CVD and ALD in the Bi-Ti-O System

BY

MIKAEL SCHUISKY

ACTA UNIVERSITATIS UPSALIENSIS
UPPSALA 2000
Dissertation for the Degree of Doctor of Philosophy in Inorganic Chemistry presented at Uppsala University in 2000

ABSTRACT


Bismuth titanate Bi₄Ti₃O₁₂, is one of the bismuth based layered ferroelectric materials that is a candidate for replacing the lead based ferroelectric materials in for instance non-volatile ferroelectric random access memories (FRAM). This is due to the fact that the bismuth based ferroelectrics consists of pseudo perovskite units sandwiched in between bismuth oxide layers, which gives them a better fatigue nature.

In this thesis thin films of Bi₄Ti₃O₁₂ have been deposited by chemical vapour deposition (CVD) using the metal iodides, BiI₃ and TiI₄ as precursors. Films grown on MgO(001) substrates were found to grow epitaxially. The electrical properties were determined for films grown on Pt-coated silicon and good properties such as a high dielectric constant (ε) of 200, low tan δ of 0.018, a remnant polarisation (Pᵣ) of 5.3 µC/cm² and coercive field (E_c) as high as 150 kV/cm were obtained. Thin films in the Bi-Ti-O system were also deposited by atomic layer deposition (ALD) using metalorganic precursors.

In addition to the ternary bismuth titanates, films in the binary oxide systems i.e. bismuth oxides and titanium oxides were deposited. Epitaxial TiO₂ films were deposited both by CVD and ALD using TiI₄ as precursor. The rutile films deposited by ALD were found to grow epitaxially down to a temperature of at least 375 °C on α-Al₂O₃(0 1 2) substrates. The TiO₂ ALD process was also studied in-situ by QCM. Different bismuth oxides were deposited by halide-CVD using BiI₃ as precursor on MgO(0 0 1) and SrTiO₃(0 0 1) substrates and the results were summarised in an experimental CVD stability diagram. The Bi₂O₂.₃₃ phase was found to grow epitaxially on both substrates.

Key words: Halide-CVD, ALD, Bismuth titanate, Bi₄Ti₃O₁₂, Titanium oxide, TiO₂, Bismuth oxide, Bi₂O₂.₃₃, Epitaxy, QCM.

Mikael Schuisky, Department of Inorganic Chemistry, The Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

© Mikael Schuisky 2000

ISSN 1104-232X
ISBN 91-554-4881-X

Printed in Sweden by Eklundshof Grafiska AB, Uppsala 2000
Till Marie
Preface

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

I. **Epitaxial growth of Bi$_2$O$_{2.33}$ by halide CVD.**
Mikael Schuisky and Anders Hårsta

II. **Chemical vapor deposition stability diagram for the BiI$_3$-O$_2$ system.**
Mikael Schuisky and Anders Hårsta

III. **Epitaxial growth of TiO$_2$ (rutile) thin films by halide CVD.**
Mikael Schuisky and Anders Hårsta

IV. **Atomic layer chemical vapour deposition of TiO$_2$: Low-temperature epitaxy of rutile and anatase.**
Mikael Schuisky, Anders Hårsta, Aleks Aidla, Kaupo Kukli, Alma-Asta Kiisler and Jaan Aarik

V. **Real time monitoring in atomic layer deposition of TiO$_2$ from TiI$_4$ and H$_2$O$_2$-H$_2$O.**
Kaupo Kukli, Aleks Aidla, Jaan Aarik, Mikael Schuisky, Anders Hårsta, Mikko Ritala and Markku Leskelä

VI. **Ultra thin TiO$_2$ films deposited by atomic layer chemical vapor deposition.**
Mikael Schuisky, Kaupo Kukli, Aleks Aidla, Jaan Aarik, Mikael Ludvigsson and Anders Hårsta
Accepted for publication in the proceedings from the Fifteenth Int. CVD Conf.

VII. **Halide chemical vapor deposition of Bi$_4$Ti$_3$O$_{12}$.**
Mikael Schuisky and Anders Hårsta

VIII. **Ferroelectric Bi$_4$Ti$_3$O$_{12}$ thin films on Pt-coated silicon by halide chemical vapor deposition.**
Mikael Schuisky, Anders Hårsta, Sergey Khartsev and Alex Grishin

IX. **Atomic layer chemical vapour deposition in the Bi-Ti-O system.**
Mikael Schuisky, Kaupo Kukli, Mikko Ritala, Anders Hårsta and Markku Leskelä
1. INTRODUCTION

Materials and their properties have fascinated mankind since the early days when man started to use tools and weapons to facilitate daily life. One of the first oxide materials to be utilised by man must have been flint stone. The very sharp edges of the flint stone splinters made it a good constructing material for tools and weapons. It was also later used to form ignition sparks to make fires by banging two rocks together. When the utilisation of the fire was controlled, man started to use different kinds of clay materials to make pottery, which probably is one of the earliest ceramic processes developed by man. During time, man has learned to utilise the properties of various oxide materials and developed several important material processes. Some of the materials have even given names to the period of human history, i.e. Bronze Era and Iron Age.

Nowadays, the electrical properties of oxides have attracted tremendous attention and have made scientists to steadily increase their work effort to fully understand and utilise these materials. One of the properties that have gained large attention both for academic reason as well as industrial applications is the dielectric nature of oxides. Dielectric materials form dipoles when polarised by an applied voltage. The polarisation is, however, lost when the applied voltage is shut off. These materials are electrical insulators and are often used as capacitors or electrical insulators in electrical devices, e.g. SiO₂ as gate dielectric in metal oxide semiconductor (MOS) structures. For a dielectric material to be useful in applications it should have a high dielectric strength i.e. it should not undergo any degradation and become electrical conducting at high voltage. The material should also have a low dielectric loss, i.e. it should not lose energy as heat in an alternating electric field.

The phenomenon of ferroelectricity was first observed by Valasek in 1921 [1], during an investigation of Rochelle salt (sodium tartrate tetrahydrate). Ferroelectric materials are a special type of dielectric materials that possess a spontaneous dipole. The dipole is reversible by an electric field of some magnitude smaller than the dielectric breakdown of the material itself. Ferroelectric materials are characterised by properties such as high dielectric constant, high piezoelectric constants, relatively low dielectric loss and high electrical resistivity. For ordinary dielectric materials the relationship between the applied electric field and the induced polarisation is linear. However, for ferroelectric materials the behaviour is more complicated and a hysteresis loop is observed (Fig. 1.1). The remanent polarisation (P_r) is the residual polarisation when the applied electric field is shut off and (E_c) is the coercive field needed to reduce the polarisation to zero. For a crystal to exhibit ferroelectricity is has to belong to a
noncentrosymmetric space group in a certain temperature range. The breakdown temperature where the noncentrosymmetry and the ferroelectric properties are lost is called the Curie temperature ($T_c$) and above this temperature the material becomes paraelectric. More detailed descriptions of ferroelectricity are given in ref. [2,3].

