diffractogram refer to MnO$_2$ (hausmanite) and those on the lower diagram to $\beta'$-MnO$_2$ ('pyrolusite'). Numbers on the right-hand side give deposition temperature in °C.

The selected AFM-topography image of a film deposited on Si(100) with 1000 cycles at 186 °C in Fig. 3a, have a rms roughness of 1.0 nm independent of the scanning area chosen. When the number of cycles is increased to 5000 (Fig. 3b), the rms roughness is increased to 4.2 nm, still independent of the area analysed. However, for films deposited at 283 °C (Fig. 3c; 1000 cycles), where the precursor is believed to decompose (see below), the rms roughness increases from 4.0 to 20 nm as the analysed area is increased from 0.25 x 0.25 to 5 x 5 μm$^2$. For comparison it should be noted that films deposited at 186 °C on soda-lime glass (Fig. 3d; 1000 cycles), showed a rms roughness of 2.5 nm independent of the area scanned, viz. more than twice as much as for the corresponding films deposited on Si(100).

Fig. 6. XPS scan of Mn(3s) profile for film grown at 186 °C. Inset shows energy splitting ($\Delta E$) vs. deposition temperature; $\Delta E$ for Mn in oxidation states +2 (MnO), +3 (Mn$_2$O$_3$), and +4 (MnO$_2$) according to Ref. [31] are indicated.

IR data for powdered samples with well-established composition and structure were compared with spectra of films deposited on both sides of Si(100) substrates (Fig. 8). There is a marked distinction in the deposits made at 210 and 234 °C. Films with an IR spectrum close to that of hausmanite are formed at higher temperatures. At lower temperatures the spectra exhibit similar features as powdered pyrolusite ($\beta'$-MnO$_2$), but with systematic shifts to lower wave numbers. This is
yet another indication that the films formed at lower temperature are structurally closely related to $\beta$-MnO$_2$.

4. Discussion

Fig. 1 indicates that a short ozone pulse of only 1.0 s could be appropriate to produce films with gradients of less than 5%. However, these growth-rate data for the front and end of the substrates measure just gradients in the flow direction. Fig. 9 shows, however, that appreciable gradients occur normal to the flow direction for short ozone pulses. These gradients are reduced when the ozone pulse exceeds 5 s, and have probably their origin in the unstable ozone gas, which enters a large chamber from a narrow tube. (However, most of the deposited films showed a smaller type of such gradients.)

The half-life for decomposition of O$_3$ to O$_2$ at room temperature is ca. 160 h, at 100 °C 210 s, and at 250 °C only 0.03 s [10]. The lifetime will be further reduced when taking collisions with other molecules into account. The ozone as such is, therefore, less likely to diffuse uniformly throughout the reaction chamber during the growth experiments at elevated temperatures, but will rather follow a straight path within the reaction chamber. Longer pulse duration of ozone results in a significant increase in the reactor pressure from 1.7 to 3.5 mbar, and helps ozone in reaching more remote locations normal to the flow direction before it decomposes. A more sophisticated design of the ozone inlet to the reaction chamber would probably allow shorter ozone pulses. Another factor that constantly reduces the amount of ozone in the chamber is the fact that the product film (MnO$_2$) itself is a well-recognized catalyst for decomposition of ozone [10]. In fact, it is likely that the ozone molecules will not be able to survive collisions with any surface in the chamber. As have been seen in ongoing work it is indeed possible to deposit gradient-free films of more non-catalytic materials such as CaCO$_3$ and La$_2$O$_3$ with ozone pulses as short as 1 s.

The measured growth rate of manganese dioxide is ca. 18 pm cycle$^{-1}$, based on mean thicknesses of films, whereas if maximum thicknesses are applied, the growth rate becomes ca. 22 pm cycle$^{-1}$. The growth mode is most probably of the columnar type with [100] normal to the substrate plane. The maximum angle of the sides on the tips of the columns is according to AFM ca. 45° (see Fig. 3), which suggests that they represent $\{110\}$ surfaces. In order to achieve columnar growth with this configuration, $\{110\}$ must have experienced a growth rate of ca. $22\sqrt{2}=15.5$ pm cycle$^{-1}$, and the inherent growth rate of $\langle 100 \rangle$ would have to be close to, or
larger than, 22 pm cycle⁻¹. By using the analogy of Ylilammi [32], viz. assuming that the adsorbed Mn(thd)₃ fragment spans over an area of ca. 11.5×13 Å² (extracted from information in Ref. [33]), and applying surface unit-cell dimensions of 2.87×4.40 and 2.87×6.22 Å² for (100) and [110], respectively, the maximum growth rate would be 23 pm cycle⁻¹ if the precursors completely fill the surface. Taking into account the periodicity on (100) it is possible to identify a pattern in which an adsorbed fragment blocks 12 active sites from further adsorption. This results in a growth rate of 18 pm cycle⁻¹ on (100). On {110} a corresponding reasoning gives a tolerable growth rate of 15.5 pm cycle⁻¹ (20 active sites blocked by one adsorbed fragment), which fits well with the periodicity on this surface. According to these surface-specific growth rates, the tips of the columns should have a flat termination with a length extension of minimum 39% compared with {110}. This is not as observed by AFM; the tips do not have such large flat surfaces, and hence the growth rate of (100) must be larger than inferred above, either by more dense packing of the adsorbed fragments, by another arrangement of the fragments (e.g., stretching out from the substrate) or the fragments are adsorbed as Mn(thd) rather than Mn(thd)₂. Owing to the nature of the β-MnO₂-like structure there may be a reason to believe that the Mn precursor fragment adsorbs on terminating oxygen atoms on {110} surfaces, and on bridging positions between two oxygen atoms on (100) surfaces. This implies that the adsorbed fragments should be of a different character on these two surfaces, covering a larger area space on {110} surfaces than on (100) surfaces, and hence reducing the growth rate of {110} surfaces compared to the other surfaces present.

In addition to the use of X-ray profilometry, growth rate (Fig. 2) was also estimated from XRF data by simply dividing mass per area with the density of β-MnO₂ (5.189 g cm⁻³; PDF 24-735). The distinction between results derived by XRF and X-ray profilometry may originate from either differences in analysed area (240 vs. 5 mm²) or from the fact that X-ray profilometry measures the absolute thickness whereas XRF measures the amount of compound per unit area. In coarse features the XRF results show good correspondence with the X-ray profilometry findings, by showing a plateau with a growth rate of ca. 20 pm cycle⁻¹ in the temperature region 140–190 °C followed by another growth-rate plateau of ca. 33 pm cycle⁻¹ in the temperature region 190–230 °C. However, the actual growth rates are slightly higher than discussed above. The latter plateau may be due to a larger fraction of the precursor being adsorbed as Mn(thd) and hence have produced a lower steric hindrance.

Decomposition experiments with Mn(thd)₃ in a gradient oven unveil that onset of thermal degradation occurs already at 240 °C [34]. The uncontrolled film growth above 240 °C is, therefore, a result of such decomposition of the Mn(thd)₃ precursor. It is interesting to note that enhanced stability of Mn(thd)₃ is observed when this precursor is used in combination with La(thd)₃ or Ca(thd)₂ for the growth of LaMnO₃ [35] or CaMnO₃ [36]. This behaviour is probably related to surface interactions between thd and La or Ca entities during the film growth and this aspect will be returned to in more detail in forthcoming papers.

This work does not draw a firm conclusion as to the relationship between β- and β'-MnO₂. On the one hand, it seems tempting to maintain that the extra reflection could reflect induced stress in the films, all the more since the reflection disappears when the film is crushed and does not appear on deposits made on curved substrates such as capillaries. On the other hand, shifts in IR spectra could favour an interpretation with a separate phase. Stress induced by thermal expansion differences between substrates and films should expectedly also have resulted in differences between the different kinds of substrates. However, one should also bear in mind that the deposition temperature is rather low when considering the effect of thermal stress.

Acknowledgments

This work has received financial support from the Research Council of Norway. The authors are indebted to Cand. Scient. Sissel Jørgensen for XPS measurements and helpful discussions, to Turid Winje for XRF measurements, to Odvar Dyrlie for help with AFM measurements, and Dr. Ero Rauhala for performing RBS measurements.

References

References

$\alpha$-MnO$_2$  $\beta$-MnO$_2$  $\epsilon$-MnO$_2$
Effect of substrate on the characteristics of manganese(IV) oxide thin films prepared by atomic layer deposition

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Abstract

Manganese(IV) oxide exhibits many different crystal structures, and growth of thin films of this compound is expected to experience a guiding effect from the substrate. This effect have been studied by deposition on different kinds of substrates by the ALD (= atomic layer deposition) technique. The types of substrates examined are: amorphous substrates such as soda-lime glass and Si(100) with a native SiO\textsubscript{x} surface layer, as well as an organic substrate – Kapton\textsuperscript{TM} foil; single-crystal substrates of oxides [\(\alpha\)-SiO\textsubscript{2}(001), \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}(012), \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}(001), muscovite(001), and MgO(100)]; and single crystal alkali-metal halide substrates [NaCl(100), KCl(100), KBr(100), and KI(100)] that may contribute with potential dopant elements to the film in the early growth stages. The films were made using Mn(thd\textsubscript{3}) (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) and ozone as precursors. Four different phases of MnO\textsubscript{2} are prepared: \(\alpha\)-MnO\textsubscript{2} (cryptomelane Q) [obtained on NaCl(100), KCl(100), and KBr(100) substrates], \(\beta\)-MnO\textsubscript{2} (pyrolusite) [obtained on \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}(012), muscovite(001), \(\alpha\)-SiO\textsubscript{2}(001), and MgO(100) substrates], a possible new phase of MnO\textsubscript{2} designated \(\beta'\)-MnO\textsubscript{2} [obtained on soda-lime-glass and Si(100) substrates], and \(\varepsilon\)-MnO\textsubscript{2} (akhtenskite) [obtained on \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}(001)]. The coherence between these phases and the substrates is discussed.

Keywords: manganese(IV) oxide (MnO\textsubscript{2}); effect of substrate; atomic layer deposition (ALD).

1. Introduction

The ALD technique (= atomic layer deposition; alternatively ALE = atomic layer epitaxy or ALCVD = atomic layer chemical vapour deposition) is a CVD type deposition technique where gas-phase reactions have been eliminated by means of purging and sequential pulsing of the individual precursors into the reaction chamber [1].
Manganese oxides adopt a range of oxidation states and structure types, and several exhibit nonstoichiometry. This makes the product very susceptible to alterations in the experimental conditions. For thin-film growth, different types of substrates may influence the nucleation kinetics and thus both the phases formed and their orientation. The main aim of the present study has been to investigate the influence of various types of substrates on ALD growth of manganese(IV) oxide thin films.

The Mn-O phases have different physical and chemical properties, especially with respect to selective oxidative catalysis [2-5]. Hence, product control is of high importance in synthesis by ALD. The manganese dioxides form a family of molecular sieves where β-MnO₂ exhibit small 1×1 channels and α-MnO₂ (OMS-2) 2×2 channels. Manganese(IV) oxides are applicable as layer material in thantalum thin-film capacitors, so-called ultracapacitors [6-8], furthermore as cathode and depolarizer in dry-cell batteries [9-17], and as sensors [18]. The molecular-sieve variants show good intercalation properties and may act as ion exchangers in, e.g., pollution removal from water [19-22].

α-MnO₂ is tetragonal (I4/m) with \(a = 9.788\), \(c = 2.865\) Å [23], Fig. 1a. The phase appears to be stabilized with inclusion of certain foreign ions, e.g., as \(X_x\text{Mn}_8\text{O}_{16}\) with \(X = \text{Na}\) (manjiroite), K (cryptomelane), Ba (hollandite) etc. The MnO₆ octahedra are connected to form the mentioned 2×2 channels. The bulk specific resistance of α-MnO₂ varies strongly between different natural occurring specimens that furthermore cover a wide range of \(X\) substituents. Reported values (in the range 1000–0.2 \(\Omega\) cm [24]) are generally larger than for β-MnO₂. α-MnO₂ may be regarded as metastable with respect to β-MnO₂ [25,26], and hence a modest heat treatment of α-MnO₂ results in oxygen deficient β-MnO₂ [23,26].

β-MnO₂ (pyrolusite) is tetragonal (\(P4_2/mnm\)) with \(a = 4.388\), \(c = 2.865\) Å [27]. The crystal structure (Fig. 1b) contains rods of edge-sharing octahedra which are interconnected at the corners, giving rise to the characteristic 1×1 channels. The bulk resistivity of β-MnO₂ may be as low as 0.0028 \(\Omega\) cm at room temperature [28], but most reported [29-31] values fall in the range 1000–0.1 \(\Omega\) cm.
\(\varepsilon\)-MnO\(_2\) (akhtenskite) is hexagonal \((P6_3/mmc)\) with \(a = 2.786\), \(c = 4.412\) Å \([32]\), and contains rods of face-sharing octahedra, the rods being interconnected at their edges (Fig. 1c).

![Diagram of crystal structure](image)

**Fig. 1.** The crystal structure for (a) \(\alpha\)-, (b) \(\beta\)-, and (c) \(\varepsilon\)-MnO\(_2\). Note that only half of the MnO\(_6\) octahedra in \(\varepsilon\)-MnO\(_2\) are filled.

Thin films of manganese oxides have hitherto been synthesised mainly by wet chemical processes; anodic oxidation \([33,34]\), electrodeposition \([35-39]\), electroless deposition \([40]\), spray pyrolysis \([41]\), and sol-gel methods \([8,39,42-45]\); but also by electron beam evaporation \([46]\), chemical vapour deposition \([47-49]\), reactive sputtering \([30,31,50]\), molecular beam epitaxy \([51,52]\), pulsed layer deposition \([53]\), and ALD \([54]\).

We have chosen several groups of substrates for the present study in order to gain insight into the structure-guiding effects on the deposited films. We have studied the effect of amorphous substrates, using soda-lime-glass and Si(100) substrates with a native SiO\(_x\) surface layer, as well as an organic Kapton\textsuperscript{TM} foil substrate. The effect of oxide substrates with surface structures with different symmetries are examined: two-fold \([\alpha\text{-SiO}_2(001)\) and \(\alpha\text{-Al}_2O_3(012)]\], three-fold [actually virtually six-fold; \(\alpha\text{-Al}_2O_3(001)\) and mineral muscovite(001)] and four-fold [MgO(100)]. We have also studied substrates that in addition to structure-geometry-guiding effects, may contribute to the film with dopant elements in the early growth stages [NaCl(100), KCl(100), KBr(100), and KI(100)].
2. Experimental

The ALD growth of manganese oxide films is described in Ref. [54]. Relevant preparation conditions with respect to the substrates are given below. All films were deposited using 5000 cycles (giving ~100 nm thickness) at a reactor temperature of 186 °C.

The soda-lime-glass substrates were regular microscope plates, the Si(100) substrates were purchased from Silicon Valley Microelectronics Inc., and Kapton™ foil from Goodfellow. Single-crystal substrates of α-SiO₂(001), α-Al₂O₃(001), and α-Al₂O₃(012) were obtained from MaTecK, MgO(100) substrates from Coating & Crystal Technology, and muscovite from a naturally occurring sample. Single crystals of KI, KBr, KCl, and NaCl were made in-house by controlled evaporation of saturated solutions of, respectively, KI (99.0 %), KBr (98.5 %), KCl (99.5 %), and NaCl (99.5 %) (all from Merck). This produced cubes with (100) surfaces. Relevant crystallographic data for the substrates are given in Table 1.

The Si(100) surface has four-fold symmetry; \( a = 5.431 \) Å. However, in oxidizing environments Si obtains an oxide layer that will possess some of the surface features of soda-lime-glass substrate. HF-etched Si(100) takes a hydrogen terminated surface, but it is doubtful that such surface remains unoxidized under the applied conditions.

The films were examined with a Siemens D5000 diffractometer equipped with a Göbel mirror to obtain parallel Cu Kα radiation. This set-up was used both for conventional 0-20 X-ray diffraction (XRD) analysis in reflection mode and for reciprocal mapping. The topography was studied by atomic force microscopy (AFM; Digital Instruments, type Dimension 3100, in tapping mode). Selected films were analyzed by transmission electron microscopy (TEM; Jeol 2000FX, 200 keV). The electronic resistance was measured at room temperature for selected as-deposited films by using a linear four-point probe. The electronic resistance as a function of temperature and at varying magnetic fields was measured using a home-built four-point probe inserted into a Quantum Design SQUID unit. The resistivity data are corrected for the sample geometry [55].
3. Results and discussion

During the analyses of the films prepared in this study, four different modifications of 
MnO$_2$ were established: $\alpha$-MnO$_2$, $\beta$-MnO$_2$, a new phase related to $\beta$-MnO$_2$ (designated $\beta'$-MnO$_2$), and $\varepsilon$-MnO$_2$ (see the compilation of results in Table 1). Attempts have been made to determine the preferred growth direction and the in-plane orientation of the various films. Some of the findings for soda-lime-glass and Si(100) substrates described below are already reported in an earlier paper [54], but are also briefly included in this contribution for the sake of completeness.

Table 1. Different modifications of MnO$_2$ obtained on thin films on the selected substrates, and their textures.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Bulk symmetry</th>
<th>Repeating surface unit / Å$^2$</th>
<th>Synthesized MnO$_2$ modification and orientation</th>
<th>Rocking curve FWHM / °</th>
<th>No. of peaks in $\varphi$-scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda-lime glass</td>
<td>Amorphous</td>
<td>−</td>
<td>$\beta'$ (100)</td>
<td>7</td>
<td>$\infty$</td>
</tr>
<tr>
<td>Kapton$^\text{TM}$ foil</td>
<td>Amorphous</td>
<td>−</td>
<td>Un-oriented $\beta$</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Si(100)</td>
<td>$Fm\overline{3}m$</td>
<td>$5.43 \times 5.43$</td>
<td>$\beta'$ (100)</td>
<td>7</td>
<td>$\infty$</td>
</tr>
<tr>
<td>Si(100), HF etched</td>
<td>$Fm\overline{3}m$</td>
<td>$5.43 \times 5.43$</td>
<td>$\beta'$ (100)</td>
<td>7</td>
<td>$\infty$</td>
</tr>
<tr>
<td>Muscovite(001)</td>
<td>$P3_112$</td>
<td>$5.21 \times 5.21$ (120°)</td>
<td>$\beta'$ (100)</td>
<td>2.2</td>
<td>12</td>
</tr>
<tr>
<td>$\alpha$-SiO$_2$(001)</td>
<td>$P3_121$</td>
<td>$4.91 \times 4.91$ (120°)</td>
<td>$\beta'$ (100)</td>
<td>8.3</td>
<td>$\infty$</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$(001)</td>
<td>$R\overline{3}c$</td>
<td>$4.76 \times 4.76$ (120°)</td>
<td>$\varepsilon$ (001)</td>
<td>0.06</td>
<td>6</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$(012)</td>
<td>$R\overline{3}c$</td>
<td>$4.76 \times 5.13$ (120°)</td>
<td>$\beta$ (101)</td>
<td>3</td>
<td>−</td>
</tr>
<tr>
<td>MgO(100)</td>
<td>$Fm\overline{3}m$</td>
<td>$4.21 \times 4.21$</td>
<td>$\beta'$ (110)</td>
<td>1.7</td>
<td>4</td>
</tr>
<tr>
<td>NaCl(100)</td>
<td>$Fm\overline{3}m$</td>
<td>$5.62 \times 5.62$</td>
<td>Un-oriented $\alpha$</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>KCl(100)</td>
<td>$Fm\overline{3}m$</td>
<td>$6.28 \times 6.28$</td>
<td>$\beta'$ (100)</td>
<td>4</td>
<td>$\infty$</td>
</tr>
<tr>
<td>KBr(100)</td>
<td>$Fm\overline{3}m$</td>
<td>$6.59 \times 6.59$</td>
<td>$\beta'$ (100)</td>
<td>6</td>
<td>$\infty$</td>
</tr>
<tr>
<td>KI(100)</td>
<td>$Fm\overline{3}m$</td>
<td>$7.05 \times 7.05$</td>
<td>$\alpha$ (110)</td>
<td>5</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

Substrate reforms to KIO$_3$ and gives un-oriented $\alpha$
3.1. Depositions on amorphous substrates

When the films are deposited on soda-lime-glass and Si(100) substrates, X-ray diffraction patterns similar to that for (h00) oriented β-MnO₂ are obtained (Fig. 2), with the exception that the (100) reflection is present. The latter reflection should be extinct in space group $P4_2/mnm$, and the MnO₂ phases occurring in these films is designated as a $\beta'$ modification to emphasize similarity with, as well as distinction from, $\beta$-MnO₂. The $\beta'$-MnO₂ films were oriented with the (100) surface parallel to the substrate plane and $\varphi$-scans of the asymmetric reflection (310) confirmed that the films were polycrystalline with no in-plane orientation, typical for columnar growth. Rocking-curve analyses of the (200) reflection for films on soda-lime-glass and Si(100) substrates had a FWHM (full width at half maximum) of ca. 7°. Reciprocal space maps for the (200) and (400) reflections of films deposited on soda-lime-glass substrates revealed that the width of the rocking curve was due to tilting and not to the in-plane crystallite size. However, films deposited on Kapton™ foil turned out to be polycrystalline with randomly oriented $\beta$-MnO₂. Topography measurements for films on soda-lime-glass and Si(100) substrates show that the in-plane crystallite size is larger for film on the former substrates Fig. 3a,b.

Fig. 2. Diffractogram of manganese(IV) oxide deposited on soda-lime-glass substrates both with (upper diagram) and without (lower diagram) full control of the Mn(thd)₃ precursor flux in the reaction chamber. Illustration quoted from Ref. [54].

In order to obtain a sample of the $\beta'$-MnO₂ phase suitable for structure determination, several different approaches were tried. Films were scraped from glass substrates using a diamond scraper, films were deposited on thin glass supports which were subsequently crushed, deposited on finely powdered silica glass, and deposited on glass capillaries. For
X-ray transmission experiments, films were also deposited on glass supports thinner than 10 μm and on 8 μm Kapton™ foil.

**Fig. 3.** Topography of β-MnO₂ film deposited on substrates of (a) soda-lime glass, (b) Si(100), (c) α-SiO₂(001), (d) α-Al₂O₃(012), (e) α-Al₂O₃(001), (f) muscovite(001), and (g) MgO(100). The depth profile black to white equals 10 nm in (b) and (g), and otherwise 30 nm.

The scraped and the crushed films turned out to consist of ordinary β-MnO₂, viz. the (001) reflection was absent. The peak had clearly vanished during the mechanical processing of the samples since it was unequivocally present on unscraped and uncrushed films. X-ray analyses of films deposited on finely powdered silica glass indicated presence of β-MnO₂, Mn₃O₄ (hausmanite), and also possibly some Mn₂O₃ (bixbyite C). Films deposited on glass capillaries (see Fig. 4) and Kapton™ foil gave polycrystalline β-MnO₂.
**Fig. 4.** Diffractogram of $\beta$-MnO$_2$ film deposited on thin capillaries. Data collected by synchrotron XRD (SNBL at ESRF) using an area detector and $\lambda = 0.71091$ Å.

This study has made further attempts to gain insight into the presence of the additional reflection at $d = 4.33$ Å [indexed as (100) of a $\beta$-MnO$_2$-like structure]. The films deposited on thin glass were used (in transmission mode) to search for the presence of other reflections that should be extinct for $\beta$-MnO$_2$ but perhaps not for $\beta'$-MnO$_2$ [e.g., (021) or (201)], but all attempts to detect such reflections were in vain. It should also be mentioned that there exist reports [56] which claim that the $\beta$-MnO$_2$ structure should rather be described in space group $P4_{2}nm$ owing to ferroelectric behaviour which would be incompatible with a centrosymmetric space group. However, nor this space group can explain the presence of a (100) reflection. Returning then to the occurrence of the (100) reflection one may speculate as to whether the film features indicate a distinct new phase or is an effect of stress in the film. If we have to do with a new phase the structural differences are likely to be rather small, most probably manifesting a degree of disorder in the $ab$-plane of the $\beta$-MnO$_2$ structure. This disorder may relax when films are crushed or deposited on uneven surfaces.

It seems tempting to maintain the explanation that the extra reflection mirrors induced stress in the films, all the more since the reflection disappears when the film is crushed and does not appear on deposits made on curved substrates such as capillaries. On the other hand, shifts in IR spectra [54] could favor an interpretation with a separate phase. Stress induced by differences in thermal expansion between substrates and films should expectedly also have resulted in distinctions between different kinds of substrates. However, one should bear in...
mind that the applied deposition temperature is rather low in relation to possible thermal induction of stress.

Finally we record the results of a 5000-cycle runs at 186 °C, in which the sublimation temperature for the Mn(thd)$_3$ precursor was set higher than the 133 °C used in the rest of the series. The XRD data for these films (Fig. 2) reveal that the thus generated enhanced (and somewhat un-controlled) Mn(thd)$_3$ flux results in un-oriented growth of $\beta'$-MnO$_2$.

3.2. Depositions on single-crystal oxide substrates

Depositions on $\alpha$-SiO$_2$(001) substrates resulted in mainly ($h00$) orientated growth of $\beta'$-MnO$_2$ [however with a rather week (100) reflection], although there was evidences of some presence of (110) oriented crystallites (with reduced intensity). $\varphi$-scans of the (301) peak of $\beta$-MnO$_2$ shows that the films did not exhibit in-plane ordering, and the topography (Fig. 3c) revealed almost the same in-plane crystallite size as for films on soda-lime-glass substrates.

The specific electrical resistivity at room temperature for typical 100 nm films deposited on soda-lime-glass and $\alpha$-SiO$_2$(001) substrate was measured to be 0.12 and 0.17 $\Omega$ cm, respectively.

Depositions on $\alpha$-Al$_2$O$_3$(012) are likely of a $\beta$-MnO$_2$ phase oriented with the (101) surface at some 1.3° to the substrate plane according to $\varphi$-resolved rocking curves of the (101) reflection (rocking-curve peaks with FWHM $\approx$ 3°). Regular $\theta$-2$\theta$ XRD diffractiongrams showed only two broad peaks of low intensity that could stem from (101) and (202) reflections from $\beta$-MnO$_2$. The (101) plane of $\beta$-MnO$_2$ and (012) of $\alpha$-Al$_2$O$_3$ have almost identical arrangements of both metal and oxygen atoms (Fig. 5), and have unit-cell dimensions corresponding to a mismatch of $-7.6$ % along [010] and 2.4 % along [101] of $\beta$-MnO$_2$. (Note: positive mismatch = compressive strain.) This match should give a fit with two-fold symmetry, but it was difficult to verify this with $\varphi$-scans due to low diffracted intensity and probably also due to tilts in the film structure. The broadening and reduced intensities of the diffracted peaks may be due to an initial strained film structure that is gradually relaxed as the film grows thicker. Theoretically viewed, according to the lattice
conformities, the film should follow the orientation scheme:
(101)[010]β-MnO₂||(012)[100]α-Al₂O₃.

Fig. 5. Schematic illustration of possible orientation of a β-MnO₂(101) film on α-Al₂O₃(012).

Films deposited on α-Al₂O₃(001) consist most likely of the ε-MnO₂ phase oriented with [001] normal to the substrate surface (in which case this is the first example of preparation of ε-MnO₂ films). Regular θ-2θ XRD diffractograms showed only presence of rather sharp (002) and (004) reflections from ε-MnO₂ (Fig. 6a). Rocking curve analyses (Fig. 6b) of the (002) reflection proved to be sharp and gave a curve with FWHM = 0.063° as compared with FWHM = 0.056° for α-Al₂O₃ (006). The φ-scan of (103) for ε-MnO₂ and (119) for α-Al₂O₃ gave six coherent peaks (Fig. 6c), which indicate an epitaxial structure with the orientation scheme (001)[100]ε-MnO₂ || (001)[110]α-Al₂O₃. The ε-MnO₂(001) and α-Al₂O₃(001) surfaces have nearly identical oxygen arrangements (Fig. 7). The oxygen atoms on the ε-MnO₂(001) surface form regular hexagons with an O–O distance of 2.786 Å, whereas the oxygen atoms on the α-Al₂O₃(001) surface form pseudo hexagons where each oxygen have four and two neighbors at a distance of 2.865 and 2.525 Å, respectively. According to the average distance (2.751 Å) the lattice mismatch is only 1.2 %. The surface cell dimensions of the ε-MnO₂ film may be calculated on the basis of the reciprocal map data for the (002), (004), and (103) reflections; giving a = 2.76 and c = 4.30, which indicate that the in-plane cell dimension is modified to match the substrate. However, it is somewhat surprising to note a compression in both a and c of the ε-MnO₂ film even though the acting
in-plane stress is of compressive character. This may be due to a different oxygen stoichiometry in the films as compared with bulk materials [32,57–59].

AFM analysis (Fig. 3d,e) of films deposited on both orientations of α-Al₂O₃ single-crystal substrates show crystallites that have terminating surfaces which are inclined from the substrate plane with angles close to 45 and 33°. The roughness was measured to be ca. 3.5 and 4.4 nm on the (001) and (012) oriented α-Al₂O₃ substrates, respectively. It should be noted that the deposition on α-Al₂O₃(001) exemplifies growth of a highly epitaxial film even though the growth dynamics results in a rough surface.

Fig. 6. (a) Sections of XRD diffractograms of ε-MnO₂ film deposited on α-Al₂O₃(001) substrate. The peak splitting in the 2θ range 90.5–92.5° is due to diffraction from both Cu
Kα1 and Cu Kα2. (b) Rocking curve analysis of the reflections in part a. (c) φ-scan on the α-Al2O3 (119) and ε-MnO2 (103) reflections.

**Fig. 7.** Schematic illustration of possible orientation of an ε-MnO2(001) film on α-Al2O3(001).

The specific electrical resistivity at room temperature for typical 100 nm films deposited on α-Al2O3(001) and α-Al2O3(012) substrates was measured to be 0.079 and 0.063 Ω cm, respectively.

Muscovite is a sheet silicate which cleaves readily and hence one can easily produce large surfaces with atomic roughness. Depositions of MnO2 on cleaved (001) surfaces of muscovite resulted in rather well oriented growth where only the (200) and (400) reflections from β-MnO2 are observed. Some minute intensity from a peak in the position where a (100) reflection would have occurred was also detected, but we were unable to positively ascribe this to β'-MnO2 (see above) rather than to effects from the substrate and/or spectral noise from the X-ray source. Anyway, owing to the minute intensity of the peak, it is appropriate to conclude that the effects which causes the presence of the (100) reflection observed for depositions on soda-lime-glass and like substrates, are of minor importance for films deposited on muscovite(001) substrates. Reciprocal-space-map analyses of the (200) reflection revealed that the films are oriented with the (100) plane parallel to the surface and have a rocking curve with FWHM = 2.2°, as compared to the substrate with FWHM = 0.7°. The in-plane ordering was analyzed by φ-scans of the (301) reflection (Fig. 8), and revealed 12 peaks with 30° separation. Reciprocal space maps of three succeeding (301) reflections proved all of them to be singular peaks and not simple overlaps with tails from reflections of
the substrate. Fig. 8 includes also a φ-scan of what we believe is the (1,1,20) reflection of muscovite (according to a trigonal space group description [60]) with the expected three peaks with a 120° separation.

![Image]

**Fig. 8.** In-plane ordering of β-MnO₂ film deposited on muscovite(001) analyzed by φ-scan of the β-MnO₂ (301) reflection and the substrate (1,1,20) reflection. Reciprocal space maps of the three selected peaks (marked I–III) from the β-MnO₂ (301) φ-scan are included at the top of the illustration.

Regarding the observed in-plane orientations on muscovite(001): It is possible to find a rather good agreement between the oxygen positions on muscovite(001) and β-MnO₂(100) by using a 2×2 surface cell on the latter surface (Fig. 9). This will give rise to half of the 12 peaks in the φ-scan for the (301) reflection of β-MnO₂ and is supported by the coherence with the positions of the (1,1,20) reflections from muscovite. This arrangement will, however, give a rather large strain since there is lattice mismatch of 10 and −0.8 % in the c and a directions, respectively. The strain can be reduced to −4.5 and 1.4 % for the c and a direction, respectively, by imagining a 6×3 surface cell rotated by 30° with respect to the 2×2 surface cell mentioned above (Fig. 9). This arrangement would give rise to the additional six peaks in the φ-scan for (301) of β-MnO₂. However, it is not so straightforward to identify a good match between the surface atoms in this setting. Neglecting this uncertainty these films may be regarded as epitaxial with the orientations (100)[001]β-MnO₂ || (001)[100]muscovite and (100)[001]β-MnO₂ || (001)[120]muscovite.
The topography of films deposited on muscovite(001) show (Fig. 3f) well crystalline surface with 30–70 nm crystallite size and with a total roughness of ca. 4.4 nm. The crystallites consist of surfaces that are typically inclined from the substrate at angles close to 45 and 30°. This is consistent with the apprehension that the (100) oriented crystallites are terminated with surfaces of \{110\} (45°) and perhaps \{201\} (37°) or rather \{301\} (27°).