![Figure 1.1. A typical P-E hysteresis loop in ferroelectrics.](image1)

A large number of ferroelectric systems adopt the perovskite structure such as BaTiO$_3$, Ba$_x$Sr$_{1-x}$TiO$_3$ (BST), PbTiO$_3$, PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) and Pb$_{1-x}$La$_x$Zr$_y$Ti$_{1-y}$O$_3$ (PLZT) [2,3]. Many of these ferroelectrics are lead-based but these are believed to be replaced in numerous applications by bismuth based layered ferroelectrics. This is due to the fact that the bismuth based ferroelectrics consists of pseudo perovskite units sandwiched in between bismuth oxide layers, which gives them a better fatigue nature [4,5]. In addition there is also a desire to limit the integration of lead containing compounds into electronic products and here bismuth based layered ferroelectrics can be a more environmental friendly alternative.

![Figure 1.2. The ideal perovskite structure of PbTiO$_3$.](image2)
Bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, is one of the bismuth based layered ferroelectric materials that is a candidate for replacing the lead based ferroelectric materials in for instance non-volatile ferroelectric random access memories (FRAM) [6-8]. In this thesis gas phase chemical routes to deposition of bismuth titanate thin films including the binary oxides have been investigated.

2. DEPOSITION TECHNIQUES

To utilise the properties of dielectric and ferroelectric materials, many applications require them to be made as thin films. There exists numerous different thin film deposition techniques, and these techniques are usually divided in two main groups, Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD) [9]. Simplified one could state that in all PVD methods no chemical exchange reactions should occur while in CVD the chemical reactions play a crucial role in the deposition process. Two typical PVD techniques are sputtering and evaporation while metalorganic chemical vapour deposition (MOCVD) and atomic layer deposition (ALD) are two typical CVD techniques. In this thesis two CVD techniques have been used, halide-CVD and ALD. The names of these two techniques might need a small explanation. The use of the prefix halide was thought to be necessary since MOCVD has lately been used to emphasise that the precursors used are metalorganic. The name ALD has been chosen for the atomic layer epitaxy (ALE) process developed by Suntola and Antson in the 1970s [10]. The main reason is that the word epitaxy implies epitaxial growth, which is usually not the case.

2.1. Chemical vapour deposition

The basic principles for the CVD technique have been know to scientist for at least 150 years [11]. A large number of materials has been deposited and a large number of process developments has been achieved during the years [12,13]. In CVD a solid film is deposited onto a substrate material from gaseous reactants that are simultaneously delivered and mixed prior to the deposition zone. The gaseous reactants will react on or in the vicinity of the substrate surface. These reactions can be activated in several ways. The most common is thermally activated (TACVD) but also plasma activated (PACVD) and laser activated (LACVD) reactions are utilised. The TACVD processes can be divided in two main categories, cold wall and hot wall processes. In a cold wall process only the substrate is heated while in a hot wall process the whole deposition chamber is heated. In a CVD process several reaction steps can occur and in Fig. 2.1 these reaction steps have been illustrated.
Figure 2.1. Chemical reaction steps occurring during a CVD process.

1. The precursors are transported to the substrate surface.
2. Adsorption of the precursors on the surface.
3. Diffusion of the precursors on the surface.
4. Reaction of precursors on the surface.
5. Desorption of gaseous reaction products.
6. Gas phase nucleation or homogenous gas phase reaction.
7. Thermal decomposition of the precursor.

2.2. Atomic layer deposition

The general principle for the ALD process is alternate exposure of the substrate surface to the precursor fluxes, *i.e.* the fluxes are separated both in space and time [14]. The precursor molecules adsorb in the form of mono-molecular layers on the surface and any excess of molecules is either flushed away by a purging pulse or simply removed by evacuation of the system for a certain period of time. In the ideal case, the adsorption process will proceed until all adsorption sites are occupied, *i.e.* the process will be self-limiting. Instead of just molecular adsorption the precursor molecules often anchor to the surface by reacting with the surface groups left after the previous precursor pulse. For instance, in ALD of oxides, an adsorbed layer of metal precursor molecules will be converted to an oxide by exposing the surface to the oxygen precursor, *e.g.* water. A film with the desired composition and thickness will thus be formed stepwise, via successive surface reactions between the alternating metal and oxygen precursors. Fig. 2.2 shows a schematic illustration of an ALD cycle.
The ALD method has several advantages compared with conventional CVD techniques. The alternate supply of precursors will allow the exploitation of aggressively reacting precursors since the homogeneous gas-phase reactions are inhibited. The increased reactivity, in turns, lowers the kinetic barriers for the film formation reactions. Therefore, rather low deposition temperatures may be utilised. As an intrinsic advantage of the ALD method, the self-limiting process can provide enhanced lateral uniformity and two-dimensional growth, ensuring appreciable quality on large-area substrates accompanied with conformal growth [15]. The major draw back with the ALD technique is the longer deposition times needed. However, this can easily be compensated for by the use of reactors that can fit large area substrates. In addition, it should also be mentioned that as the device sizes continue to decrease the deposited layers in the devices needs to be grown with an atomic level control. In this context the surface saturation of the ALD technique giving self-limiting control of the growth mechanism is a very attractive feature especially for manufacturing of ultra-thin layers for the semiconductor industry [16,17].

2.3. The choice of precursors in CVD and ALD

The precursors used in any chemical deposition experiment should first of all be easy to handle i.e. not be extremely poisonous, explosive or dangerous in any other way. If the precursors have any of these unwanted properties the utilisation of them will demand much more careful handling and storage. However, when a suitable precursor is found, it must have a high enough vapour pressure to be useful in either CVD or ALD. It should also have a good
thermal stability \textit{i.e.} it should not decompose in the temperature range used and it should easily react at the desired temperature, preferably without leaving any precursor residues in the film. The chemical state (\textit{i.e.} gas, liquid or solid) of the precursor is of less importance as long as a continuous precursor delivery is possible throughout the whole experiment. However, precursors that are gaseous at room temperature (RT) are preferable since the monitoring of the gas flows is much easier compared to condensed precursors. Liquids are usually evaporated from a heated/cooled reflux condenser and solids are usually sublimated from open boats inside the reactor at suitable temperatures. Here one should keep in mind that the powder area and the powder packing affects the sublimation of the precursor and this might complicate a continuous precursor delivery in time-consuming experiments. This problem is not so critical in ALD, since here the dose of precursor only has to be large enough to obtain a complete mono-molecular layer. The chemistry in ALD processes is more delicate than in conventional CVD processes and the precursor must therefore be more carefully selected. The thermal stability of the precursors is highly important in ALD. If the precursor will decompose uncontrollably, the surface saturation will be lost and the deposition process will not be self-limiting. Moreover, the precursors in ALD must adsorb onto or react with surface groups on the substrate to form a mono-molecular layer. If the precursor molecules do not stick to the surface, film growth will accordingly not occur. For more detailed descriptions of precursor selections in CVD and ALD the reader is referred to ref. [12,13,18,19].