Depositions on MgO(100) substrates resulted in (110) oriented β-MnO₂ (Fig. 10). Rocking curve analyses of the (110) reflection showed two overlapping peaks which could be fitted by two Gaussian shaped curves, FWHM = 1.7 and 6.5° (Fig. 11), whereas a similar analysis of the substrate gave FWHM = 0.7°. This indicates that these films are not perfect single crystals, but probably consists of one set of rather oriented crystals and another set that are more tilted or minor in size. Reciprocal space maps of the (110) and (220) reflections revealed that the broadening of the rocking curves are due to random tilting and not to the in-plane crystallite size. The in-plane orientation was analyzed by φ-scans of the (210) peak from β-MnO₂ films and the (311) peak of MgO substrates (Fig. 12). This examination shows that both the film and the substrate have four peaks at the same positions in the φ-scans. The (210) plane of the β-MnO₂ structure should occur only twice with 180° separations in a φ-scan since (110) of β-MnO₂ has two-fold symmetry. This indicates that the films are
deposited with two specific orientations on the MgO(100) surface (Fig. 13). The film may thus be regarded as epitaxial with the orientations (110)[001]β-MnO₂ || (100)[011]MgO and (110)[001]β-MnO₂ || (100)[01–1]MgO. Topography measurements show a pattern that reflects this orientation scheme (Fig. 3g), since it consists of elongated crystallites oriented at ca. 90° to each other. The tops of these crystallites are rather flat and less than 2° inclined off a plane parallel to the substrate plane. This is consistent with the assumed lowest growth rate of the (110) surface argued for in Ref. [54]. The film thickness on a MgO(100) substrate was also measured by RBS giving a growth rate of 18.0 pm/cycle which is somewhat larger than the previous [54] estimated 15.5 pm/cycle growth rate for {110} surfaces. This may imply that also our previous assumptions about the maximum growth rate were underestimated (should be increased from 22.0 to 25.5 pm/cycle).

![Diffractogram](image)

**Fig. 10.** Diffractogram of (110)-oriented β-MnO₂ film deposited on MgO(100). Reflections marked β corresponds to diffraction from the substrate by Cu Kβ radiation.

The specific resistance as a function temperature for a 100 nm film deposited on a MgO(100) substrate is shown in Fig. 14 (0.047 Ω cm at room temperature). This is similar to the findings described in Ref. [61] for a bulk sample except that the resistance minimum at around 50 K in Fig. 14 is less marked than for bulk samples. This may be due to a larger amount of grain boundaries in the film. Fig. 14 also unveils a small hysteresis between ~50 and 250 K and we have found no indication of magnetoresistance for deposited films on application of a magnetic field of 5 T.
Fig. 11. Rocking curve analysis of the $\beta$-MnO$_2$ (110) reflection on MgO(100) substrate (thicker line) The deconvoluted experimental profile in two Gaussian shaped curves is shown by thinner lines.

Fig. 12. $\varphi$-scan of $\beta$-MnO$_2$ (321) and (210), and MgO (311) reflections for $\beta$-MnO$_2$ film deposited on MgO(100).

Fig. 13. Schematic illustration of possible adjustment of (110)-oriented $\beta$-MnO$_2$ on a MgO(100) surface.
Fig. 14. Temperature dependence of specific resistance for $\beta$-MnO$_2$(110) deposited on MgO(100).

3.3. Depositions on alkali-metal halide crystals

$\alpha$-MnO$_2$ was obtained in films deposited on (h00) surfaces of single crystals of NaCl, KCl, KBr, and KI. Conventional 0-20 XRD analyses proved to be difficult since the substrate and the film had too many overlapping reflections, hence it was not possible to find any asymmetric XRD reflections for in-plane analysis. However, the $\alpha$-MnO$_2$ (110) and/or $\beta$-MnO$_2$ (200) reflections were well resolved and could be used for identification and analyses of tilting by reciprocal mapping. When single crystals of KI were used, the surface was oxidized to KIO$_3$ by the first ozone pulses which prevented direct comparisons with the other substrate materials in this context. In addition, the films on the latter substrates had scaled off during the cooling down from the reactor temperature. Nevertheless, some results from TEM analyses of these scales are included in this report.

The XRD analyses showed that the $\alpha$-MnO$_2$ phase was oriented with the (110) plane parallel to the (100) surface of the substrates on both KCl and KBr whereas it was difficult to identify any diffraction peaks for the film deposited on NaCl(100) substrates (Fig. 15). Rocking curve analyses of the (110) reflection for films deposited on KBr(100) and KCl(100) gave FWHM $\approx$ 4 and 5°, respectively. There is a marked increase in the intensity of the $\alpha$-MnO$_2$ (110) reflection as the substrate lattice is increased from NaCl via KCl to KBr. Film deposited on KCl(100) also seems to contain (100) oriented $\beta'$-MnO$_2$ crystals with a rocking
curve with FWHM $\approx 4^\circ$. When KBr(100) was used as substrate the intensity of the $\alpha$-MnO$_2$ (110) reflection increased markedly but was also split into at least two peaks. Also the $\alpha$-MnO$_2$ (330) reflection was identifiable for films on the latter substrates, but these films still proved to contain some (100) oriented $\beta'$-MnO$_2$ with a rocking curve with FWHM $\approx 6^\circ$. The splitting of the $\alpha$-MnO$_2$ (110) reflection on films grown on KBr(100) substrates may be due to a sharp interfacial separation where the first layers are richer in potassium than the following layers. The potassium richer layers will exhibit larger (110) plane separation than those which have less (or lack) potassium and may be regarded as relatively pure binary $\alpha$-MnO$_2$.

Fig. 15. Diffractogram of MnO$_2$ deposited on NaCl(100), KCl(100), and KBr(100) single crystals.

Elemental analysis of the $\alpha$-MnO$_2$ films on KBr(100) substrates by TEM revealed presence of potassium in the films. This supports the just advanced explanation for the observed splitting of the (110) reflection, but there is also a possibility that the potassium originates from the preparation of the TEM specimen (viz. have been introduced during the dissolution of the KBr substrate by water).

The films were analyzed with TEM after removing them from the substrates by dissolution with water. The films on the KBr(100) substrates consisted of $\alpha$-MnO$_2$ grains with dimensions 20–30 nm. The same dimensions were also found for the $\alpha$-MnO$_2$ grains on films on KCl(100) and NaCl(100) substrates, but the films on the latter substrates also contained
needles of $\beta$-MnO$_2$ with approximate dimensions 1000×50 nm (Fig. 16). The films deposited on polycrystalline KIO$_3$ (formed on the exposure of KI(100) substrates to ozone), consisted of nanocrystalline (~5 nm) $\beta$-MnO$_2$ with no preferred orientations.

![Fig. 16. Electron micrograph of films on KCl(100). (a) Microstructure of $\alpha$-MnO$_2$. (b) Enlarged section showing also needles of $\beta$-MnO$_2$.](image)

As the results indicate, the amount of (110) oriented $\alpha$-MnO$_2$ increases with increasing match in surface cell dimensions on going from NaCl(100) (~23% mismatch) to KBr(100) (~5% mismatch) substrates. We assumed that the match would be further improved on turning to of KI(100) substrates (2% mismatch), but as mentioned, the KI(100) surface was oxidized to KIO$_3$ and this hypothesis could accordingly not be tested.

The specific resistivity at room temperature for a 100 nm film deposited on NaCl(100), KCl(100), and KBr(100) single crystal substrates was measured to be 0.27, 0.42, and 6.1 $\Omega$ cm, respectively.

The stabilization of $\alpha$-MnO$_2$ on alkali-metal halide crystals is more likely due to the introduction of alkali-metal ions in the film than due to match with the surface crystal structure (see the introduction). The alkali-metal ions may in turn be washed away to produce a pure $\alpha$-MnO$_2$ phase. In the present film synthesis the alkali-metal ions have probably functioned as nucleation aids that direct the growth toward $\alpha$-MnO$_2$, and at the same time a certain amount of alkali-metal ions is diffused into the first layers of the film. After the first nucleating layers of potassium rich $\alpha$-MnO$_2$ have been formed, the further growth probably results in relative pure $\alpha$-MnO$_2$. 
Acknowledgment

We are grateful to prof. Poul Norby for performing the synchrotron diffraction measurements. This work has received financial support from the Research Council of Norway.

References

Growth of calcium carbonate by the atomic layer chemical vapour deposition technique

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Abstract

Thin films of CaCO$_3$ (calcite) have been grown with the ALCVD (= atomic layer chemical vapour deposition) technique, using Ca(thd)$_2$ (Hthd = 2,2,6,6-tetramethylheptan-3,5-dione), CO$_2$, and ozone as precursors. Pulse parameters for the ALCVD-type growth are found and self-limiting reaction conditions are established between 200 and 400 °C. Calcium carbonate films have been deposited on soda-lime-glass, Si(100), α-Al$_2$O$_3$(001), α-Al$_2$O$_3$(012), α-SiO$_2$(001), and MgO(100) substrates. The observed textures were: in-plane orientated films with [100](001)CaCO$_3$||[100](001)Al$_2$O$_3$ and [100](001)CaCO$_3$|[110](001)Al$_2$O$_3$ on α-Al$_2$O$_3$(012), amorphous films on α-Al$_2$O$_3$(001) when grown at 250 °C, and columnar oriented films on soda-lime-glass, Si(001), α-SiO$_2$(001), and MgO(100) substrates with (00$l$) and (104) parallel to the substrate plane at 250 and 350 °C, respectively. The film topography was studied by atomic force microscopy and AC impedance characteristics were measured on as-deposited films at room temperature. The films were found to be insulating with a dielectric constant ($\varepsilon_r$) typically round 8.

Thin films of CaO were obtained by heat treatment of the carbonate films at 670 °C in a CO$_2$-free atmosphere, but the thermal decomposition led to a significant increase in surface roughness.

Keywords: Atomic layer deposition (ALD), Calcium carbonate (CaCO$_3$).

1. Introduction

ALCVD (= atomic layer chemical vapour deposition; also known as ALD = atomic layer deposition and ALE = atomic layer epitaxy) is a thin-film technique that relies on self-limiting surface reactions. Each precursor is sequentially pulsed into the reaction chamber with a purge of an inert gas between the different precursor doses [1]. In this way all gas-
phase reactions are eliminated and the growth is self limited to one monolayer of precursor per pulse. The method ensures conformal growth and pin-hole-free films over large areas [2].

Thin films of calcium carbonate are commonly made by liquid-phase techniques with the aid of different types of templates [3–10], but has also been reported synthesized by organo-metallic CVD [11]. Calcium oxide have, on the other hand, previously been made by a variety of techniques: dehydration of hydroxide films [12,13], spin coating [14], molecular-beam epitaxy [15,16], electron-beam evaporation [17], and pulsed layer deposition [13,18]. The growth dynamics of CaO from Ca(thd)₂ and H₂O by an ALCVD approach have previously been studied by a quartz-crystal microbalance set-up, but the thus obtained films were not characterized [19]. This paper reports syntheses of CaCO₃ thin films with the ALCVD technique and the subsequent preparation of CaO thin films by calcination of CaCO₃ films.

CaCO₃ (calcite) adopts a trigonal structure with unit-cell dimensions \( a = 4.991(2) \) and \( c = 17.062(2) \) Å in hexagonal setting [20]. CaCO₃ also crystallizes with the hexagonal vaterite-type and orthorhombic aragonite-type structure, but these modifications have not been obtained by the present preparation procedure.

The main motivation for this study has been to survey the growth conditions for CaCO₃ by the ALCVD technique in order to shed light on the corresponding manufacture of more complex oxides with calcium as constituent, e.g., \( \text{Ca}_1-x\text{La}_x\text{MnO}_3 \).

2. Experimental

Films were grown in a commercial F-120 Sat reactor (ASM Microchemistry) by using Ca(thd)₂ (Strem Chemicals; 99.9%; Hthd = 2,2,6,6-tetramethylheptan-3,5-dione) and ozone as precursors, with CO₂ (AGA; 99.99 %) as controlling atmosphere in selected runs. Ozone gas with a flow of 500 cm³ min⁻¹ was produced by feeding pure O₂ (AGA 99.999%) into an ozone generator (OT-020, OzoneTechnology; giving an ozone concentration of 15 vol.% according to specifications). The applied sublimation temperature for Ca(thd)₂ was 195 °C. The reactor pressure was maintained at ca. 1.8 mbar by employing an N₂ carrier-gas flow of 300 cm³ min⁻¹, supplied from a Nitrox 3001 nitrogen purifier with a purity of 99.9995% inert.
gas (N₂ + Ar) according to specifications. The soda-lime-glass substrates were cleaned as described in Ref. [21], whereas Si(100), α-SiO₂(001), α-Al₂O₃(001), α-Al₂O₃(012), and Mg(100) substrates were used as purchased from the supplier. Calcium oxide films were prepared by heat treatment of calcium carbonate thin films in a CO₂-free O₂ atmosphere.

The films were examined both as deposited and calcined with a Siemens D5000 diffractometer equipped with a Göbel mirror to obtain parallel Cu Kα radiation. This set-up was used both for thickness measurements with X-ray profilometry and conventional 0–20 X-ray diffraction (XRD) analysis in reflection mode and reciprocal mapping. The topography of selected films was studied by atomic force microscopy (AFM; Digital Instruments, type Dimension 3100, in tapping mode). Selected films were analyzed with transmission FT-IR spectroscopy on a Perkin Elmer system 2000 FT-IR spectrometer. The films for IR analyses were deposited on both sides (both sides polished) of Si(100) substrates. An uncoated substrate was used as reference. Powdered samples were pressed and measured in KBr pellets using a blank pellet as reference.

Impedance measurements were performed in ambient air at 25 °C with a HP 4192A impedance analyzer, at 100 kHz and 1 V. For this purpose the films were deposited on 2.5 × 2.5 cm² stainless steel plates which also served as electrode. A gold contact of typically 1 × 1 cm² was sputtered on the films as a counter electrode. Care was taken to eliminate the parasitic elements of the set-up.

3. Results

The effect of pulse and purge parameters on the growth rate of CaCO₃ at 200 °C was first investigated without introduction of additional CO₂ in order to ascertain that ALCVD-type growth really takes place (Fig. 1). Such growth can in the present case be achieved with a 1.0 s pulse of Ca(thd)₂ followed by a purge over an almost neglectable time interval, and then a 2.0 s O₃ pulse followed by a 0.8 s purge. It was possible to obtain films with less than 1 % thickness gradients over a 5 × 5 cm² substrate area by using the just mentioned pulse and purge times.
Fig. 1. CaCO₃ growth-rate dependence (at 200 °C) on Ca(thd)₂ and O₃ pulsing and purging parameters. Measurement points refer to Si(100) substrates, and symbols ■, ○, and ▲ denote readings taken in front, middle, and back of the substrates, respectively.

The growth linearity was checked by measuring the thickness of films grown with different number of pulses at a reactor temperature of 200 °C. As seen from the inset to Fig. 2 there is a strict linear relation between the thickness of a given film and the number of pulse cycles used to form it and there is no initiation period involved with the formation of the first layer(s).

Fig. 2. Temperature dependence of the growth rate of CaCO₃. Symbols ■, ○, and ▲ refer to readings taken on Si(100) substrates in front, middle, and back of the substrates, respectively, and ◇ refers to readings in the middle of soda-lime-glass substrates. Inset shows thickness of CaCO₃ films (grown at 200 °C) as a function of number of pulses.
The influence of the temperature on the growth rate was investigated by varying the reactor temperature while keeping all other parameters constant. Only a small decrease in the growth rate is observed (Fig. 2) on increasing temperature. This effect escalates at higher temperatures and thickness gradients develop as the temperature is increased above 400 °C. It is interesting to note that films grown on soda-lime-glass substrates appear to decompose at 450 °C whereas those grown on Si(100) substrates did not. Thermal decomposition tests [22] of Ca(thd)2 suggest that this precursor should be stable up to 590 °C.

As-deposited films with thicknesses of only ca. 45 nm on soda-lime-glass and Si(100) substrates showed no sign of periodic crystal structure by XRD analyses, regardless of the deposition temperature. For thicker films (ca. 230 nm) on soda-lime-glass substrates, diffraction peaks from (00l)-oriented CaCO3 were observed at a deposition temperature of 250 °C. When the deposition temperature was increased to 350 °C these substrates gave mixtures of (111)-oriented CaO and (00l)-oriented CaCO3 (Fig. 3).

**Fig. 3.** XRD diffractogram cuts for films deposited on soda-lime-glass substrates without CO2 pulses in the procedure. Profiles are shifted for clarity; numbers on the right-hand side give deposition temperature in °C.

Films were also deposited with an additional CO2 pulse (pulse time: 3 s at a flow of ca. 400 cm3 min−1) introduced after each O3 pulse. This resulted in the same film thicknesses (viz. within the present measurement accuracy of ca. 1 %) as obtained in the corresponding experiments without the additional CO2 pulses in the procedure. However, the explicit introduction of CO2 made the films better crystalline and occasioned also other orientations
[(001) orientation at 200 °C, (104) orientation at 350 °C; roughly the same for all kinds of substrates; see Fig. 4].

Depositions on Si(100) and soda-lime-glass substrates gave identical products with regards to phases and orientations. This is most probably due to a native amorphous layer of SiO$_x$ on the Si(100) surface. The soda-lime-glass substrate is chosen to represent these substrates in Fig. 4 due to disturbing diffraction effects from the crystalline Si(100) substrates.