Metal iodides are usually solids at RT but several of them have reasonable high vapour pressures to make them good precursor candidates for both CVD and ALD [20]. Despite this the use of metal iodides as precursors in both CVD and ALD have been sparse [21-31]. However, the high volatility of metal iodides has been utilised for a long time in chemical transport reactions [32]. In these experiments pure metal and iodine are sealed in an evacuated tube which is placed in a furnace with a temperature gradient. The iodine is used as the transport agent to carry the metal to the deposition zone. The formation of volatile metal iodides can be used in CVD to generate metal iodide precursors \textit{in-situ} by passing iodine vapour over the metal. The utilisation of metal iodides in CVD and ALD are believed to be more advantageous compared to the use of the corresponding metal chlorides, since the iodides are less aggressive. An additional advantage is that the use of metal iodides in CVD does not require water as oxygen source, which is the case when chlorides are used [33]. The hydrogen from the water is needed to take care of the chlorine in the metal chloride to form hydrogen chloride, HCl. The use of only oxygen in iodide based processes will eliminate the formation of aggressive reaction products such as hydrogen iodide, HI. The elimination of
such reaction products will suppress unwanted etching reactions of the deposited film or substrate.

3. STRUCTURAL AND GENERAL PROPERTIES

3.1 Bismuth oxides

The crystal structures of bismuth oxides have been investigated by scientists for almost a century [34-43]. The most common stoichiometry of bismuth oxide is the bismuth sesquioxide, Bi$_2$O$_3$, which is known to have four polymorphs. The thermodynamically stable polymorph at room temperature and ambient pressure is the monoclinic $\alpha$-Bi$_2$O$_3$. When heating the $\alpha$-Bi$_2$O$_3$ phase up to 730 °C it transforms to the $\delta$-Bi$_2$O$_3$ phase, with a fluorite-type structure, which is stable up to 825 °C, the melting point of bismuth oxide. An interesting property of this phase is that it is the best oxygen ion conductor of any material. It can be applied in solid oxide fuel cells (SOFC) where the bismuth oxide can increase the oxygen ion conductivity of the cell [44,45]. The two metastable polymorphs, $\beta$-Bi$_2$O$_3$ and $\gamma$-Bi$_2$O$_3$ can be formed on cooling the high temperature $\delta$-Bi$_2$O$_3$ phase at 650 °C and 640 °C, respectively.

The phase equilibria and thermodynamics of the Bi-O system have been thoroughly investigated by Risold et al. and Oniyama et al. [46,47]. The Bi-O binary system also includes the mono-oxide BiO and two non-stoichiometric oxides, Bi$_2$O$_2.75$ and Bi$_2$O$_2.33$. Noteworthy here is that the occurrence of the latter oxides was first reported in thin film studies [48,49]. The lattice parameters for the bismuth oxides are given in Appendix.

3.2. Titanium oxides

The most common stochiometry of titanium oxide is the dioxide, TiO$_2$, which exist in five polymorphs. The stable polymorph at all temperatures and at ambient pressure is the tetragonal rutile phase while the anatase and the brookite polymorphs are low-pressure and low-temperature forms (see Fig. 3.1 for the rutile and anatase structures). The lattice parameters for the rutile and the anatase phases are given in Appendix. In addition to these three, two high-pressure polymorphs of titanium dioxide exist, denoted TiO$_2$-II and TiO$_2$-III, as well as a large number of lower oxides, the so-called Magnelli phases such as Ti$_2$O$_3$ and Ti$_3$O$_5$, etc. The titanium dioxides have excellent properties such as high refractive index, good transmittance in the visible and near-infrared range, and high chemical and abrasion resistance [50]. Due to these outstanding properties titanium oxide has been extensively studied for the use in opto-electronic devices, as antireflecting coating and waveguides. The rutile phase of
TiO$_2$ has a high dielectric constant (170) \cite{51} and has therefore been thought as a candidate material for replacing silicon dioxide as gate oxide in MOS structures \cite{52,53}.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig31}
\caption{The structures of A) rutile and B) anatase.}
\end{figure}

### 3.3. Bismuth titanates

Bismuth titanate, Bi$_4$Ti$_3$O$_{12}$ is a bismuth based layered ferroelectric oxide and it belongs to the family of structures which were closely investigated by Bengt Aurivillius in the late 1940s and early 1950s \cite{54,55}. The structure of the so-called Aurivillius phases can simply be described by the general formula $(\text{Bi}_2\text{O}_2)^{2+} (\text{M}_{n-1}\text{R}_n\text{O}_{3n+1})^{2-}$ where $n$ can have the number 1 to 6. The $(\text{M}_{n-1}\text{R}_n\text{O}_{3n+1})^{2-}$ formula unit consists of $n$ pseudo perovskite units which are sandwiched in between two $(\text{Bi}_2\text{O}_2)^{2+}$ layers. The M cation is a rather large mono-, di- or trivalent cation (\textit{e.g.} Na$^+$, Pb$^{2+}$, Bi$^{3+}$) and the R cation is smaller in size and is either a tri-, tetra-, penta- or hexavalent cation (\textit{e.g.} Fe$^{3+}$, Ti$^{4+}$, Ta$^{5+}$, W$^{6+}$). Several different compounds having this general formula have been synthesised and structurally determined since the original work of Aurivillius, \textit{e.g.} SrBi$_2$Ta$_2$O$_9$ (n=2), Bi$_4$Ti$_3$O$_{12}$ (n=3) and BaBi$_4$Ti$_4$O$_{15}$ (n=4) \cite{56-59}. In Fig. 3.2 a simplified crystal structure of Bi$_4$Ti$_3$O$_{12}$ is shown. The three pseudo perovskite units and the bismuth oxide layers have been marked.

In addition to the ferroelectric Bi$_4$Ti$_3$O$_{12}$ phase \cite{60-62} the ternary Bi–Ti–O system contains several other bismuth titanates such as the dielectric Bi$_2$Ti$_2$O$_7$ phase \cite{63} and the electro-optical and photo-conducting Bi$_{12}$TiO$_{20}$ phase \cite{64}. The phase diagram of the Bi$_2$O$_3$-TiO$_2$ system has been investigated by Speranskaya \textit{et al.} \cite{65} who reported the existence of two additional phases Bi$_8$TiO$_{14}$ and Bi$_2$Ti$_4$O$_{11}$. 
There are some divergent opinions about the true symmetry of the ferroelectric Bi₄Ti₃O₁₂ phase. It has optically been determined to be monoclinic but diffraction studies have defined it as orthorhombic [54,62,66,67]. The reason for this is that the optically determined monoclinic β-angle is very close to 90°. The lattice parameters of the Bi₄Ti₃O₁₂, Bi₂Ti₂O₇ and Bi₁₂TiO₂₀ phases are given in Appendix.

The ferroelectric Bi₄Ti₃O₁₂ phase has a high Curie temperature of 675 °C, possesses a high dielectric strength and a relatively high dielectric constant ~ 200. Bi₄Ti₃O₁₂ single crystals demonstrate bi-axial polarisation. Along the a-axis they can be polarised up to 50 µC/cm² while the polarisation along the c-axis does not exceed 4 µC/cm² [62]. Strong in-plane polarisation in c-axis oriented bismuth titanate films make them candidates for integrated electro-optic device applications while the low coercive field and high dielectric constant look promising for use as gate electrode in a ferroelectric FET memory [8]. Bi₄Ti₃O₁₂ films also have a unique rotation of the optical indicatrix upon polarisation switching [68]. Ceramics of the Bi₄Ti₃O₁₂ type of materials are also candidate materials for high temperature acoustic piezo-sensors [69].
4. EXPERIMENTAL

4.1. The CVD system

All the films deposited by conventional CVD (I-III, VII & VIII) were deposited in the same horizontal low-pressure hot-wall CVD reactor (Fig. 4.1). The reactor was made of fused silica and consisted of an outer reactor tube both for the evaporation of metal iodide precursors and the depositions. The evaporation zones and the deposition zone were protected by an exchangeable inner tube, which was cleaned between each experiment. The oxygen was introduced in a separate tube to avoid oxidation of the metal iodide precursors prior to the deposition zone. The CVD reactor was equipped with an 8-zone furnace, where each zone could be independently monitored to obtain a suitable temperature profile.