![Fig. 4. XRD analysis of films grown at the different temperatures specified on the right-hand side of the illustration (in °C). Substrate specifications are given within each panel and Miller indices are marked at each reflection [CuKβ peak for (104) is labeled β]. Profiles in each panel are shifted for clarity.](image-url)
Calcium carbonate was also deposited on single crystals of $\alpha$-SiO$_2$(001) and $\alpha$-Al$_2$O$_3$(001) in attempts to obtain oriented growth, since CaCO$_3$, $\alpha$-SiO$_2$, and $\alpha$-Al$_2$O$_3$ adopt trigonal structures with only small lattice mismatches (see Sec. 4). This may be suspected to facilitate epitaxial growth, but the XRD analyses of the depositions on the $\alpha$-SiO$_2$(001) substrates (Fig. 4) showed largely the same orientations as those on the other substrates: (00l) orientation for deposition at 250 °C and (104) orientation at 350 °C. Depositions on MgO(100), Si(100), and soda-lime-glass substrates gave under corresponding conditions virtually identical XRD diagrams to those on $\alpha$-SiO$_2$(001) substrates (Fig. 4). Depositions on $\alpha$-Al$_2$O$_3$(001) gave, on the other hand, in-plane oriented growth (Fig. 5) and $\alpha$-Al$_2$O$_3$(012) substrates gave amorphous CaCO$_3$ films when deposited at 250 °C and (104) oriented films at 350 °C (Fig. 6). A $\varphi$-scan of the (106) peak for films deposited on $\alpha$-Al$_2$O$_3$(012) at 350 °C proved that these films are unoriented in the substrate plane. $\varphi$-scans of the (1,0,10) peak for films deposited on $\alpha$-Al$_2$O$_3$(001) at 250 and 350 °C gave six peaks with 60° separation, half of these peaks having a higher intensity than the others. Half of these peaks coincides with the (1,0,10) peaks from the substrate. Reciprocal space mapping of CaCO$_3$ was performed for two of the (1,0,10) peaks separated by 60° in the $\varphi$-scan. This was done in order to determine whether they were genuine peaks or tails from substrate reflections due to the energy spread in the X-ray source. This examination revealed that the intensity difference detected by the $\varphi$-scans was due to overlap with a tail from the (108) peak of the substrate. This proves that the CaCO$_3$ films on $\alpha$-Al$_2$O$_3$(001) substrates consist of domains that are well oriented with the $c$-axis normal to the substrate plane, but randomly rotated 60° with respect to each other.
Fig. 5. In-plane orientation analysis of film grown on $\alpha$-$\text{Al}_2\text{O}_3$ (001) at 350 °C. Left side: $\varphi$-scan of CaCO$_3$ (1,0,10) together with $\alpha$-$\text{Al}_2\text{O}_3$ (1,0,10) and (108). Profiles are not scaled. Right side: reciprocal mapping of CaCO$_3$ (1,0,10) at $\varphi = 130$° and 190°. The intensity scale is logarithmic for the reciprocal maps.

Fig. 6. Cuts from XRD diffractogram of films grown at the temperatures specified on the right-hand side of the illustrations (in °C). Substrate specifications are given within each panel and Miller indices are marked at each reflection [CuK$\beta$ peaks in the upper panel are labeled $\beta$, peaks at $2\theta = 24 – 28°$ in the lower panel originate from the substrate]. Profiles are shifted for clarity.
Rocking curve analyses were performed for the (006) peak for all films deposited at 250 °C and films deposited on α-Al2O3(001) at 350 °C as well as (104) peaks for films deposited at 350 °C (see Table 1). The rocking curves of (104) peaks for films deposited on soda-lime-glass and Si(100) substrates are split into two profiles separated by 1.5° (Fig. 7).

Table 1. FWHM of rocking curve data for CaCO3 peaks (104) and (006) deposited on selected substrates.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>FWHM of (104) / °</th>
<th>Substrate</th>
<th>FWHM of (006)/ °</th>
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<td></td>
<td></td>
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<td>15</td>
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</table>

a Deposited at 350 °C. b Deposited at 250 °C.

Fig. 7. Rocking curve analysis of (104) on films deposited at 350 °C. The different profiles are reproduced in scale.

ϕ-scans of the (1,0,10) and (116) peaks were measured for all kinds of substrates to determine the in-plane ordering of films deposited at 250 and 350 °C. Except for the films deposited on α-Al2O3(001), no sign of in-plane ordering could be detected, and this, together with the rocking curve analyses, suggest that all other films were grown in a columnar manner.

The IR spectra of the CaCO3 films (Fig. 8b,c) showed sharper absorption bands than those observed in the IR spectrum of CaCO3 powder in KBr pellets (Fig. 8a), probably owing to a more ordered structure in the films as compared to powdered samples. The IR spectra of
films deposited at 250 °C coincide well with the spectrum for calcite, and although these films are oriented with the CO$_3^{2-}$ groups along the substrate plane, excitations of in-plane asymmetric CO stretching vibration ($\nu_3$) are observed (Fig. 8c). This indicates that the films are not perfectly oriented with the CO$_3^{2-}$ groups parallel to the substrate plane, which is also seen from a rather large FWHM (~10°) detected by the rocking curve analyses of (006) on Si(100) substrates, and/or that a certain amount of X-ray amorphous material is present. On increasing the deposition temperature, an additional absorption band at 1482 cm$^{-1}$ appeared (Fig. 8c). This band is not active for the calcite-type modification, but is observed for aragonite-, vaterite-, and amorphous-type CaCO$_3$ [23] where the $\nu_3$ mode is split into $\nu_{3a}$ and $\nu_{3b}$. However, XRD analyses of the samples were unable to detect traces of either the aragonite- or vaterite-type variants, and we therefore believe that the occurrence of $\nu_{3a}$ originates from amorphous CaCO$_3$ which is formed in increasing amounts with increasing deposition temperature. Selected as-deposited films were heat treated in a CO$_2$-free O$_2$ atmosphere at 670 °C for 12 h to convert the carbonate into oxide. The XRD analyses of these films confirmed that they were phase-pure polycrystalline CaO (NaCl type). However, the IR technique detected also minor traces of carbonate (Fig. 8d), which most probably have been introduced during the handling of the specimens prior to the IR analyses.

The topography of films deposited on soda-lime glass with 5000 pulse cycles at 200 – 350 °C with and without sequential CO$_2$ pulses was analyzed with AFM (Fig. 9). For films deposited with CO$_2$ support, different growth regimes were identified: Films deposited at 200 °C (Fig. 9a) have surfaces with mixed rough and flat areas, which give rise to rather large variations in measured surface roughness (rms ranging between 3 and 12 nm). For films grown at 250 °C (Fig. 9b) the surfaces are more uniform and form a triangular shaped pattern with a surface roughness of ca. 9 nm rms. The triangular shapes have sides with angles in the range 24 – 30°. A marked change in surface morphology was observed for films deposited at 300 °C (Fig. 9c), where the surfaces turned out to be featureless and flat, with a rms roughness (of 0.3 nm) which is even smaller than in the original substrate (rms = 0.4 nm). When the reactor temperature was increased to 350 °C (Fig. 9d) the surfaces again became rather rough and consisted of some larger grains with a triangular shape and a background of extended areas that consisted of parallel ridges with low-angle slopes (one side typically inclined around 8° and the other around 10–25°; note: rather uncertain values).
Films deposited according to the procedure without CO\(_2\) pulses exhibit (see Fig. 9e and f) generally a somewhat lower roughness (rms = 4 and 8 at 250 and 350 °C, respectively) than those with CO\(_2\) pulses included. (This is probably due to larger amounts of amorphous material in the former series).

Films, deposited on Si(100) at 250 °C gave on annealing at 670 °C for 12 h a dramatically altered surface with increased roughness, rms ≈ 150 nm (see Fig. 9g). This treatment has clearly generated a total reconstruction of the films when CaCO\(_3\) is converted to CaO.
Fig. 9. Topography of as-grown CaCO₃ films on soda-lime-glass substrates with 5000 pulse cycles at different reactor temperatures (in °C) with and without extra CO₂: (a) 200, with; (b) 250, with; (c) 300, with; (d) 350, with; (e) 250, without; (f) 350, without; and (g) 250, without and then annealed at 670 °C for 12 h.

The complex admittance obtained by the electrical measurements, was resolved into conductance and capacitance and on introduction of the area of the gold electrode and the thickness of the CaCO₃ films the specific conductance and relative dielectric constant were derived. A problem occurred in that the sputtered gold for the electrodes (especially when thicker gold layers were used) appeared to penetrate the films and gave unreliable conductivity values across the film. However, it was established that the capacity of the films is of the order of 70 pF/m corresponding to a relative dielectric constant of 8. The measurements indicate that the films are well insulating, with conductivities in the 10 nS/m range, behaving similar in this respect to the alumina films of similar thickness used as reference.
4. Discussion

According to thermodynamic calculations made by the HSC program [24] for the Ca–O–CO$_2$ system, CaCO$_3$ is more stable than CaO at temperatures below 400 to 500 °C depending on the partial pressure of CO$_2$. When calcium-based film are grown with the present precursors the surface layer is first saturated with Ca(thd)$_x$. In the next step ozone is introduced in order to burn off the organic ligands under the formation of CO$_2$ and H$_2$O. Hence after each O$_3$ pulse the films will be subjected to an atmosphere of CO$_2$ and H$_2$O with rather significant partial pressures. This explains why the CaO phase can not be deposited directly as a film but require post heat treatment. However, the present findings show that the amount of CO$_2$ formed as a product during the O$_3$ pulse is not sufficient for formation of phase-pure crystalline CaCO$_3$ (Fig. 3).

The attempts to deposit in-plane oriented films of CaCO$_3$ on α-SiO$_2$(001) failed despite the low mismatch between the two sets of unit-cell dimensions; 100×(4.991–4.9128)/4.9128 = 1.6 % (compressive strain). However, the oxygen surface structure of α-SiO$_2$(001) has a twofold symmetry which is rather different from that in the basal plane of CaCO$_3$. In fact the films deposited on α-SiO$_2$(001) adopts the same preferred orientations as those deposited on soda-lime-glass substrates, which has an amorphous surface structure and hence should not guide the depositions. The same pattern of orientations is moreover found for films deposited on MgO(100) and Si(100) substrates. CaCO$_3$ was deposited with an in-plane ordering on α-Al$_2$O$_3$(001), as the ϕ-scans reveal, where domains of the film are rotated by 60° with respect to each other. The lattice mismatch of this constellation is 100×(4.991–4.761)/4.761 = 4.8 % which introduces a rather large compressive strain for epitaxial growth. The most probable reason for the observed in-plane orientation is that the oxygen surface structure of α-Al$_2$O$_3$(001) has a virtual six-fold symmetry. The substrate surface may also be stepped so that surface positions unsuitable for bonding with Ca (owing to short distances to the underlying Al) become distributed with a six-fold symmetry. For films deposited at 250 °C there are also indications of grains with a (104) orientation, but these disappear as the deposition temperature is increased to 350 °C. [Note that the XRD intensity of (104) is 33 times more intense than (006).]
The texture of films grown with the ALCVD technique is less influenced by the surface energy of the different surfaces than by the surface density of the adsorbed precursors. Surfaces that hold a high density of precursors also exhibit a high growth rate. However, it is not the rapid growing surfaces that form the outer surfaces on the columnar forms, but rather surfaces with the lower growth rates. The reason for this is that surfaces with high growth rates will soon grow to self extinction and leave those with lower growth rates to develop further.

It is evident that the CaCO₃ growth experiences a change in dynamics when the deposition temperature is increased from 250 to 350 °C. At 250 °C the columns take (00l) orientation with triangular tips and facet angles of around 26°, the termination planes are therefore possibly of the {108} type. At 250 °C these surfaces apparently have the lowest surface density of adsorbed precursors and hence the lowest growth rate among the relevant alternatives for CaCO₃ (calcite). The adsorbed precursor layer probably experiences a reconstruction somewhere between 250 and 350 °C. This either reduces the precursor surface density for some additional surfaces or increases the precursor surface density for the surfaces dominating the growth at 250 °C, so that at 350 °C also {108} grow to extinction and then opens up for a new set of surfaces for growth. What is observed is a somewhat lower growth rate at higher temperatures as seen from Fig. 2, and a change in the orientation of the columnar growth. The reduction in growth rate favours the idea that the precursor surface density is decreased for an additional set of surfaces. A rearrangement within the adsorbed precursor layer may reflect changes on the CaCO₃ surface, or more probably originate from changes in the composition of the gas phase Ca(thd)ₓ molecules (see also Ref. [25]).

The surfaces developed at 350 °C have features (see Fig. 9) which indicate that (104) oriented columns are terminated by two different crystal surfaces. One of these surfaces has an angle of ca. 8° toward the substrate, which makes it a vicinal {104} type with ca. 22.5 Å between the steps. The angle of the second surface is as mentioned more uncertain and, we hesitate to speculate further. It is impossible to construct two surfaces with similar surface structures on (104) oriented columns that are terminated with parallel ridges in the way we observe here. This is due to the crystal symmetry, which forces the CO₃²⁻ units of calcite to protrude with different angles from the two terminating surfaces. This likely leads to different adsorption arrangements of the precursors and hence different surface density of adsorbed
precursors. The growth rate of the two surfaces needs not be symmetric around (104) and this can result in an inclination of the columns which in turn can explain the splitting in the rocking curves for films deposited at 350 °C on amorphous substrates (Fig. 7). The fact that the rocking curves of the films deposited on α-SiO2(001) and MgO(001) do not reflect such splitting may result from the influence of the first nucleation centers on these surfaces.

It should be noted that although the XRD analyses of the films deposited at 350 °C show only reflections from the (104) orientation, AFM reveals presence of some scattered features with threefold symmetry. These features must be of another orientation than (104) and reflect most probably (00l) orientation. The reason why these features do not show up in the XRD analyses is most probably due to their limited number and extension as well as the much lower scattered intensity of (006) than (104), see above.

The experimental results of this work indicates that Ca(thd)2 and ozone are unsuitable precursors for growth of more complex oxides such as Ca1-xLaₓMnO3, due to formation of carbonate. However, although we have hitherto been unable to make carbonate-free films of CaO by the ALCVD technique, we have preliminary findings that show it is indeed still possible to grow carbonate-free films of just Ca1-xLaₓMnO3 by usage of the same precursors. This is most probably due to increased stability of the Ca1-xLaₓMnO3 phase with regards to the CaCO3 phase.

Acknowledgement

This work has received financial support from the Research Council of Norway. The authors are grateful to prof. Truls Norby for performing the electrical measurements and contributing to their analyses and to dr. Ingvil Gausemel for helpful comments on the IR data.

References


Effect of magnetic field on the growth of $\alpha$-Fe$_2$O$_3$ thin films by atomic layer deposition

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Abstract

Effect of magnetic field on the growth of $\alpha$-Fe$_2$O$_3$ thin films on soda-lime-glass and $\alpha$-Al$_2$O$_3$(001) substrates with the ALD (= atomic layer deposition) technique is reported. Alterations in texture of the deposited films have been investigated by XRD and TEM, and topography by AFM. It is possible to alter the preferred growth orientation of films on soda-lime-glass substrates from preferred [001] to random polycrystalline orientation by application of a magnetic field. The epitaxial growth on $\alpha$-Al$_2$O$_3$(001) is, however, not affected by application of a magnetic field. The growth rate of films deposited on soda-lime-glass substrates is reduced by a factor of $3/2$ by application of a magnetic field, whereas the growth rate on $\alpha$-Al$_2$O$_3$(001) is not affected. The complete mechanism behind the occurrence or absence of modified growth in external magnetic fields is not uncovered, but factors such as: presence/absence of iron sites, activation of surface iron to accept thd liberated during the chemisorbtion of Fe(thd)$_2$, and presence of parasitic ferromagnetism may be of importance in the present case.

Keywords: Atomic layer deposition (ALD), effect of magnetic field, hematite $\alpha$-Fe$_2$O$_3$.

1. Introduction

In the ALD (= atomic layer deposition, also known as ALE = atomic layer epitaxy and ALCVD = atomic layer chemical vapour deposition) process molecular precursors are alternately pulsed into the growth chamber where they saturate all surfaces with one monolayer of precursor [1]. Each reactant pulse is followed by an inert gas purge in order to remove excess precursor from the gas phase before the next reactant is admitted. In this way gas-phase reactions are eliminated and the film-forming reactions become self-limited.
Several interesting examples are known where growth of thin films has proved to be influenced by magnetic fields. First of all, there are thin-film methods which actively depend on the presence of magnetic fields, e.g., magnetron sputtering [2–8]. Secondly, magnetic fields have been applied to regular film growth where charged species occur, such as depositions from ionic solutions [9–11], different types of electro deposition [12–17], redox deposition [18–20], electrophoresis [21], as well as influencing particles in the plumes produced in pulsed-laser depositions [22–26] and alterations of the plasma in plasma-enhanced chemical vapour deposition processes [27–30]. Magnetic fields have also been applied in cases where no charged species is involved; e.g., cyclic organic compounds may undergo orientation effects due to induced currents in the cyclic parts of the molecules [31–33]. Along this line one also finds carbon nanofibers made by metal-organic chemical vapour deposition (MOCVD) [34]. Large magnetic fields have moreover been shown to affect the MOCVD growth of paramagnetic compounds such as YBa2Cu3O7 [35,36]. However, we have failed to find examples where magnetic fields have been applied to the growth of ferromagnetic or antiferromagnetic compounds by precursors that do not possess an electric charge.