![Fig. 4.1. A schematic drawing of the CVD reactor used.](image)

The leak rate of air into the system was in the range of $10^{-6}$ Pa•m$^3$•s$^{-1}$, which corresponds to an air contamination level of less than 5 ppm and the purity of the gases was 99.9999 % for argon and 99.998 % for oxygen. Argon was used as carrier gas for the metal iodide precursors in all experiments. The amounts of metal iodide precursor admitted into the reactor were controlled by the temperature of the evaporation zones and by the argon carrier gas flow over the evaporation zones.

Table 4.1. Process parameters for the CVD experiments.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>$T_{\text{vap.}}$ (°C)</th>
<th>$T_{\text{dep.}}$ (°C)</th>
<th>$P_{\text{tot.}}$ (Torr)</th>
<th>Substrates</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiI$_3$(99.999%)</td>
<td>200</td>
<td>600-800</td>
<td>10</td>
<td>MgO(001);SrTiO$_3$(001)</td>
<td>I</td>
</tr>
<tr>
<td>BiI$_3$(99.999%)</td>
<td>175-225</td>
<td>490-800</td>
<td>10</td>
<td>MgO(001)</td>
<td>II</td>
</tr>
<tr>
<td>TiI$_4$(99.99%)</td>
<td>120</td>
<td>275-710</td>
<td>10</td>
<td>$\alpha$-Al$_2$O$_3$(012)</td>
<td>III</td>
</tr>
<tr>
<td>BiI$_3$(99.999%)</td>
<td>175-225</td>
<td>600;700</td>
<td>3.6;10;16</td>
<td>MgO(001); Pt/Ti/SiO$_2$/Si</td>
<td>VII;VIII</td>
</tr>
</tbody>
</table>
4.2. The ALD systems

Two types of reactors were used for the ALD experiments. The experiments made in paper IV, V and VI were performed in a hot-wall flow-type ALD reactor [70] at the University of Tartu, Estonia (Fig. 4.2). The reactor consisted of an outer stainless steel reactor tube with a diameter of 51 mm and contained inner quartz tubes with the diameters 40 mm and 36 mm. The latter of those tubes had a conical part connecting the deposition zone with the precursor inlets. The precursors were fed into the carrier gas through microprocessor-controlled valves which allowed switching on and off the precursors pulses in less than 0.1 s. This reactor has a limitation in the number of different precursors that can be utilised in each experiment and therefore only binary compounds were deposited. However, the design of the reactor made it possible to place several different substrates at the deposition zone in each experiment. The reactor also had the possibility to connect a quartz crystal microbalance (QCM) for in-situ studies of the deposition mechanism.

In paper IX the experiments were carried out in a commercial flow-type ALCVD reactor F-120 (ASM Microchemistry Ltd, Espoo, Finland [71]) at the University of Helsinki, Finland. The commercial reactor has greater possibilities to deposit multi-component films and was therefore used to deposit ternary compounds. The design of the substrate holder of the reactor made it possible to put two substrates with the size 5x5 cm$^2$ parallel to each other in the deposition zone.
The metal precursors in both reactors were evaporated from open or semi-open boats inside the reactor and nitrogen was led over the boats to carry the reactant vapour into the heated reaction zone and was also used as purging gas after each precursor pulse. Hydrogen peroxide solution (IV-VI) and water (IX) were used as oxygen precursors and were evaporated at room temperature from external reservoirs connected to the cold end of the reactor through a capillary and a needle valve. From the cold end of the reactor the oxygen precursors were transported further into the deposition zone by nitrogen. In the table below the process parameters for the depositions by ALD is summarised.

Table 4.2. Process parameter for the ALD experiments.

<table>
<thead>
<tr>
<th>Metal precursor</th>
<th>Oxygen source</th>
<th>$T_{\text{dep.}}$ (°C)</th>
<th>Substrates</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiI$_4$(99.99%)</td>
<td>H$_2$O$_2$ (30%)</td>
<td>230-455</td>
<td>MgO(001); Si(100); Pt/Ti/SiO$_2$/Si; α-Al$_2$O$_3$(012); (001) &amp; (110)</td>
<td>IV-VI</td>
</tr>
<tr>
<td>Bi(C$_6$H$_5$)$_3$ Ti(i-OC$_3$H$_7$)$_4$</td>
<td>H$_2$O</td>
<td>200-325</td>
<td>Soda lime glass; Corning 7059; ITO-coated glass</td>
<td>IX</td>
</tr>
</tbody>
</table>

4.3. Film characterisation

The deposited films have been analysed by several different techniques. The main technique for phase determination has been X-ray diffraction (XRD) but additional analysis has been made with Raman spectroscopy. The XRD analysis was also made to determine epitaxial relationships. The chemical composition of the films was characterised by X-ray fluorescence spectroscopy (XRFS), energy dispersive spectroscopy (EDS) or X-ray photoelectron spectroscopy (XPS). The morphology of the films was characterised by scanning electron microscopy (SEM) or atomic force microscopy (AFM). In-situ monitoring of ALD growth mechanism was studied by QCM. Frequency and temperature dependencies of the permittivity ($\varepsilon$) and the dielectric loss factor ($\tan \delta$) were measured for the ferroelectric films. Non-linear ferroelectric hysteresis $P$-$E$ loops were measured as well as the electric field dependence of the permittivity (C-V) and the I-V characteristics.

The major analysis technique used in all papers has been XRD and therefore a short description of the technique and the different geometries used is given here. For phase analysis of thin films the $\theta$-2$\theta$ geometry was employed. With this geometry the X-ray tube $i.e.$ the incidence angle of the X-rays is locked at $\omega=\theta$ and the detector is locked at 2$\theta$ throughout the scan. This type of scan will only give diffraction from crystal planes perpendicular to the normal of the sample. It should be noted that the $\theta$-2$\theta$ scan can not distinguish between highly textured and epitaxial films $i.e.$ a film can show only one set of reflections without being epitaxial.
Table 4.3. Summary of the techniques used for characterisation.