The present target compound, α-Fe2O3 (hematite), orders antiferromagnetically below $T_N = 955$ K [37]. The rhombohedral crystal structure (space group $R\overline{3}c$), has unit-cell dimensions $a = 5.0353$ and $c = 13.7495$ Å in the hexagonal setting [38]. The magnetic moments are oriented normal to [001], i.e., in the $ab$-plane [39]. Although α-Fe2O3 is considered as a pure antiferromagnetic material [40] below $T_N$ [37], it is reported to develop weak ferromagnetism [41] after having been subjected to an external magnetic field.

The aim of the present study is to explore the possibility of using a magnetic field to alter the texture of thin films of α-Fe2O3 grown by the ALD technique, and explore whether films grown in an external magnetic field will develop orientation effects dependent on the configuration of the field. Furthermore, we want to establish whether such a modified process is able to modify an epitaxial growth of α-Fe2O3 on α-Al2O3(001).
2. Experimental

The thin-film growth of $\alpha$-Fe$_2$O$_3$ was performed with Fe(thd)$_3$ (Hthd = 2,2,6,6-tetramethylheptan-3,5-dione) as iron precursor and ozone as oxygen source. Most films were grown with 10 000 cycles at 186 °C, which gave films with a thickness of ca. 110 nm (11 pm/cycle). One cycle consisted of a 1-s Fe(thd)$_3$ pulse, 1-s purge with N$_2$, 2-s O$_3$ pulse, and 1-s purge with N$_2$. The iron precursor was sublimed at 114 °C.

Amorphous soda-lime-glass substrates were chosen in order to possibly eliminate effects that a crystalline substrate may have on the film growth. In addition, film deposition was also made on $\alpha$-Al$_2$O$_3$(001) (sapphire) substrates (which have an isotypic crystal structure with $\alpha$-Fe$_2$O$_3$) to test whether an external magnetic field is able to break down the highly oriented growth on this kind of substrate.

An F120-Sat (ASM Microchemistry) thin-film reactor was used. The reaction chamber was modified in order to accommodate magnetic fields, by building insertions (Fig. 1) with permanent magnets of Sm$_2$Co$_{17}$ (10 × 20 × 30 mm). The Sm$_2$Co$_{17}$ is beneficial since demagnetization occurs first around 300 °C, compared to ca. 200 °C for NdFeB magnets. Two different spacers were made, one with iron plates and another with aluminium plates. The magnetic fields between the plates of these insertion devices were measured by a Hall probe at room temperature to be 0.14 T for the iron-plate insertion and 0.30 T for that with aluminium plates. The magnetic field is expected to decrease somewhat with increasing temperatures. Films were grown with the magnetic field parallel and normal to the substrate surface by changing the orientation of the substrate (see Fig. 1).

The films were analyzed by X-ray diffraction (XRD) with Cu K$_\alpha$ radiation on a Siemens D5000 unit equipped with a Göbel-mirror. The same diffractometer was also used for thickness measurements of thinner films with X-ray profilometry. The topography was analyzed by atomic force microscopy (AFM; Digital Instruments, type Nanoscope E, in contact mode). Cross sections of films deposited on soda-lime-glass substrates were analyzed by transmission electron microscopy (TEM; Jeol 2000FX, 200 keV) in order to obtain information about the microstructure. Selected substrates were also measured by Rutherford
back scattering (RBS) with 2 MeV He ions and fitted with SIMNRA [42] as an alternative method for thickness measurement.

Fig. 1. Modified reaction chamber with attached permanent magnets. Upper part shows the location of the insert in the reaction chamber with substrates positioned parallel to the magnetic field. Middle and lower parts show insert in top and side view with substrates normal to the magnetic field. Arrows indicate the direction of the magnetic field.

3. Results

Normal grown thin films of $\alpha$-Fe$_2$O$_3$ on soda-lime-glass substrates, viz. without the presence of a magnetic field, show a dominating (00$l$) orientation according to XRD, however, with some minor traces of (104) and (116) (Fig. 2a). Rocking curve analyses of the (006) peak revealed a split curve with two peaks with an FWHM (full width at half maximum) of 6 and 7° separated by ca. 8.5°. A $\varphi$-scan of (1,0,10) revealed that there is no in-plane ordering of the crystallites. This indicates that the orientation is far from perfect and that the films grow in a columnar way with (00$l$) parallel to the surface plane or actually some 4–5° tilted from the surface.
A significant difference was observed when a magnetic field was applied to the growth process. The resulting films showed reproducibly no dominating crystal orientation, regardless of the orientation of the magnetic field toward the substrate and for both strengths of the magnetic field (Fig. 2b-e). Rocking curve analyses of the (104) and (110) reflections confirmed that as-grown films were without preferred orientation.

![Fig. 2. X-ray diffraction patterns of $\alpha$-Fe$_2$O$_3$ grown on soda-lime-glass substrate (a) without (b) with magnetic field (0.14 T) normal to the substrate (directed upward) and (c) downwards, (d) parallel to the substrate, and (e) normal to the substrate (0.30 T; directed upward). Miller indices are marked on the upper and lower diffractograms.](image)

The growth of $\alpha$-Fe$_2$O$_3$ on (isotypic) $\alpha$-Al$_2$O$_3$(001) substrates resulted in a much stronger orientation of the films than those on soda-lime glass. Applications of magnetic fields were not able to influence the orientation of the deposited $\alpha$-Fe$_2$O$_3$ films on this substrate.

Fig. 3 shows the typical topography of films grown on soda-lime-glass substrates with and without magnetic field. The topographies are similar, but with larger grains on the films deposited in magnetic fields (~45 nm) than on those deposited without magnetic fields (~35 nm). The rms surface roughness of films with and without magnetic fields was measured to be ca. 6 and 4 nm, respectively.

Examples of the microstructure of films, grown on soda-lime-glass substrates with and without the influence of a magnetic field, are illustrated by the cross-sectional TEM pictures shown in Fig. 4. These indicate that all films have an initial growth stage of nanocrystalline
character up to an overall thickness of ca. 10 nm. After the initiation period, the texture of the films grown without magnetic fields becomes of a columnar type with ca. 30 nm broad columns. The total thickness of such films was measured as ca. 100 nm. For films grown in magnetic fields the growth is not of a columnar type above the initial layer, but consists rather of randomly oriented crystals extending right out to the surface. The total film thickness was in this case ca. 65 nm, which gives a thickness reduced by a factor of \((100/65 \approx) 3/2\).

**Fig. 3.** Typical topography of film grown on soda-lime-glass substrates (a) with and (b) without a magnetic field (0.14 T).

**Fig. 4.** TEM cross-section images of film grown on soda-lime-glass substrate (a) with and (b) without a magnetic field (0.14 T).

A set of thinner films was made in order to determine whether the difference in growth rate observed with TEM was due to the initial growth stage or connected with the second columnar stage. When using only 1000 pulsing cycles, an expected film thickness of ca. 11 nm should be obtained within the initial growth regime. The actually observed thickness of such films grown with magnetic fields were ca. 6.6 nm whereas those without magnetic fields
were ca. 10.0 nm thick, again leading to a thickness reduction by a factor of $(10.0/6.6 \approx 3/2$.

In contrast to this, the growth rate of the oriented films on $\alpha$-$\text{Al}_2\text{O}_3(001)$ was measured by RBS to be ca. 11 pm/cycle regardless of presence of the magnetic fields or not.

There is a possibility that the observed alterations in growth could be due to the influence of the magnetic field on the precursor, since cyclic compounds (Fig. 5) may be affected by magnetic fields [31-33]. In order to elucidate this aspect, different sets of thin films of $\beta'$-MnO$_2$ (paramagnetic) and CaCO$_3$ (diamagnetic) were grown with and without magnetic fields, and for thicker as well as thinner films, using the procedure in Refs. [43, 44] (which makes use of the same category of metal precursor, viz. thd complexes). For both of these materials at the chosen deposition temperature, columnar growth with [100] and [001] as preferred growth directions was observed regardless of the presence or absence of the magnetic fields. The growth rates were also unaffected by the magnetic fields. Hence, it is evident that an influence of the cyclic parts of the thd complexes does not appear to be significant for the effects observed with $\alpha$-Fe$_2$O$_3$.

![Fig. 5. Cyclic part of a thd-ligand connected to the central metal atom (M) of a complex.](image)

**Discussion**

The present study shows that both the texture and the growth rate behaviour of $\alpha$-Fe$_2$O$_3$ on soda-lime-glass substrates are affected by application of a magnetic field. These effects may be linked since columnar growth appears to be closely related to the growth rate.

When a film grow on an amorphous substrate, all orientations should be possible for the first crystallites formed. When these grow further, those that are oriented with the fastest growth direction normal to the substrate plane will soon enclose other oriented crystals and dominate the film structure. This is the regular columnar growth mechanism. Columnar
structures formed by ALD are grown in a slightly different way than those by other techniques like chemical vapour deposition, solution growth, vapour growth etc. The pulse times in ALD growth are regulated to allow all crystallite surfaces to become saturated with precursor for each pulse, regardless of the orientation of the surfaces. The relative growth rates of different surfaces will accordingly be determined by the saturation density of the precursors on the various surfaces, and effects such as nucleation rate and surface diffusion should not be of importance. The facets seen on the obtained film will be those with the lowest saturation density of the (decisive) precursor, viz. the surfaces with the lowest growth rate. However, the orientation of the columnar crystallites will be along the direction with the highest growth rate with the basis in the crystal surfaces with the lowest growth rate. Hence, in general, columnar growth occurs when one particular constellation of surfaces with low growth rates gives rise to a relatively higher growth direction than other constellations.

On the basis of the split rocking curve, the terminating $\alpha$-Fe$_2$O$_3$ surfaces forming the columnar crystallites should be oriented toward each other so that the highest growth rate occurs at a direction some 4–5° off [001]. The traces of (104) and (116) orientations that were detected by XRD may originate from crystals formed during the initial growth stage that later become enclosed by columns of (00l) crystals. An initial growth stage of randomly ordered crystallites is shown by cross-section TEM analyses of films grown on soda-lime-glass substrates (Fig. 4b).

In order to grow a film with a random texture there will have to be no apparent dominating growth direction, and hence no set of surfaces with appreciably lower saturation density than the rest. A possible hypothesis for the observed change in texture is that a magnetic field induces surface reconstructions which render the surface densities of the iron precursor to rather similar values for all surfaces.

One consequence of the above reasoning is that when the growth rates of all surfaces take similar values, also the growth rates sideways will be similar and none of the crystallites will be enclosed. One should then expect the films to consist of narrow elongated columns with a column density similar to that for the first nucleation. This is, however, not observed; broad crystallites with random orientations are indeed formed. The reason for this may be that the presence of the magnetic field does not render the growth rate of all surfaces to a similar low value, but rather affects a large enough number of surfaces to give the overall texture a
random character. Another possibility is some sort of selective adsorption on selected crystallites on or along their boundaries, thus producing a spreading sideways.

By using the observed growth rate of the (001) surface (ca. 11 pm/cycle) for $\alpha$-Fe$_2$O$_3$ on $\alpha$-Al$_2$O$_3$(001) and the analogy of Ylilammi [45], it is reason to believe that the iron species are chemisorbed as Fe(thd)$_2$ rather than Fe(thd). If we then assume that the Fe(thd)$_2$ fragment spans over an area of ca. $11.5 \times 13$ Å$^2$ (extracted from information in Ref. [46]), and applying the surface unit-cell dimensions of $\alpha$-Fe$_2$O$_3$(001) $a = 5.035$ Å, $\beta = 120^\circ$, a growth rate of 12.8 pm/cycle is obtained if the precursor fragment blocks 9 active sites on adsorption. If the Fe(thd)$_2$ fragment is allowed to rotate freely, it will block 12 sites and give a growth rate of 9.6 pm/cycle. The observed growth rate of ca. 11 pm/cycle indicates an intermediate situation. By considering that this surface should have a higher growth rate than those terminating the [001] oriented columns, it is likely that the latter surfaces also contain adsorbed Fe(thd)$_2$ fragments.

The observations show that growth on the $\alpha$-Al$_2$O$_3$(001) substrate is not affected by the presence of a magnetic field, whereas both a change in texture and a reduction of the growth rate by a factor of 3/2 are observed for films grown on soda-lime-glass substrates. For the growth rate to be reduced by a factor of 3/2, some additional mechanism for surface blocking of active sites must be in operation. This could come about if the thd fragment which is normally lost to the exhaust gas in the introductory reaction stage when the Fe(thd)$_3$ precursor adsorbs on a terminating surface oxygen, now is caught by a nearby surface iron site (say a jammed-in surface iron which rules an area large enough to host one thd group, see Fig. 6). The thus produced Fe(thd) fragment would cover about half the area of a Fe(thd)$_2$ fragment, provided it is prevented from rotation (see above). Accordingly the growth rate will be reduced by the observed factor of 3/2. In order for such films to grow randomly oriented, the surface density of the two iron precursor fragments must take similar low values on several surfaces.

As mentioned the growth rate was not altered by a magnetic field for films grown on $\alpha$-Al$_2$O$_3$(001). The resulting $\alpha$-Fe$_2$O$_3$ films has been shown to be highly epitaxial on this substrate and AFM analyses reveal that the films are very smooth with only low angle features. Hence such films grow with only one type of surface exposed, the (001) surface.
Films grown on soda-lime-glass substrates are expected not to have (001) terminated surfaces due to the [001] orientation of the columns and of their terminating facet angles as observed by AFM, Fig. 4.

![Diagram of Fe(thd)$_3$ adsorption scheme](image)

**Fig. 6.** Pictorial illustration of a possible adsorption scheme for Fe(thd)$_3$ on a weakly guiding substrate which is subjected to an external magnetic field. Note the interception of the thd fragment by the surface iron rest valence.

The central question is then why different surfaces respond differently to the presence of a magnetic field. In order for a surface to take on additional thd ligands, it has to have available Fe sites. Unpolar surfaces [such as the (012) surface] will always have both types of atoms present, but the termination of the polar (001) surface will depend on the oxygen pressure. It is reasonable to believe that the surface will be oxygen terminated during the ozone pulse, but it is questionable if the kinetics is fast enough to alter the surface to a partial iron termination during a purge of 1 s at a reactor temperature of 186 °C. According to the experiments described by Shaikhutdinov and Weiss [47] this is rather doubtful, and we may assume the (001) surface of α-Fe$_2$O$_3$ films grown on α-Al$_2$O$_3$(001) to be oxygen terminated when the Fe(thd)$_3$ is pulsed. This may be one reason why growth on this surface is unaltered by a magnetic field. At the used reaction temperature, the magnetic moments on this surface lie in the surface plane, and hence any surface with an angle to this surface will have magnetic moments protruding out from it. This may also be a prerequisite for activation of iron sites to act as host for a thd group librated by the mechanism illustrated in Fig. 6.

Already the fact that both the orientation and the growth rate remain unaltered for α-Fe$_2$O$_3$ grown on α-Al$_2$O$_3$(001) rules out that the modified growth is due to alterations of the
precursor alone. The control experiments with Ca(thd)$_2$ and Mn(thd)$_3$ rule out the possibility that any perturbation of the electronic properties of the precursor complex by a magnetic field has major effect on the growth process. Hence, neither magnetic effects set up in the cyclic parts (viz. the β-diketonato rings of the complexes) of the precursor nor the central metal atom is the source for the modified growth. (Note that MnO$_2$ films grown by Mn(thd)$_3$ and ozone are expected to exhibit non-polar terminating surfaces [43]. Furthermore Mn(thd)$_3$ and Fe(thd)$_3$ paramagnetic complexes are expected to behave similarly to perturbation by external fields.) On this basis, the effects induced by magnetic fields for α-Fe$_2$O$_3$ thin films, appear not to be connected with the Fe(thd)$_3$ precursor alone. It is therefore plausible that the observed effects for α-Fe$_2$O$_3$ are due to interplay between the precursor and magnetic nature of the film. Regarding the observations, it natural to assume that a complex between a surface terminated iron and thd will be additionally stabilized in a magnetic field.

Weak parasitic ferromagnetism will develop in α-Fe$_2$O$_3$ in external magnetic fields ([41]; confirmed also in the present study) and this property may also occasion modifications in the growth process. The atomic arrangement in the first α-Fe$_2$O$_3$ layers on the substrates is ruled by the structure of the supporting substrate. When the film has obtained a certain thickness, the parasitic ferromagnetism induced in the underlying α-Fe$_2$O$_3$ layers could be imagined to take over the directing role. The growth pattern already developed would then largely rule the subsequent layers.

The present study has revealed that activation of Fe(thd)$_3$ on an α-Fe$_2$O$_3$(001) surface is not influenced by a magnetic field, whereas other surfaces are influenced. The complete mechanism behind the occurrence or absence of such modified growth is uncertain, but effects such as: presence/absence of iron surface sites, activation of surface iron to accept liberated thd groups, and presence of parasitic ferromagnetism may be of importance. These observations should be an invitation for further studies of the phenomena, e.g., by more powerful surface analysis techniques, computational theoretical chemistry, etc.

Acknowledgement

We are grateful to Oddvar Dyrlie for performing the AFM measurements. This work has received financial support from the Research Council of Norway.
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Thin film deposition of lanthanum manganite perovskite by the ALE process

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Received 14th April 1999, Accepted 3rd June 1999

Deposition of thin films of LaMnO₃ from β-diketonate-type (thd) precursors and ozone in an ALE reactor has been demonstrated. At low temperatures, the Mn–O growth from the Mn(thd)₃ precursor is retarded by the growth of the La–O deposit. By tuning of the pulsing ratio, full control of the stoichiometry of the deposited film is achieved in the temperature interval 300–400 °C. In this temperature range, the composition set by the pulsing ratio is transferred, within a few percent accuracy, to the deposited thin film. Indications for an ‘ALE window’ are found around 250–300 °C. Amorphous LaMnO₃ films could be deposited at temperatures as low as 250 °C, however, the deposition of crystalline films requires temperatures above 350 °C. X-Ray diffraction analyses show that the crystalline LaMnO₃ film was of the rhombohedral type with a = 5.46(2) Å and α = 60.28(10)°.

Introduction

Materials with the ABO₃ perovskite-type structure exhibit a vast range of electric and magnetic properties dependent on the elements (A,B) as well as the exact composition. This class of materials therefore provides potential components for electric and magnetic devices. Their properties are often controlled and monitored by variation in the oxygen stoichiometry or by substitution on the A and/or B sites. In recent years there has been a marked increase in research on thin film processing, motivated by the fact that several advanced applications require material in thin film form. This also applies to research on thin oxide films, where materials with the perovskite-type structure are well represented. The growth of the same thin film material has typically been attempted by a variety of methods. One motivation for this is that different methods often produce materials with different microstructures, which in turn can affect their properties. 1–5

The present work focuses on the growth of thin films of the LaMnO₃₊ₓ₋ₓ perovskite-type oxide via the atomic layer epitaxy (ALE) method. Owing to its intriguing physical properties and potential applications, LaMnO₃ and its solid-solution derivatives have received considerable attention. For instance, materials with partial substitution of La by divalent cations (Ca, Ba, Sr, Pb, Cd) or with vacancies introduced at the La sites show colossal magnetoresistance (CMR) properties, 6–8 whereas (La,Sr)MnO₃ materials are commonly used in solid oxide fuel cell (SOFC) prototypes working at high temperatures 9 and are also of interest as oxygen sensors. 10 The CMR effect is believed to result from a mixed valence situation with the presence of both Mn²⁺ and Mn⁴⁺ species. 11 Thin films of La₁₋ₓCaₓMnO₃ (A=Ca, Ba, Sr, Pb) are reported to give larger CMR values than bulk samples. There is also interest in exploiting their catalytic activity for combustion of gases like CO and NOₓ as well as for volatile organic compounds (VOC).12–14

Thin films of (A,La)MnO₃ (A=Ca, Sr, Ba, Pb) have previously been deposited by methods such as pulsed laser deposition (PLD), 3,5,15–17 facing-target sputtering, 18 RF sputtering, 19,20 ion beam sputtering, 21 molecular beam epitaxy (MBE), 22,23 chemical vapour deposition (CVD) 24 and its metalorganic variant (MOCVD), 25,26 spray pyrolysis, 27 spin coating with sol–gel epitaxial growth, 28 metalorganic deposition from solution 29 and electrodeposition. 30 Among these, PLD is the most frequently used method and it allows control over the stoichiometry up to a certain level. All these methods, except for spin coating, (MO)CVD and electrodeposition, are so-called ‘line of sight’ methods where a uniform coating cannot be expected. Furthermore, most of them require either post-annealing or deposition at a rather high temperature in order to arrive at a crystalline film.

Only a few ternary oxides have so far been grown with the ALE technique 31–32 However, its potential for growing thin films of perovskite-type oxides has been demonstrated for LaNiO₃ and LaCoO₃ 33,34 and more recently for SrTiO₃. 35 The ALE method is attractive since it can provide excellent control of thickness, stoichiometry, step coverage and uniformity over large area substrates. Furthermore, a crystalline film can often be achieved at lower temperatures than with other techniques. 36 This would be important if one considers applications such as integrated circuit units.

Experimental

Thin films were grown in a flow-type ALE reactor which has been described elsewhere. 37 Freshly synthesised La(thd)₃ and Mn(thd)₃ (thd = 2,2,6,6-tetramethylheptane-3,5-dionate) were used as precursors and ozone as the oxidiser. The stability and volatility of the precursors were checked by TG under simulated ALE conditions (reduced pressure of 1–2 mbar). Ozone was produced by feeding oxygen gas (99.999%) into the reactor through an ozone generator (Fischer model 502). The reactant pulses were separated by nitrogen gas (99.999%) purging. The pulsing period for the lanthanum and manganese precursors was 1.8 s, whereas the N₂ purging period was 2.5 s. Ozone was pulsed for 1 s followed by N₂ purging for 3 s. The pulsing and purging times were chosen on the basis of earlier ALE studies on LaNiO₃ and LaCoO₃ 33,34 and these parameters are not the subject of more detailed study here. However, a few tests were performed with variation of the pulsing and purging times without observing any notable difference. For the deposition of films with varying composition and thickness, the pulsing sequences were chosen to maximise the probability of proper mixing of the components, i.e. first La(thd)₃, then O₃, followed by Mn(thd)₃ and finally O₃ again.

The films were grown on Si(100), soda lime and aluminium foil substrates under a pressure of 1 mbar. Altogether six
50 × 50 mm² substrates were vertically accommodated in a back-to-back configuration (see Fig. 1). Substrate 1 and 2 (left hand side) were of silicon, 1 and 2 (right hand side) were of soda lime and for substrate 3 both sides were of aluminium foil. Depositions were made in the temperature interval 200–400 °C. Film growth was studied as a function of deposition temperature and of pulsing ratio. The films were characterised in the as-deposited state.

As a preliminary test, films of MnOₓ were grown with Mn(thd)₃. The growth was found to proceed in a manner similar to that described for Ni(thd)₃ and Co(thd)₃. However, a major difference stems from the fact that Mn shows a larger variation in oxidation states than Ni and Co. As a consequence, a variety of manganese oxide phases were formed: MnOₓ at 180 and 200 °C, MnₓOᵧ at 250 °C and Mn₃O₄ at 350 °C.

Characterisation

Phase identification was performed by X-ray diffraction (XRD) measurements with a Philips MDP 1880 powder diffractometer using Cu-Kα radiation. La and Mn concentrations were determined using a Philips PW 1480 X-ray fluorescence spectrometer equipped with a Cr X-ray tube. La Lα was measured with 40 kV, 60 mA and a LiF(220) analysing crystal. For Mn Kz, settings of 60 kV, 40 mA and a Ge(111) analysing crystal were used. A self-supporting LaMnO₃ pressed powder sample served as a standard for defining instrumental sensitivity factors corresponding to the analytical lines. Subsequent data analysis was performed with UNIQUANT 2.5 software based on fundamental parameters. UNIQUANT utilises the DJ Kappa model to calculate simultaneously the composition and mass thickness of an unknown bulk or thin film sample. Since oxygen could not be quantified with the present spectrometer set-up, it was assumed that there were 1.5 oxygen atoms for each La and Mn atom in the thin film layer. Furthermore, the growth rate was evaluated, when possible, by fitting of transmittance curves recorded with a Hitachi U-2000 double-beam spectrophotometer in the region 370–1100 nm. However, only the thinner films were sufficiently transparent to be evaluated spectrophotometrically.

Results and discussion

A major motivation for this work was to demonstrate the feasibility of growing multi-element films with controlled stoichiometry in an ALE reactor. Hence, the work was focused on growing films at different deposition temperatures and by variation of the pulsing ratio of the precursors. The thin films were deposited from La(thd)₃ and Mn(thd)₃ precursor batches heated in separate furnaces. By varying the source temperature, the optimum sublimation temperature was found to be 115 °C for Mn(thd)₃ and 175 °C for La(thd)₃. After completion of deposition, neither of the source crucibles showed any residue which could indicate a partial decomposition of the precursors. The precursors are hence considered to be relatively stable, in accordance with the TG data and our earlier experiences.

The deposition temperature showed a significant influence on the growth rate of the thin films, see Fig. 2. Thickness measurements were made for both the first and the second substrate in the flow direction. The thickness was measured as an average over a 450 mm² circular area in the middle of the substrate, i.e. over an area which in all cases was considered uniform.

The temperature dependence of the growth rate indicates that at least three different growth mechanisms are operative. For the range 200–250 °C, the rate increases steadily with temperature. It is believed that deposition is kinetically hindered in this range and that only a small amount of the precursor has sufficient energy to bond chemically to the surface.

In the temperature region 250–300 °C, there is no significant variation in the growth rate with the deposition temperature. This region, marked II in Fig. 2, appears to represent an 'ALE window' since the growth is surface controlled and only affected by the temperature to a small extent.

The small variation of growth rate that is nevertheless observed in the 'ALE window' could indicate rearrangement of the surface species at different temperatures. It is indeed possible that the growth rate is influenced by the packing of the bulky La and Mn precursors on the surface.

For temperatures above ca. 250 °C, substrate 1 shows a systematically slightly larger growth rate than the succeeding substrate, Fig. 2. This may be caused by several effects: (i) full surface saturation cannot be achieved within the length of the pulsing cycles chosen, (ii) CVD-type growth may take place for substrate 1 and/or (iii) the concentration gradient in the flow direction is due to the fact that thd ligands released at an early stage will deposit on later parts and this will partially prevent the subsequent adsorption of the precursors. The ALE system was tested for possible gas leakage of the thd precursors which could lead to CVD-type growth. However, on pulsing of the ozone reactant only, no film was obtained and CVD-type growth could therefore be excluded. In the growth of manganese oxide films, only a slight thickness variation was observed when the length of the Mn pulses was varied. A few tests were carried out to study the effect of the pulsing cycles on the growth of LaMnO₃ films, but no large variation was found either.

A third growth mechanism is indicated at temperatures between 300 and 400 °C (region III of Fig. 2). The growth rate in this interval increases with temperature. This is believed to reflect a partial decomposition of the precursors (the thd compound may lose one or two of its three ligands) which makes it possible that a larger amount of the precursor can chemically bond to the surface in one cycle.

The obtained films are not uniform in all directions and exhibit a rather sharp decrease in thickness towards the edges that were parallel to the flow direction (see Fig. 1). This type of gradient was also found with pure Mn(thd)₃, Ni(thd)₃ and Co(thd)₃ precursors and is therefore believed to be related.

Fig. 2 Growth rate as a function of temperature for substrates 1 and 2. Open and filled symbols refer to substrate positions.

Fig. 1 Substrate arrangement with respect to the direction of the gas flow. Dimensions in mm.
to reactor gas flow characteristics or to reactions between these precursors, the substrate and ozone.

The choice of deposition temperature has a pronounced effect on the stoichiometry of the film. Fig. 3 shows how the Mn content of the obtained films varies with deposition temperature for fixed 1 : 1 (La : Mn) pulses. The films become poor in Mn content at temperatures below 250 °C. The film deposited at 200 °C consists almost entirely of lanthanum oxide and the growth rate is very low. However, at the same temperature it is possible to grow oriented MnO$_2$ films at a growth rate of at least 0.2 Å per cycle by pulsing Mn(thd)$_3$ and ozone. This shows that presence of La–O retards the growth of Mn–O at lower temperatures. The retarding effect on Mn–O growth may possibly be caused by unfavourable surface sites for Mn(thd)$_3$ to adsorb at. However, this hypothesis requires further investigation.

In order to achieve control of the La : Mn stoichiometry of the film, depositions were performed at 300 and 400 °C with varying pulsing ratios. The resulting Mn content is shown in Fig. 4. It appears possible to control the La : Mn stoichiometry of the film within a few percent by adjusting the pulsing ratio. It can be seen that the films grown at 400 °C on substrate 2 show consistently higher Mn contents than those on substrate 1, in particular at higher Mn pulsing ratios. The films grown on substrate 1 at 300 °C show a slight decrease in their Mn contents as the La : Mn ratio increases. This may indicate that La–O is retarding the growth of Mn–O, even at this temperature.

XRD measurements were conducted on films grown on Si(100) substrates (in position 2). The observed diffraction profiles of some samples from selected deposition conditions are shown in Fig. 5. The data indicate that it is possible to grow reasonably crystalline films at a temperature as low as 350 °C. The degree of crystallinity, as judged from the FWHM of the peaks, improves with increasing deposition temperature as expected. The XRD patterns fit well with that of LaMnO$_3$ and show that the films are polycrystalline with a rhombohedral type structure, $a = 5.46(2)$ Å and $c = 60.28(10)$ Å, being thus quite similar to powder samples.

**Conclusion**

Thin film growth of LaMnO$_3$ in an ALE reactor has been demonstrated from β-diketonate-type precursors and ozone. It was shown that La–O retards the growth of Mn–O from Mn(thd)$_3$ at low temperature. Film growth with a good control of stoichiometry has been demonstrated at temperatures between 300 and 400 °C. At these temperatures the stoichiometry of the pulsing ratio is transferred, within a few percent accuracy, to the thin film. LaMnO$_3$ can be deposited at temperatures as low as 250 °C, but crystalline films can be achieved at temperatures above 350 °C.

**Acknowledgement**

The authors are indebted to Ms. Minna Nieminen, Lic. Tehn., for assistance and helpful discussions concerning the thin film deposition.

**References**

Preparation and characterization of La$_{1-x}$Ca$_x$MnO$_3$ thin films grown by atomic layer chemical vapour deposition

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Abstract

Thin films of calcium substituted lanthanum manganite (La$_{1-x}$Ca$_x$MnO$_3$) have been made by the ALCVD (= atomic layer chemical vapour deposition) technique using Mn(thd)$_3$ (Hthd = 2,2,6,6-tetramethyl-3,5-heptadione), La(thd)$_3$, Ca(thd)$_2$, and ozone as precursors. The effect of each of these precursors on the product stoichiometry has been investigated, and growth of the ALCVD-type was achieved in the temperature range 200–330 °C. This is the first example of the use of the ALCVD technique for growth of films of a phase with three types of metal components, with control (or partial control) of variable stoichiometry, and at the same time obtain samples suitable for magnetoresistance measurements. The films of La$_{1-x}$Ca$_x$MnO$_3$ are grown carbonate-free although Ca(thd)$_2$ and ozone used alone as precursors give CaCO$_3$. Mn(thd)$_3$ may be used as precursor for ALCVD growth of oxides up to 330 °C when Mn is deposited together with Ca and La than whereas 240°C is the upper temperature limit when Mn is deposited alone. Films have been deposited on substrates of (amorphous) soda-lime glass and single crystals of Si(100), MgO(100), SrTiO$_3$(100), and LaAlO$_3$(100), and growth with a cube-on-cube epitaxy has been achieved on SrTiO$_3$(100) and LaAlO$_3$(100) substrates. The substrates affect the growth and the physical properties of the resulting films. Magnetoresistive properties are recorded for films with composition close to La$_{0.7}$Ca$_{0.3}$MnO$_3$.

Keywords: Atomic layer deposition (ALD), calcium lanthanum manganite (CaLaMnO$_3$).

Introduction

The substituted manganites, A$_{1-x}$A$'$$_x$MnO$_3$ (where A is a trivalent and A' divalent cation), adopt a perovskite-related structure where the Mn$^{3+}$ : Mn$^{4+}$ ratio depends on the substitution level of the A' and the oxygen stoichiometry. The different types of such
substituted manganites have gained much attention after the discovery of colossal magnetoresistance (CMR; for $x \approx 0.15–0.5$, with a maximum for $x \approx 0.3$) and charge ordering (CO; for $x \approx 0.5$). Electron hopping gives rise to double exchange (DE), thereby also high electronic conduction combined with ferromagnetic interactions. In addition superexchange is important for the magnetic properties. Both the electrical and magnetic properties of the manganites are very susceptible to external effects such as magnetic fields and also stresses that may alter the angle of the corner sharing MnO$_6$ octahedra, viz. the Mn-O-Mn bond angle. Any deviation from 180° will decrease the conduction. The physical properties of thin films of manganites are therefore very influenced by the microstructure and compositional variations. Hence, numerous techniques have been tried for synthesis of $A_{1-x}A'$,MnO$_3$ phases and the readers should consult Refs. [1–3] and references therein for comprehensive surveys of the field.

The lowest resistivities and the largest magnetoresistances at high magnetic fields are found among the most epitaxial films; nevertheless, presence of grain boundaries is shown to give large contribution to the magnetoresistance at low magnetic fields. It is therefore of importance to be able to control this when applications are in mind. A systematic search performed by deposition on different types of nearly lattice-matched substrates should be performed in order to explore the effects of tensile and compressive strains, as well as to map the influence of various deposition parameters. Perovskite-related manganite films have in the past been grown by modifying the synthesis conditions developed for high-temperature superconductor materials [2,3]: Reactive sputtering, ion beam sputtering, co-evaporation, molecular beam epitaxy, spray pyrolysis, sol-gel spin coating, chemical vapour deposition (CVD), and pulsed laser deposition. Most of these techniques either suffer from problems with narrow windows for the deposition parameters and limited substrates sizes, or insufficient compositional control over larger areas. Nevertheless, high quality films have successfully been produced. The manganites have mostly been grown at 600–700 °C in order to assure single-crystal epitaxial microstructure.