<table>
<thead>
<tr>
<th>Phase identification</th>
<th>Abbreviation</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray diffraction</td>
<td>(XRD)</td>
<td>I-IX</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td>(Raman)</td>
<td>VI</td>
</tr>
<tr>
<td>Morphology</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scanning electron microscopy</td>
<td>(SEM)</td>
<td>I, II, VI &amp; VIII</td>
</tr>
<tr>
<td>Atomic force microscopy</td>
<td>(AFM)</td>
<td>II; III, VI &amp; VII</td>
</tr>
<tr>
<td>Chemical composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy dispersive spectroscopy</td>
<td>(EDS) or (EDX)</td>
<td>IX</td>
</tr>
<tr>
<td>X-ray fluorescence spectroscopy</td>
<td>(XRFS) or (XRF)</td>
<td>I, II, III &amp; VI</td>
</tr>
<tr>
<td>X-ray photoelectron spectroscopy</td>
<td>(XPS)</td>
<td>IX</td>
</tr>
<tr>
<td>In-situ monitoring</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz crystalline microbalance</td>
<td>(QCM)</td>
<td>V</td>
</tr>
<tr>
<td>Electrical measurements</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacitance-Voltage</td>
<td>(C-V)</td>
<td>VIII</td>
</tr>
<tr>
<td>Leakage current</td>
<td>(I-V)</td>
<td>VIII</td>
</tr>
<tr>
<td>Ferroelectric hysteresis</td>
<td>(P-E)</td>
<td>VIII</td>
</tr>
</tbody>
</table>

To evaluate highly oriented and epitaxial films rocking curve (ω–scan) measurements are usually performed. Here the incident angle (ω) is scanned while the detector is locked at the Bragg angle 2θ. The shape of the resulting peak from the rocking curve measurements will give information of the film quality, which is usually evaluated from the full width at half maximum (FWHM) value of the peak. A small rocking curve FWHM value thus corresponds to highly ordered crystals and will indicate epitaxial growth while a larger rocking curve FWHM value will show that the films is less oriented. It should be noted that the rocking curve FWHM value also depends on strain and the number of defects in the film.

Fig. 4.3. Schematic picture of the XRD φ–scan geometry used. The enlargement shows typical crystal planes not parallel to the surface used for φ–scan measurements.
If a small rocking curve FWHM value is obtained it is possible that the film has grown epitaxially which can be proven by φ–scan measurements. A φ–scan measurement is performed by studying two crystallographic planes P, one from the substrate and one from the film, not parallel with the sample surface (see enlargement in Fig. 4.3). The geometry for the φ–scan set up is so that the incident X-ray is locked at an angle ω determined by the chosen plane and the detector is locked at the diffraction angle 2θ for the same plane. The sample is then rotated around the sample normal while the intensity of the plane P is simultaneously recorded. The in-plane orientational relationship can then be determined by comparing the positions of the resulting peaks in the two φ-scans. A good description of the φ-scan method is given in reference [23].

![Image](image_url)

*Figure 4.4. The different subgroups of films with the corresponding results of XRD characterisation. A) Amorphous B) Non-textured polycrystalline C) Textured D) Epitaxial polycrystalline and E) Single crystalline (ideal epitaxial) film.*

The deposited film can be classified in different subgroups depending on the crystallinity of the film. Illustrations of the different subgroups are shown in Fig.4.4 together with the expected results of XRD characterisation by θ-2θ, rocking curve and φ-scans. The first subgroup is amorphous films, *i.e.* films without long range order, usually deposited at low temperatures and with high deposition rates (see Fig. 4.4A). These films can posses short
range order so that phase characterisation is possible by Raman spectroscopy. The next subgroup is non-textured polycrystalline films (see Fig. 4.4B). Since the crystallites are randomly oriented all allowed reflections will be visible in the θ-2θ XRD patterns. The third subgroup is textured films with preferred orientation which are usually deposited at higher temperatures and with moderate deposition rates (Fig.4.4C). Here many crystallites grow in a specific direction but no epitaxial relationship exists between films and substrate. The degree of texture can be determined from the intensity ratio of the diffraction peaks but also by XRD rocking curve measurements.

Epitaxial polycrystalline films are usually deposited at even higher temperatures and with low deposition rates. An epitaxial film is here defined as a polycrystalline film where the crystallites have specific in-plane orientational relationships with the substrate surface (Fig.4.4D). This in-plane orientational relationship can be determined by XRD φ–scans or X-ray pole figures. Finally, in the ideal case the epitaxial film is not polycrystalline but single crystalline and deposited on a single crystalline substrate (Fig.4.4E). In addition to these subgroups nano-crystalline films might be mentioned. These are polycrystalline films with nanometer sized grains.

One of the key parameters to grow epitaxial films is the lattice mismatch between the film and the substrate. This mismatch is defined as \((d_{\text{film}} - d_{\text{substrate}})/d_{\text{substrate}}\) where \(d_{\text{substrate}}\) = the in-plane lattice parameter for the substrate and \(d_{\text{film}}\) = the in-plane lattice parameter for the film. The \(d\) values are taken from the bulk atomic distances of the compounds and will not account for any surface reconstruction that might occur. A small lattice mismatch will favour epitaxial growth while larger mismatch values might induce strain and stress in the grown film so that the epitaxy is lost. For a good and thorough description of epitaxy and related topics, please refer to ref. [9].

5. DEPOSITION OF BISMUTH OXIDES

Thin films of bismuth oxide have previously been prepared by methods such as thermal evaporation of bismuth followed by annealing in air [72], activated reactive evaporation [73], evaporation [74], chemical spray pyrolysis [75], sputtering [76], electrodeposition [77] and CVD [78-81]. The utilisation of bismuth iodide, BiI₃, as precursor in CVD of bismuth oxide has never previously been reported.
5.1. By CVD

Bismuth oxides and bismuth oxyiodides were deposited by conventional CVD on MgO(0 0 1) and SrTiO₃(0 0 1) substrates (I, II) and the results were summarised in an experimental CVD stability diagram (II), see Fig.5.1. In the diagram the flow ratio of oxygen and bismuth iodide is plotted vs. the deposition temperature. Each deposited phase and/or phase mixture is marked with different symbols and a solid line was included as a guideline to show the limit for deposition of iodine free films. The films grown above this line were iodine free while films deposited below the line contained bismuth oxyiodides.

![Diagram showing experimental CVD stability diagram for the BiI₃-O₂ system.]

From the CVD stability diagram in Fig. 5.1 some general trends can be seen. First and most obvious, low deposition temperatures gave films containing bismuth oxyiodides while high deposition temperatures gave iodine free films. Furthermore, an increased \([O₂]/[BiI₃]\) ratio reduced the temperature limit for depositing iodine free films. It should also be noted that the observed growth rate showed large variations within the CVD stability diagram. The highest growth rate was about 0.5 \(\mu\)m/h obtained for the \(\alpha\)-Bi₂O₃ phase in the upper left side of the diagram while much lower growth rates (100-500 Å/h) were observed for the other deposited phases. It can be mentioned that the growth rate decreased at the highest deposition temperatures for all \([O₂]/[BiI₃]\) ratios. No films could be grown above a certain temperature and this temperature decreased with increasing \([O₂]/[BiI₃]\) ratio. For example, attempts to deposit films at 800 °C using a \([O₂]/[BiI₃]\) ratio of 3.38 and at 700 °C using a \([O₂]/[BiI₃]\) ratio of 4.64 were not successful. The reduction of the growth rate at higher oxygen/bismuth ratios is explained by the low bismuth iodide flows. Since the total pressure of the reactor was kept...
constant, the partial BiI$_3$ pressure will decrease to the right in the stability diagram. The unsuccessful depositions at higher temperatures can easily be explained by the high volatility of bismuth oxides at these temperatures. The upper temperature limit for the depositions decreased with increasing oxygen/bismuth ratios. This is due to the fact that the decrease in the partial BiI$_3$ pressure will shift the solid-gas equilibrium (Bi$_2$O$_3$(s) ⇌ Bi$_2$O$_3$(g)) of bismuth oxide to the right, leading to a reduced deposition rate.

\[ \text{Fig. 5.2. XRD patterns for films deposited at a log} \left[ \frac{O_2}{[\text{BiI}_3]} \right] \text{ratio of 4.64.} \]

Some typical XRD patterns for films grown with an [O$_2$]/[BiI$_3$] ratio of 4.64 is shown in Fig. 5.2. Both Bi$_2$O$_{2.33}$ and BiOI were found to grow highly oriented. The Bi$_2$O$_{2.33}$ films deposited on both MgO(0 0 1) and SrTiO$_3$(0 0 1) substrates grow with strong [0 0 1] orientation and only 0 0 l reflections were detected in the diffractograms (I). The rocking curve FWHM for the 0 0 l reflections, were found to be about 0.2° for both substrate materials indicating epitaxial growth, which was also confirmed by ϕ-scans (Fig. 5.3A-B).

\[ \text{Fig. 5.3.} \ \text{ϕ-scans for the Bi$_2$O$_{2.33}$ phase grown on A) SrTiO}_3(0 0 1); B) MgO(0 0 1) and C) ϕ-scan for the BiOI phase grown on MgO(0 0 1). \]
The for the Bi$_2$O$_2$$_{3.33}$ films grown on the SrTiO$_3$(0 0 1) substrate contained a set of four peaks 90° separated. The in-planar orientational relationships determined from the $\varphi$-scan was found to be [1 0 0]$_{\text{SrTiO$_3$}}$/[1 0 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$. However, for Bi$_2$O$_2$$_{3.33}$ grown on the MgO(0 0 1) substrate an additional set of four peaks with weaker intensities appeared in the $\varphi$–scan. This set of peaks was shifted 45° from the other set with stronger intensities and corresponds to the in-plane orientational relationship [1 0 0]$_{\text{MgO}}$/[1 0 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$. This gives that the two in-plane orientational relationships [1 0 0]$_{\text{MgO}}$/[1 0 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$ and [1 0 0]$_{\text{MgO}}$/[1 1 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$ co-exists. The difference in epitaxial growth behaviour between the two substrate materials can be explained by considering the lattice mismatch between the substrate and the deposited Bi$_2$O$_2$$_{3.33}$ films. For the SrTiO$_3$(0 0 1) substrate, the [1 0 0]$_{\text{SrTiO$_3$}}$/[1 0 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$ orientation gives a lattice mismatch of less than 2 %. In contrast, for the MgO(0 0 1) substrate the calculated lattice mismatches are much larger, about 9 % for the [1 0 0]$_{\text{MgO}}$/[1 0 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$ orientation and about 29 % for the [1 0 0]$_{\text{MgO}}$/[1 1 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$ orientation. This larger mismatch may explain why two orientations were observed when Bi$_2$O$_2$$_{3.33}$ was deposited on MgO(0 0 1) substrates. It is also interesting to note that the peaks corresponding to the [1 0 0]$_{\text{MgO}}$/[1 0 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$ orientation have stronger intensities than the peaks corresponding to the [1 0 0]$_{\text{MgO}}$/[1 1 0]$_{\text{Bi$_2$O$_2$$_{3.33}$}}$ orientation. This agrees well with the fact that the first orientation exhibits a lower value for the lattice mismatch than the second orientation.

The BiOI phase was also found to grow epitaxially on MgO(0 0 1) substrates with the same two in-planar orientational relationships, [1 0 0]$_{\text{MgO}}$/[1 0 0]$_{\text{BiOI}}$ and [1 0 0]$_{\text{MgO}}$/[1 1 0]$_{\text{BiOI}}$, as the Bi$_2$O$_2$$_{3.33}$ phase (Fig. 5.3C). The lattice mismatch values for these two epitaxial relationships are 5 and 34 %, respectively.

The morphology of the films varied depending on the phase grown and in Fig. 5.4, AFM micrographs of the $\alpha$-Bi$_2$O$_3$ and BiOI phases and a SEM micrograph of the Bi$_2$O$_2$$_{3.33}$ phase are shown. The BiOI crystals can be seen to grow with two main orientations shifted 45°, which corroborates the results from the above mentioned $\varphi$-scan measurements.
Fig. 5.4. AFM micrographs of the A) α-Bi₂O₃ and B) BiOI phases grown on MgO(0 0 1) substrates and C) SEM micrograph of the Bi₂O₂.₃₃ phase grown on a SrTiO₃(0 0 1) substrate.

5.2. By ALD

The deposition of pure bismuth oxide films by ALD was never successfully accomplished. Three different bismuth precursors were unsuccessfully tried, bismuth iodide (BiI₃), bismuth chloride (BiCl₃) and triphenyl bismuth (Bi(C₆H₅)₃). All three precursors were tried in combination with water and/or hydrogen peroxide. Bismuth iodide gave no films whatsoever, while the experiments with triphenyl bismuth gave films that mostly contained carbon but no bismuth oxide. The most successful bismuth precursor was BiCl₃, which at least gave films that contained bismuth. However, XRD and EDS of these films revealed that the films formed were bismuth oxychlorides. At lower deposition temperatures, 300-400 °C the films consisted of the BiOCl phase while an increment of the temperature to 500 °C gave bismuth oxychlorides with a lower chloride content, i.e. Bi₂₄O₃₃Cl₁₀.
6. DEPOSITIONS OF TITANIUM OXIDES

Titanium oxide is probably one of the most studied oxide materials in thin films. It has been deposited by several different PVD and CVD methods such as ion beam sputtering (ISB) [82], reactive ionised cluster beam (RICB) [83], sol-gel [84], CVD [85, 86] and ALD [87-95]. The utilisation of titanium iodide as precursor in CVD and ALD of titanium oxides has never previously been reported.

6.1. By CVD

Titanium oxide films were successfully deposited from TiI$_4$ and O$_2$ in the temperature range 275 °C to 710 °C on α–Al$_2$O$_3$(0 1 2) substrates (III). All films were iodine-free according to XRFS measurements. Phase pure rutile films were deposited above 490 °C and the rutile phase grow with a strong [1 0 1] orientation, since only the 1 0 1 and 2 0 2 reflections were visible in the diffractograms (Fig. 6.1). As can be seen, films deposited below 490 °C contained the anatase phase.