This study will explore the possibility for the ALCVD (ALCVD = atomic layer chemical vapour deposition; also known as ALD = atomic layer deposition or ALE = atomic layer epitaxy) technique to deposit manganites with three metal components and variable stoichiometry. The present contribution leans on earlier work which shows that the ALCVD technique is able to deposit material over large areas, with low compositional variations, and
at typically lower deposition temperatures than other techniques. ALCVD is a gas-phase deposition technique closely related to CVD, but gas-phase reactions are eliminated by alternately pulsing one precursor at the time into the reaction chamber (see Ref. [4]).

The main aim of the present study is to demonstrate the ability to grow films of multi-component, nonstoichiometric phases with the ALCVD technique; and in addition produce materials with favourable magnetoresistant properties. A crucial challenge was to grow carbonate-free calcium-containing complex oxides with the Ca(thd)\(_2\) and ozone precursors. These precursors are known to form calcium carbonate films when used alone [5]. The preparation of oxide films of each of the metal constituents of La\(_{1-x}\)Ca\(_x\)MnO\(_3\) have been characterised earlier in the Refs. [5–7].

**Experimental**

Films were grown in a commercial F-120 Sat reactor (ASM Microchemistry) by using Mn(thd)\(_3\) (Hthd = 2,2,6,6-tetramethylheptan-3,5-dione), La(thd)\(_3\), and Ca(thd)\(_2\), and O\(_3\) as precursors. The precursors were made in-house as described in Ref. [8]. Ozone gas was used at a flow of 500 cm\(^3\) min\(^{-1}\). It was produced by feeding pure O\(_2\) (AGA 99.999\%) into an ozone generator (OT-020, OzoneTechnology) giving an ozone concentration of 15 vol.% according to specifications. The applied sublimation temperatures for the precursors (Mn(thd)\(_3\), La(thd)\(_3\), and Ca(thd)\(_2\)) were 135, 185, and 195 °C, respectively. The reactor pressure was maintained at ca. 1.8 mbar by employing a carrier gas flow of 300 cm\(^3\) min\(^{-1}\) N\(_2\), supplied from a Nitrox 3001 nitrogen purifier with a purity of 99.9995\% inert gas (N\(_2\) + Ar) according to specifications. The soda-lime-glass substrates were cleaned as described in Ref. [6], whereas Si(100), Mg(100), SrTiO\(_3\)(100), and LaAlO\(_3\)(100) substrates were used as purchased from the supplier since they were epi-polished. In addition to this, all substrates have been subjected to a cleaning procedure with ozone treatment just prior to the film deposition.

For all composition- and thickness-variation measurements, a total of ca. 1000 basic cycles was applied where one basic cycle comprises the pulsing scheme: 1.5 s metal-thd precursor [La(thd)\(_3\), Ca(thd)\(_2\) or Mn(thd)\(_3\)], 0.3 s purge, 6 s ozone and 1.5 s purge. The sequence of the different metal-thd injections were alternated in specific patterns that
facilitated optimum mixing of the metal components at the predetermined composition. For example, an Mn-precursor-containing basic cycle should follow both La- and Ca-precursor-containing basic cycles in the order predetermined by the Mn stoichiometry in the La_{1-x}Ca_{x}MnO_{3} films. The typical thickness of the resulting film by 1000 basic cycles was ca. 20 nm. In selected runs and for the single crystal substrates [MnO(100), SrTiO_{3}(100), LaAlO_{3}(100), α-SiO_{2}(001), and α-Al_{2}O_{3}(012)] a pulsing scheme with a total of 5000 basic cycles were used.

The post-annealing of selected films was performed in a CO_{2}-free O_{2} atmosphere at 850 °C for 30 min. In the annealing treatment the films where rapidly heated and cooled by moving the films quickly between hot and cold zones of a furnace. The films for composition- and thickness-variation measurements were mainly performed on 5×5 cm² soda-lime-glass and Si(100) substrates mounted in a back-to-back configuration. Smaller substrates were placed on a horizontal insertion that divided the reaction chamber in two.

Deposited and annealed films were examined with a Siemens D5000 diffractometer equipped with a Göbel mirror that produces parallel Cu Kα radiation. This set-up was used both for thickness measurements with X-ray profilometry and conventional 0–20 X-ray diffraction (XRD) in reflection mode and reciprocal mapping. The topography of selected films was studied by atomic force microscopy (AFM; Digital Instruments, type Dimension 3100, in tapping mode). Selected films were analyzed with transmission FT-IR spectroscopy on a Perkin Elmer system 2000 FT-IR spectrometer. The films for IR analyses were deposited on both sides (both sides polished) of Si(100) substrates. An uncoated substrate was used as reference. Powdered samples were pressed and measured in KBr pellets using a blank pellet as reference.

X-ray fluorescence (XRF) measurements were performed for determination of the composition and as an alternative method for thickness assessments of the films. The UniQuant analysis software was used to interpret the results. This method uses only fundamental parameters for the extraction of composition and thickness data from the observed intensities [9]. Rutherford back scattering (RBS) was used as an additional means to derive information on thickness and composition for selected films. 2.0 MeV He-particles were used with an incident angle of 0°, exit angle of 13°, and scattering angle of 167°. Large-
scale distribution mapping of the different components in selected films was performed with an Itrax XRF microscope (Cox Analytical Systems) by using a 1 mm capillary and a Cu X-ray source.

The room temperature resistivity of the films was measured by a linear four-point probe set up with 1 mm spacing between the pins and probe tips with a curvature of 500 μm. The latter precaution was taken to prevent damage of the films. Resistivity values given in this report have been corrected for the sample geometry [10]. The magnetoresistance measurements were performed with a four-point set up in a Quantum design PPMS unit with a maximum magnetic field of 9 T.

Results

This work builds on Ref. [11] where LaMnO₃ was grown with slightly different ALCVD equipment. In order to grow La₁₋ₓCaₓMnO₃ films with the ALCVD technique one needs to explore how each constituent affects the deposition of the others. One can only anticipate coherence between the pulse pattern used for each constituent (viz. the fraction of equal basic cycles in the growth process) and the composition of the resulting film when precursors of the same type and with the same number of ligands are used. It was therefore necessary to explore how the deposition of one constituent affects the depositions of the others. Recent studies [5–7] on the ALCVD growth of the binary oxides (CaCO₃, La₂O₃, and MnO₂) of the metal constituents of La₁₋ₓCaₓMnO₃ represent a convenient starting point for the endeavours reported here (Fig. 1).

The effect of the La(thd)₃ : Mn(thd)₃ pulse ratio [viz. the relative number of basic cycles] on the composition and growth rate of deposited La₁₋ₓMnₓO₃ (y ≈ 3, but note that attention has not focused on the oxygen content at this stage; and for convenience y = 3 is used in the rest of this paper) films at 235 °C is shown in Fig. 2. The composition defined by the applied fraction of the basic cycles is nearly quantitatively deposited on the substrates. It is interesting to note that the growth rate and hence the thickness goes through a minimum near the composition LaMnO₃ and the thickness gradients over the films are also rather minor near the equiatomic La : Mn composition. Films deposited in the composition range 10–40% Mn pose particularly large thickness gradients.
Fig. 1. Growth rate as a function of deposition temperature for La$_2$O$_3$ (circles; half-filled mark data quoted from Ref. [6], others are from in-house work), MnO$_2$ (triangles; quoted from Ref. [7]) and CaCO$_3$ (squares; quoted from Ref. [5]). Filled and open symbols refer to measurements on Si(100) and soda-lime-glass substrates, respectively.

Fig. 2. Effect of La : Mn pulse ratio on composition and growth rate for films prepared at 235 °C. Open symbols refer to composition and filled symbols to growth rate. The symbols △, ●, and ▼ refer to measurements made in front, middle, and back of films on soda-lime-glass substrates, respectively, and ◆ and ▼ to corresponding data for film on Si(100) substrates.

Keeping the La(thd)$_3$ : Mn(thd)$_3$ pulse ratio at 1 : 1 while varying only the reactor temperature the relationship depicted in Fig. 3 was obtained. This shows a slight relative increase in the manganese content with increasing temperature, and indicates, moreover, that the films grown on Si(100) substrates contain slightly less (ca. 5 at%) manganese than films
deposited on soda-lime-glass substrates. However, this feature is seen (Fig. 3) to be dependant on the reactor temperature and may, in fact, rather result from the location of the (5×5 cm²) substrates in the reactor chamber [Si(100) substrates on the same side as the metal-precursor inlet in the “Sat” reaction chamber]. The results show that it is possible to deposit LaMnO₃ in a temperature interval from ca. 180 to 325 °C without a dramatic increase in thickness gradients and with fairly constant thickness, viz. representing conditions typical of an ALCVD-window [12]. We have with this system been able to deposit films with a composition close to LaMnO₃ with a La(thd)₃ : Mn(thd)₃ pulse ratio of 1 : 1 at much lower temperatures than previously reported in Ref. [11], and hence we did not observe the same depletion in the manganese content by introduction of lanthanum as previously reported in the latter paper.

![Fig. 3.](image)

**Fig. 3.** Growth rate and relative Mn content as a function of temperature for films prepared with a 1 : 1 pulse ratio of Mn(thd)₃ and La(thd)₃. Open symbols refer to composition and filled symbols to growth rate. The symbols ▲, ▼, and ▼ refer to thickness measurements made in front, middle, and back of films on soda-lime-glass substrates, respectively, and ◆, ●, and ■ to corresponding data for films on Si(100) substrates.

The result of varying the Ca(thd)₂ : Mn(thd)₃ pulse ratio on the composition of Ca₁₋ₓMnₓO₃ films at 235 °C is shown in Fig. 4. It is evident that the deposited films contain more Ca than according to the applied pulsing ratio. It proved necessary to enhance the relative number of Mn(thd)₃-containing basic cycles to a ca. 60 % Mn (and 40 % La) in order to achieve a composition close to CaMnO₃. Also in this case the film thickness and the film-thickness gradients are at minimum close to the equiatomic Ca : Mn content of the formula CaMnO₃. The growth rate and composition of films with a Ca(thd)₂ : Mn(thd)₃ pulse ratio of 2 : 3 (60 % Mn) is shown in Fig. 5. A slight increase in the manganese content with
increasing temperature is noted, but there should be a reasonable good ALCVD window from ca. 180 to 335 °C.

**Fig. 4.** Effect of Ca : Mn pulse ratio on composition and growth rate for films prepared at 235 °C. Open circles refer to composition and filled symbols to growth rate. The symbols ▲, ◄, and ▼ refer to measurements in front, middle, and back, of films on soda-lime-glass substrates, respectively, and ● to data collected in the middle of films on Si(100) substrates.

**Fig. 5.** Growth rate and relative Mn content as a function of temperature for films prepared with a 2 : 3 pulse ratio of Mn(thd)$_3$ and Ca(thd)$_2$. Open symbols refer to composition and filled symbols to growth rate measurements. The symbol ◄ refers to measurements made in the middle of films on soda-lime-glass, and ●, ○, and ■ to measurements in the front, middle, and back of films on Si(100) substrates, respectively.

Since the object of the present endeavours is to produce films within the homogeneity range of the La$_{1-x}$Ca$_x$MnO$_3$ phase, the effect of the Ca(thd)$_2$ : La(thd)$_3$ pulse ratio on the composition of the deposited films was studied. This was done by varying the pulsed Ca(thd)$_2$ : La(thd)$_3$ ratio while keeping the pulsed (Ca(thd)$_2$ + La(thd)$_3$) : Mn(thd)$_3$ ratio fixed.
at 1 : 1. The result of this examination is shown in Fig. 6. It is evident that again the deposited films contain more Ca than expected according to the applied pulse ratio.

![Graph showing growth rate and content variations](image)

**Fig. 6.** Effect of Ca : La pulse ratio on composition and growth rate for films prepared at 235 °C. The symbols ▲, ▼, and ▼ refer to growth rate in front, middle, and back of films on soda-lime-glass substrates, respectively, and ● to growth rate in the middle of films on Si(100) substrates. The symbols △, ▽, and ○ refer to La, Ca, and Mn content, respectively, whereas ★ give the sum La and Ca contents.

On the basis of the findings outlined above it seemed clear that an iterative procedure with alternating growth and characterization of the resulting film must be applied in order to obtain a specific composition for a system with the present complexity. This is even the case when the precursors are as similar with respect to type and number of ligands as La(thd)₃ and Mn(thd)₃.

An Si(100) substrate was cut to the shape of the cross section of the “Sat” reaction chamber and mounted horizontally in order to map the long range compositional variations for a film with desired composition close to La₄₋₇Ca₀₃₋₇Mn₀₈₋₀₂O₃ (using 5000 basic cycles at 235 °C). The resulting film was scanned with the XRF microscope and the raw data were normalized to the regular XRF measurements to give the compositional variations (Fig. 7). The outcome is that there is only a small increase in Mn content along the flow direction over this special 12 cm long substrate. This may be due to a slightly increasing temperature gradient noted also previously along that same direction, and the fact that the Mn content
increases with increasing deposition temperature. In view of the enlarged dimensions of the test substrate (see Fig. 7), we may therefore safely assume that the growth conditions are similar on all smaller substrates included in the same run.

![Diagram](image_url)

**Fig. 7.** XRF microscopy scans of the variations in Mn (■), La (○), and Ca (▲) content on a La$_{0.7}$Ca$_{0.3}$MnO$_3$ film deposited at 235 °C on a Si(100) substrate formed as the cross section of the reaction chamber and positioned horizontally. ★ denotes positions for the thickness measurements. Flow direction is from top to bottom on the illustration.

There is generally good agreement between the relative contents determined by XRF on 3×3 cm$^2$ Si(100) substrates and RBS analyses on cuts of the same substrates and on MgO(100) substrates, Table 1. Most of the films are seen to have a manganese deficiency which suggests formation of grain boundaries and precipitation of calcium and/or lanthanum along these which in turn will be reflected in the electrical properties of the films.
Table 1. Analyzed compositions of La$_{1-x}$Ca$_x$MnO$_3$ films specified by $x$, $y$, $z$ of the empirical formula La$_x$Ca$_y$Mn$_z$O$_3$. Uncertainties are: $\Delta x = \Delta y = \Delta z = \pm 0.02$, for XRF data, and $\Delta x = \pm 0.04$, $\Delta y = \pm 0.04$, $\Delta z = \pm 0.05$ for RBS. A, B, and C mark different samples for the same growth parameters.

<table>
<thead>
<tr>
<th>Pulsed composition</th>
<th>XRF Si(100)</th>
<th>RBS Si(100)</th>
<th>RBS MgO(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x$(La)</td>
<td>$y$(Ca)</td>
<td>$z$(Mn)</td>
</tr>
<tr>
<td>Temperature: 235 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>$1.00$</td>
<td>$-0.91$</td>
<td>$1.00$</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>$1.00$</td>
<td>$-0.89$</td>
<td>$1.00$</td>
</tr>
<tr>
<td>La$<em>{0.8}$Ca$</em>{0.2}$MnO$_3$</td>
<td>$0.71$</td>
<td>$0.29$</td>
<td>$0.80$</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>$0.72$</td>
<td>$0.28$</td>
<td>$0.82$</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.6}$Ca$</em>{0.4}$Mn$_{1.2}$O$_3$</td>
<td>$0.47$</td>
<td>$0.53$</td>
<td>$0.80$</td>
</tr>
<tr>
<td>A</td>
<td>$-1.00$</td>
<td>$0.83$</td>
<td>$-1.00$</td>
</tr>
<tr>
<td>Temperature: 283 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>$1.00$</td>
<td>$-0.88$</td>
<td>$1.00$</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La$<em>{0.8}$Ca$</em>{0.2}$MnO$_3$</td>
<td>$0.72$</td>
<td>$0.28$</td>
<td>$0.83$</td>
</tr>
<tr>
<td>A</td>
<td>$0.72$</td>
<td>$0.28$</td>
<td>$0.86$</td>
</tr>
<tr>
<td>B</td>
<td>$0.72$</td>
<td>$0.28$</td>
<td>$0.86$</td>
</tr>
<tr>
<td>C</td>
<td>$0.73$</td>
<td>$0.27$</td>
<td>$0.81$</td>
</tr>
<tr>
<td>La$<em>{0.6}$Ca$</em>{0.4}$Mn$_{1.2}$O$_3$</td>
<td>$0.49$</td>
<td>$0.51$</td>
<td>$0.88$</td>
</tr>
<tr>
<td>A</td>
<td>$-1.00$</td>
<td>$0.88$</td>
<td>$-1.00$</td>
</tr>
<tr>
<td>CaMn$_{1.5}$O$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>$1$</td>
<td>$-0.98$</td>
<td>$1$</td>
</tr>
<tr>
<td>B</td>
<td>$0.66$</td>
<td>$0.34$</td>
<td>$1.09$</td>
</tr>
<tr>
<td>C</td>
<td>$0.49$</td>
<td>$0.51$</td>
<td>$1.14$</td>
</tr>
<tr>
<td>Ca$<em>{0.64}$Mn$</em>{0.357}$O$_3$</td>
<td>$-1$</td>
<td>$0.98$</td>
<td>$1.06$</td>
</tr>
</tbody>
</table>

The fact [5] that films made with Ca(thd)$_2$ and ozone as precursors consist of CaCO$_3$ would perhaps indicate that the Ca(thd)$_2$ precursor is unsuitable for growth of calcium-containing manganites. FT-IR spectra of as-deposited films of LaMnO$_3$ and CaMnO$_3$ on Si(100) substrates were rather featureless, see Fig. 8, but after annealing several absorption bands appear. The absorption band at 590 cm$^{-1}$ is also found for powder standards of CaMnO$_3$ and LaMnO$_3$. The other absorption bands are believed to be due to phases that are formed at the interface of the film and the Si(100) substrate. Nevertheless, all films (including those with amorphous XRD signatures) deposited on Si(100) lacked the absorption band at 1430 cm$^{-1}$, which would be indicative of carbonate [13]. Hence, contrary to the findings in Ref. [5], no carbonate was formed when Ca is deposited together with Mn.
Fig. 8. IR spectra of as-deposited and annealed films of LaMnO$_3$ (top panel) and CaMnO$_3$ (middle panel) deposited on Si(100) substrates. Lower panel shows IR spectra of powdered reference materials of CaCO$_3$, LaMnO$_3$, and CaMnO$_3$.