![XRD patterns for titanium oxide films (A=anatase, R=rutile) deposited at different temperatures.](image)

ω-scans were recorded for all the 1 0 1 reflections of the rutile phase and it was found that an increased deposition temperature gave more oriented rutile films. The rocking curve FWHM value for the 1 0 1 reflection was found to be as low as 0.43° for a film grown at 600 °C, suggesting epitaxial growth. The φ-scans for the rutile and the α–Al$_2$O$_3$ substrate are shown in Fig. 6.2 where it can be seen that both φ-scans contain one strong peak at the same φ-angle.
The occurrence of only one peak in the $\varphi$-scans might need some explanation. For the $\alpha$-Al$_2$O$_3$ substrate, the (0 2 10) plane has six symmetry equivalents, (0 2 10), (2 0 10), (0 2 10), (2 0 10), (2 2 10) and (2 2 10). However, the interplanar angles between these planes and the (0 1 2) surface plane are all different, i.e. only one peak will be observed in the $\varphi$-scan. The same is true for the rutile film, where the (3 0 1) plane has four symmetry equivalents, (3 0 1), (0 3 1), (3 0 1) and (0 3 1). The in-planar angles between these planes and the (1 0 1) plane are again all different and only one peak will be recorded in the $\varphi$-scan. The in-plane orientational relationships was determined to be $[0 1 0]_{\text{rutile}}/[1 0 0]_{\alpha\text{-Al}_2\text{O}_3}$ and $[1 0 \bar{T}]_{\text{rutile}}/[\bar{T} 1 \bar{2}]_{\alpha\text{-Al}_2\text{O}_3}$, i.e. the b-axis of the rutile film is aligned with the a-axis of the $\alpha$-Al$_2$O$_3$ substrate. A close inspection of the $\varphi$-scan for the rutile 3 0 1 reflection reveals an additional weak peak, which is shifted 180° from the strong peak, thus corresponding to a 180° in-plane rotation. The above determined in-plane orientational relationships could maybe be more easily visualised by looking at the atomic arrangements of the rutile (1 0 1) surface and the $\alpha$-Al$_2$O$_3$(0 1 2) surface. In Fig. 6.3 these atomic arrangements are shown together with two rectangles representing the in-plane unit cells of the film and the substrate. The edge lengths were calculated from the lattice parameters of rutile and $\alpha$-Al$_2$O$_3$ (see Appendix) and the corresponding directional lattice mismatches were found to be -3.57 % along the $[0 1 0]_{\text{rutile}}$ direction and 6.43 % along the $[1 0 \bar{T}]_{\text{rutile}}$ direction, respectively.
When superimposing the rutile in-planar unit cell on the \(\alpha\)-Al\(_2\)O\(_3\) in-planar unit cell, the atomic arrangement at the interface is obtained. The atomic arrangement corresponding to the weak peak in the \(\varphi\)–scan for the rutile 3 0 1 reflection is now obtained by rotating the rutile in-planar unit cell 180°. This atomic arrangement at the interface might be less favoured due to the fact that the oxygen atoms located inside the unit cell are not superimposed, as they are in the other in-plane orientational relationship.

### 6.2. By ALD

Titanium oxide thin films were deposited by ALD using TiI\(_4\) and H\(_2\)O\(_2\) (IV-VI). The film growth of rutile and anatase on various substrates were investigated (IV, VI) and the growth mechanism was studied \textit{in-situ} by QCM (V). Several titanium precursors have been used in ALD of titanium oxides and some of these processes have been \textit{in-situ} studied by QCM, for instance TiCl\(_4\)-H\(_2\)O [92,93] and Ti(O\(_2\)C\(_2\)H\(_5\))\(_4\)-H\(_2\)O [94]. The QCM study of ALD films grown from metal iodides is very favourable, because of the rather large mass changes occurring when iodine adsorbs and desorbs. It can be mentioned that other \textit{in-situ} methods have also been applied to study the growth mechanisms in ALD processes such as Fourier transformed infrared spectroscopy (FTIR) and quadrupole mass spectrometry (QMS) [96,97].

---

\textit{Fig. 6.3. Schematic atomic arrangements of the rutile (1 0 1) and the \(\alpha\)-Al\(_2\)O\(_3\)(0 1 2) surfaces. The letter z denotes the distances from the surface planes.}
6.2.1. *In-situ* monitoring

The mass-changes during the chemisorption and desorption processes of TiI₄ and H₂O₂ (aq.) in the ALD cycles were investigated *in-situ* by QCM. An increase in the surface mass upon TiI₄ adsorption was recorded as an increment in the QCM oscillation during the TiI₄ pulse, t₁. The increment tended to saturate at a certain level, ∆m₁ (Fig. 6.4). The saturation was more obvious at temperatures below 200 °C, while at higher temperatures, ∆m₁ increased slowly but continuously during t₁. During the first purge period, t₂, a certain mass decrease, ∆m_p₁, became apparent. This indicated desorption of some species from the surface. At the beginning of the subsequent H₂O-H₂O₂ pulse time, t₃, the mass was rather abruptly decreased by ∆m₂. Obviously, a certain amount of the material adsorbed during t₁ was released or replaced in this reaction step. Most likely, oxygen and/or OH-groups replaced the heavy iodine atoms and terminated the surface after the H₂O-H₂O₂ pulse. Eventually, the mass of the TiO₂ layer deposited in a completed cycle was measured as the difference, ∆m₀, between the initial and final levels of QCM signal. In Fig. 6.4, t₄ denotes the second purge period.

![Diagram](image)

*Fig. 6.4. QCM signal as function of time, recorded during a long deposition cycle.*

Figure 6.4 also shows that, at 200 °C, the stabilisation of the QCM output signal during t₃ was a rather time-consuming process. However, the stabilisation was considerably faster at higher growth temperatures and, as exemplified by Fig. 6.5, only a few seconds were needed to complete the surface reactions at 275 °C.
Henceforth, multiple growth cycles were recorded at particular growth conditions (Fig. 6.5) while the cycle time parameters were kept short enough (2-6 s) to provide a reasonable growth rate. In this case, however, entire saturation of the surface and the maximum in the growth rate per cycle were not necessarily attained. The features seen by the *in-situ* QCM monitoring were that the TiI₄ pulse was not completely self-limiting, but instead a moderate increase of both $\Delta m_1$ and $\Delta m_0$ was observed with longer TiI₄ pulses. It was also observed that when shorter $t_1$ pulses were used higher TiI₄ evaporation temperatures were needed to achieve pseudo-saturation. The effect of the partial pressure of the $\text{H}_2\text{O}-\text{H}_2\text{O}_2$ pulse was also investigated and had a minor increasing effect on both $\Delta m_1$ and $\Delta m_0$. The effect of the length of the first purge time $t_2$ was also investigated and it was found that the mass released during the purge $\Delta m_{p1}$ was increased with the pulse length. However, $\Delta m_0$ was not affected by the pulse length *i.e.* it was concluded that the released groups during the purge pulse did not contain titanium. Finally, it was observed that the growth rate was highly affected by the deposition temperature. Both $\Delta m_1$ and $\Delta m_0$ increased 3-4 times when the deposition temperature was increased from 200 to 300 °C.

**6.2.2. Film growth and epitaxy**

TiO₂ films were deposited on several different substrate materials to investigate the substrate influence on the phase content in the films. Three different cuts of $\alpha$-Al₂O₃ substrates were
used (1 1 0), (0 0 1) and (0 1 2). All three different \(\alpha\)-\(\text{Al}_2\text{O}_3\) substrates favoured the formation of the rutile phase. On the \(\alpha\)-\(\text{Al}_2\text{O}_3\)(1 1 0) substrate two different rutile orientations were observed, 1 0 1 and 2 0 0. However, on the (0 0 1) and (0 1 2) cut \(\alpha\)-\(\text{Al}_2\text{O}_3\) substrates rutile films with only one orientation were deposited and for these rutile films the in-plane orientational relationships were determined.

In the XRD patterns for the films deposited on the \(\alpha\)-\(\text{Al}_2\text{O}_3\)(0 0 1), only the 2 0 0 reflection of the rutile phase was detected at both deposition temperatures (Fig. 6.6). The rocking curve FWHM value for this reflection from the film deposited at 455 °C was 0.038°, a very low value strongly suggesting epitaxial growth (see the inserted \(\omega\)-scan in Fig. 6.6), while the corresponding value for the film deposited at 375 °C was 0.68°.