Thin films deposited at 235 and 283 °C on all kinds of substrates were characterized by regular XRD, both as-deposited and as-annealed. Despite numerous attempts it proved impossible to detect diffraction peaks from as-deposited films on soda-lime-glass, Si(100), α-SiO$_2$(001), α-Al$_2$O$_3$(012), and MgO(100). The films deposited on silicon-containing substrates suffered from interface reactions during annealing and were accordingly not characterised further. Those on MgO(100) and α-Al$_2$O$_3$(012) revealed mostly the same featureless patterns before and after annealing which indicated that the films are
polycrystalline without any preferred orientation. The low XRD intensities were taken as indications of a nanocrystalline texture.

A more thorough structural characterisation was performed for films with compositions close to CaMnO₃, La₀.₅Ca₀.₅MnO₃, La₀.₇Ca₀.₃MnO₃, and LaMnO₃. These compositions were assumed to be of particular interest owing to their technological potentials in relation to colossal magnetoresistance (near $x = \frac{1}{3}$) or special features like strong orbital ordering (near $x = \frac{1}{2}$).

The oriented films showed a cube-on-cube epitaxy with the substrate, and the films will therefore in the following be treated as pseudo cubic. When depositions were made on SrTiO₃(100) and LaAlO₃(100) substrates, highly oriented films were obtained (Fig. 9), but an annealing was necessary in order to increase the crystallinity (Fig. 9). It proved possible to observe a clear variation in the out-of-plane cell dimension of the films as the composition of La₁₋ₓCaₓMnO₃ is varied. Although the films were (100) oriented, the annealed films with composition close to La₀.₇Ca₀.₃MnO₃ showed presence of a weak (110) reflection at 2.714 Å (viz. corresponds to the most intense reflection of a cubic perovskite/type structure).

**Fig. 9.** Sections of XRD diffractograms of La₁₋ₓCaₓMnO₃ films deposited on SrTiO₃(100) (left side) and LaAlO₃(100) (right side). The full and dotted lines refer to films deposited at 283 and 235 °C, respectively. The nominal film composition for each pair of diffractograms are (a) LaMnO₃, (b) La₀.₇Ca₀.₃MnO₃, (c) La₀.₅Ca₀.₅MnO₃, and (d) CaMnO₃. For as-analyzed composition see Table 1. The recordings for the annealed films were made with Ni filter.
The textures of the films were analyzed for selected specimens. For as-deposited films, only those prepared at 283 °C with the compositions La$_{0.7}$Ca$_{0.3}$MnO$_3$ and La$_{0.5}$Ca$_{0.5}$MnO$_3$ deposited on SrTiO$_3$(100) and LaAlO$_3$(100) showed well-defined signs of crystallinity. The XRD characterisations of these as-deposited films (Figs. 10–13) reveals a good cube-on cube epitaxy between the substrates and the films. The typical FWHM (full width at half maximum) rocking curves for as-deposited films ranged between 0.44 and 0.76°, whereas the substrates had rocking curves with FWHM = 0.05–0.13°. The reciprocal map of the as-deposited film of La$_{0.7}$Ca$_{0.3}$MnO$_3$ at 283 °C on SrTiO$_3$ indicated that the film consisted of two layers, where one is either a continuous layer or has very broad crystallites, and the other probably narrower crystallites. This is a common observation for growth of materials on nearly matched substrates. The first layer is strained to follow the substrate, but as the material grows thicker, the film cracks up into domains. The FWHM of the rocking curves was close to 0.45° for the annealed films. The in- and out-of-plane cell dimensions for the films considered in Figs. 10–13 have been extracted by using the positions of the (200), (300), (310), and (311) reflections (Table 2) which moreover reveal that there is no notable strain due to the substrate, even though it was expected according to Fig. 14.
Fig. 10. XRD characterization of La$_{0.5}$Ca$_{0.5}$MnO$_3$ deposited at 283 °C on SrTiO$_3$(100). (a) φ- scan of the (310) reflections for the substrate and the film. (b-d) reciprocal space maps of the (200), (310), and (311) reflections, respectively, for film and substrate together.
Fig. 11. XRD characterization of La$_{0.7}$Ca$_{0.3}$MnO$_3$ deposited at 283 °C on SrTiO$_3$(100). (a) ϕ- scan of the (310) reflections for the substrate and the film. (b-d) reciprocal space maps of the (200), (310), and (311) reflections, respectively, for film and substrate together.
Fig. 12. XRD characterization of La$_{0.7}$Ca$_{0.3}$MnO$_3$ deposited at 283 °C on LaAlO$_3$(100).
(a) φ- scan of the (310) reflections for the substrate and the film. (b-d) reciprocal space maps of the (200), (310), and (311) reflections, respectively, for film and substrate together.
Fig. 13. XRD characterization of La$_{0.5}$Ca$_{0.5}$MnO$_3$ deposited at 283 °C on LaAlO$_3$(100). (a) φ- scan of the (310) reflections for the substrate and the film. (b-d) reciprocal space maps of the (200), (310), and (311) reflections, respectively, for film and substrate together.

Table 2. In-(∥) and out-of-plane (⊥) cell dimensions (in Å) for films grown on SrTiO$_3$(100) and LaAlO$_3$(100) substrates compared with bulk samples with the targeted composition. Estimated error limits for the film data are: ± 0.005 (⊥); ± 0.01 (∥). Last column gives observed in-plane lattice mismatch (in %).

<table>
<thead>
<tr>
<th>Composition</th>
<th>⊥</th>
<th>∥</th>
<th>Mismatch</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$</td>
<td>3.905</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{0.3}$La$</em>{0.7}$Mn$_{0.8}$O$_3$</td>
<td>3.833</td>
<td>3.85</td>
<td>-1.4</td>
</tr>
<tr>
<td>Ca$<em>{0.5}$La$</em>{0.5}$Mn$_{0.8}$O$_3$</td>
<td>3.806</td>
<td>3.82</td>
<td>-2.2</td>
</tr>
<tr>
<td>LaAlO$_3$</td>
<td>3.789</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$<em>{0.3}$La$</em>{0.7}$Mn$_{0.8}$O$_3$</td>
<td>3.844</td>
<td>3.85</td>
<td>1.6</td>
</tr>
<tr>
<td>Ca$<em>{0.5}$La$</em>{0.5}$Mn$_{0.8}$O$_3$</td>
<td>3.808</td>
<td>3.83</td>
<td>1.0</td>
</tr>
<tr>
<td>Bulk</td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>Ca$<em>{0.3}$La$</em>{0.7}$MnO$_3$</td>
<td>3.875</td>
<td>3.860</td>
<td>3.863</td>
</tr>
<tr>
<td>Ca$<em>{0.5}$La$</em>{0.5}$MnO$_3$</td>
<td>3.837</td>
<td>3.820</td>
<td>3.831</td>
</tr>
</tbody>
</table>
Fig. 14. Cell parameters $a$ (○), $b$ (●), and $c$ (□) per $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ formula unit, and $a$ (△), $b$ (★), and $c$ (◇) for $\text{LaMnO}_3$.15 bulk materials. Unit-cell parameter for $\text{SrTiO}_3$ and pseudo cubic $\text{LaAlO}_3$ substrates are also marked. Data are taken from the ICSD crystal structure database version 2002.

The morphology of the as-deposited films (see Fig. 15) were rather smooth with a rms roughness ranging between 0.15–0.32 nm for films on $\text{SrTiO}_3$(100), 0.05–1.0 nm for films on $\text{LaAlO}_3$(100), and 0.28–0.90 nm for films on $\text{MgO}(100)$. The films roughened during annealing so that the rms ranges increased to 1.5–2.0 nm for films on $\text{SrTiO}_3$(100) and $\text{LaAlO}_3$(100), and 3–5 nm for films on $\text{MgO}(100)$. Most of the as-deposited films were smooth and featureless, however, an island pattern with depletions in the films had developed on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films deposited on $\text{MgO}(100)$ (see Fig. 15f). The depth of the depletions were of the order of 4–6 Å for films deposited at 235 °C and 5–8 Å for films deposited at 283 °C. It is at first glance reasonable to assume that these depletions are due to singular or multiple steps in the crystal structure. However, this becomes questionable in view of the absence of well-defined intensity in the X-ray diffractograms of the samples. At the moment, we have no good explanation for this effect.
The room temperature resistivity of as-deposited and as-annealed films on different substrates is given in Table 3. This shows that the lowest resistivities are to be found among the films deposited with a composition close to La$_{0.5}$Ca$_{0.5}$MnO$_3$ which indicate that these films are somewhat rich in Mn$^{4+}$ ([Mn$^{4+}$] : [Mn$^{3+}$] > 1) since the earlier study [14] suggest that this composition should exhibit somewhat higher resistivity. The distinction may perhaps be ascribed to the deficiency of Mn in the deposited films. The largest resistivities are as expected found among the films of the end members, viz. the films of LaMnO$_3$ and CaMnO$_3$. 

Fig. 15. Topography of La$_{0.7}$Ca$_{0.3}$MnO$_3$ film on (a) SrTiO$_3$(100) substrate as-deposited, (b) SrTiO$_3$(100) substrate as-annealed, (c) LaAlO$_3$(100) substrate as-deposited, (d) LaAlO$_3$(100) substrate as-annealed, and (e,f) MgO(100) substrate as-deposited and (g) MgO(100) substrate as-annealed.
Films with the approximate composition $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ deposited at 283 °C were annealed and then characterized with regard to magnetoresistance by measuring the electronic resistivity as a function of temperature, with and without application of 9 T magnetic field. Measurements on films deposited on SrTiO$_3$(100), LaAlO$_3$(100), MgO(100), $\alpha$-Al$_2$O$_3$(012) and $\alpha$-SiO$_2$(001) (Fig. 16) show a large diversity in transition temperature depending on the substrate. For films deposited on SrTiO$_3$(100) and $\alpha$-Al$_2$O$_3$(100) a colossal magnetoresistance with $100 \cdot (R_{9T} - R_{0T})/R_{9T}$ of ca. 500 and 2150 %, respectively, was found at 205 and 150 °C. It is interesting to note that films deposited on $\alpha$-SiO$_2$(001) where an interface reaction is believed to have occurred show a significant magnetoresistance over a large temperature range. The field effect on such films is also rather sensitive at temperatures below the transition temperature of 260 °C for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. These findings exhibit large effects on the resistivity at low magnetic fields, especially at low temperatures, suggesting that the films are rich in grain boundaries [15,16].

Table 3. Room temperature electronic resistivity (in $\Omega$ cm) for as-deposited and as-annealed films on different single-crystal oxide substrates.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SrTiO$_3$(100)</th>
<th>LaAlO$_3$(100)</th>
<th>MgO(100)</th>
<th>$\alpha$-Al$_2$O$_3$(012)</th>
<th>$\alpha$-SiO$_2$(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>235 °C; annealed:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaMn$_{0.9}$O$_3$</td>
<td>0.280</td>
<td>0.334</td>
<td>4.50</td>
<td>1.59</td>
<td>0.196</td>
</tr>
<tr>
<td>Ca$<em>{0.3}$La$</em>{0.7}$Mn$_{0.8}$O$_3$</td>
<td>0.538</td>
<td>0.550</td>
<td>0.982</td>
<td>0.149</td>
<td>0.200</td>
</tr>
<tr>
<td>Ca$<em>{0.5}$La$</em>{0.5}$Mn$_{0.8}$O$_3$</td>
<td>0.0130</td>
<td>0.0116</td>
<td>0.0703</td>
<td>–</td>
<td>740</td>
</tr>
<tr>
<td>CaMn$_{0.8}$O$_3$</td>
<td>1.61</td>
<td>0.860</td>
<td>18.2</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>283 °C; annealed:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaMn$_{0.9}$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.375</td>
</tr>
<tr>
<td>La$<em>{0.7}$Ca$</em>{0.3}$Mn$_{0.8}$O$_3$</td>
<td>0.0753</td>
<td>0.239</td>
<td>0.449</td>
<td>0.114</td>
<td>0.210</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$Mn$_{0.9}$O$_3$</td>
<td>0.00968</td>
<td>0.343</td>
<td>3.60</td>
<td>–</td>
<td>5.54</td>
</tr>
<tr>
<td>CaMn$_{0.9}$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>283 °C as-deposited:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaMn$_{0.9}$O$_3$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>La$<em>{0.7}$Ca$</em>{0.3}$Mn$_{0.8}$O$_3$</td>
<td>0.704</td>
<td>0.425</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>La$<em>{0.5}$Ca$</em>{0.5}$Mn$_{0.9}$O$_3$</td>
<td>0.261</td>
<td>0.100</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CaMn$_{0.9}$O$_3$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Specific resistivity as function of temperature measured with and without a magnetic field of 9 T for La$_{1-x}$Ca$_x$MnO$_3$ films deposited at 283 °C on substrates of SrTiO$_3$(100), $\alpha$-Al$_2$O$_3$(012), $\alpha$-SiO$_2$(001), LaAlO$_3$(100), and MgO(100). The dotted frame panel shows magnetic field dependence of the resistivity at 298 K of films on substrates of SrTiO$_3$(100), $\alpha$-Al$_2$O$_3$(012), and $\alpha$-SiO$_2$(001).

**Discussion**

From the information in Fig. 1, it is reasonable to assume that it should not be possible to deposit La$_{1-x}$Ca$_x$MnO$_3$ in an ALCVD manner at temperatures above the decomposition temperature of ca. 240 °C for Mn(thd)$_3$. However, the growth results for LaMnO$_3$ and CaMnO$_3$ state otherwise (Figs. 3 and 5), and their ALCVD-windows is stretch up to some 325–335 °C. The reason for this apparently increased stability may be illustrated if one first assumes that Mn(thd)$_3$ precursor when used for manganese oxide growth decomposes in the way that absorbed Mn(thd)$_x$ ($x = 1$ or 2) fragments looses ligands rapidly at temperatures above 240 °C. In this way new active sites are revealed for further growth and the self-controlled growth that is seen at lower temperatures is destroyed. Secondly one must assume that calcium and lanthanum have a larger affinity toward thd ligands than manganese. If so, the thd ligands freed from the adsorbed Mn(thd)$_x$ fragment will be lost to calcium or lanthanum when they are present on the growing surface. Even though thd ligands now have
been transferred from one manganese atom to a calcium or lanthanum atom self-controlled growth is achieved due to the bulky appearance of the thd ligands.

This effect can also be seen in our data for the variation of the La : Mn or Ca : Mn ratio at 235 °C (Figs. 2 and 4). At this temperature the MnOₓ films is growing in an uncontrolled fashion and hence produce thicker films and with larger gradients than what expected with the regular ALCVD growth. As can be seen from Figs. 2 and 4, the growth rate of MnOₓ film is dramatically reduced when even small amounts of La or Ca are introduced. There is a minimum in the growth rate for ca. 20 % Ca or ca. 40 % La introduced. At these levels the thickness gradients of the films are also very small (less than 2 %).

In this study, we were not able to grow crystalline films on substrates of Si(100) and soda-lime glass, as reported in Ref. [11]. This must be due to the lower deposition temperature used. In this study no attempt was made to grow thicker films at temperatures above 300 °C since we were interested in controlled growth within the ALCVD regime (the previously used [11] 400 °C is outside the ALCVD regime for the present equipment).

Acknowledgement

This work has received financial support from the Research Council of Norway. The authors are indebted to Turid Winje (University of Oslo, Department of Geology) for XRF measurements, to director of research Antoine Maignan and dr. Erwan Rawel (Laboratoire CRISMAT-ENSICAEN) for performing the CMR measurements, and dr. Anders Hallén (Uppsala University, Ångström Laboratory) for performing the RBS measurements.

References