![XRD patterns of rutile films deposited on \(\alpha\)-\(\text{Al}_2\text{O}_3\)(0 0 1) substrates at two different temperatures. The insert shows the \(\omega\)-scan for the 2 0 0 rutile reflection.](image)

The \(\phi\)-scan for the 3 0 1 reflection of the rutile phase together with a \(\phi\)-scan for the 1 1 9 reflection of the substrate is shown in Fig. 6.7. The occurrence of six peaks in the \(\phi\)-scan for the 1 1 9 reflection of the substrate is expected since the (0 0 1) surface plane has a six-fold symmetry. For the rutile film, the (3 0 1) plane has two-fold symmetry towards the (2 0 0) plane. However, since the substrate has six equivalent directions, the growing film can be rotated in six different ways shifted by 60°, thus giving six peaks in the \(\phi\)-scan. Furthermore, since the peaks in the two \(\phi\)-scans are shifted 30°, this means that the b-axis of rutile is aligned along the [1 2 0] direction of the \(\alpha\)-\(\text{Al}_2\text{O}_3\)(0 0 1) surface. Due to the hexagonal symmetry of the \(\alpha\)-\(\text{Al}_2\text{O}_3\)(0 0 1) substrate six equivalent in-plane orientational relationships co-exist (IV) one being [0 0 1]\(_{\text{rutile}}/[1 2 0]_{\alpha\text{-Al}_2\text{O}_3}\) and [0 1 0]\(_{\text{rutile}}/[1 0 0]_{\alpha\text{-Al}_2\text{O}_3}\).
Fig. 6.7. $\varphi$-scans for the 1 1 9 reflection of $\alpha$-Al$_2$O$_3$ and the 3 0 1 reflection of rutile.

The in-plane orientational relationships might be visualised by looking at the atomic arrangements of the $\alpha$-Al$_2$O$_3$(0 0 1) and the rutile (2 0 0) surfaces (Fig. 6.8). In the figure two rectangles are included that represent the in-plane unit cells for the substrate and the film. The edge lengths were calculated from the lattice parameters of rutile and $\alpha$-Al$_2$O$_3$ given in Appendix. The directional lattice mismatch values were calculated to be $-3.57\%$ along the [0 1 0] rutile direction and $8.74\%$ along the [0 0 1] rutile direction. These lattice mismatch values are identical for all six co-existing epitaxial relationships.

Fig. 6.8. Schematic atomic arrangements of the rutile (2 0 0) and the $\alpha$-Al$_2$O$_3$(0 0 1) surfaces. The letter $z$ denotes the distances from the surface planes.
The rutile films deposited on $\alpha$-Al$_2$O$_3$(0 1 2) by ALD grow in a similar manner as films grown by CVD on the same substrate. However, phase pure [1 0 1] textured rutile films were here obtained down to a deposition temperature of 275 °C (see Fig. 6.9A). $\varphi$–scans measurements showed that the in-plane orientational relationship was identical with that previously determined for the CVD grown rutile films on $\alpha$-Al$_2$O$_3$(0 1 2).

For TiO$_2$ films deposited on MgO(0 0 1) substrates the films contained a phase mixture of anatase and rutile at the highest deposition temperature (Fig. 6.9B). However, when the deposition temperature was lowered to 375 °C and below only the 2 0 0 anatase reflection could be detected in the diffractograms. The rocking curve FWHM value for the 2 0 0 anatase reflection was found to be 1.29° for the film deposited at 375 °C. Despite this rather large value $\varphi$–scan measurements were carried out and the $\varphi$-scans for the anatase 3 0 1 and the MgO 0 2 4 reflections are shown in Fig. 6.10.

![Fig. 6.9. XRD patterns of TiO$_2$ films deposited on A) $\alpha$-Al$_2$O$_3$(0 1 2) and B) MgO(001) substrates at different temperatures (A = anatase and R = rutile).](image)

![Fig. 6.10. $\varphi$-scans for the 0 2 4 reflection of MgO and the 3 0 1 reflection of anatase for a film deposited at 375 °C.](image)
It can be seen that both $\varphi$-scans contain four peaks and that the peaks are located at the same $\varphi$-angles. The occurrence of four peaks in the $\varphi$–scan for the anatase 3 0 1 reflection needs an explanation, since the corresponding (3 0 1) plane has two-fold symmetry towards the (2 0 0) plane. The reason is that two symmetry equivalent orientations co-exists, the [0 1 0] direction of anatase being parallel with either the [1 0 0] or the [0 1 0] direction of the MgO(0 0 1) substrate. From the positions of the peaks in the two $\varphi$–scans, it can now be deduced that the in-plane orientational relationships are [0 1 0]$_{\text{anatase}}$/[0 1 0]$_{\text{MgO}}$ and [0 0 1]$_{\text{anatase}}$/[1 0 0]$_{\text{MgO}}$. The epitaxial relationship between the anatase film and the MgO substrate can be visualised by looking at the atomic arrangements of the surfaces at the interface (Fig. 6.11). In the figure two rectangles have been included to show the in-plane unit cells for the film and the substrate. The edge lengths of these unit cells were calculated from the lattice parameters given in Appendix. The lattice mismatch was found to be -10.12 % along the [0 1 0]$_{\text{anatase}}$ direction and 12.96 % along the [0 0 1]$_{\text{anatase}}$ direction. These rather large values can explain the relatively broad peaks in both the $\omega$–scan and the $\varphi$–scan for the anatase 3 0 1 reflection.

![Fig. 6.11. Schematic atomic arrangements of the anatase (2 0 0) and the MgO(0 0 1) surfaces. The letter z denotes the distances from the surface planes.](image)

Comparing the results on $\alpha$-Al$_2$O$_3$(0 1 2) and MgO(0 0 1) substrates, it becomes evident that the temperature of the anatase/rutile phase boundary is strongly affected by the substrate material chosen. Phase-pure rutile with [1 0 1] orientation was obtained on $\alpha$-Al$_2$O$_3$(0 1 2) substrates at a deposition temperature remarkably reduced down to 275 °C, while in contrast, phase-pure anatase with [2 0 0] orientation was obtained up to 375 °C on MgO(0 0 1) substrates.
6.2.3. Thickness dependence

Films with different thicknesses were deposited at 305 °C on MgO(0 0 1) substrates to investigate how the phase content in the films depended on the film thickness. The X-ray diffractograms and the Raman spectra of films with thicknesses 10-188 nm are shown in Fig. 6.12. The XRD patterns for the 27-74 nm thick films revealed that these films contained phase pure anatase, which grew with a strong \((h00)\) orientation and only the 2 0 0 reflection was detected. When thicker films, 125-188 nm, were grown the 1 1 0 and the 2 2 0 rutile reflections also appeared in the diffractograms in addition to the 2 0 0 anatase reflection. The same results were obtained by the Raman investigation (Fig.6.12). It can thus be concluded that rutile and/or anatase formation in the films is dependent also on the film thickness, in addition to the deposition temperature and the substrate material.

![Fig. 6.12. A) XRD patterns and B) Raman spectra of TiO_2 films with different thicknesses grown on MgO(0 0 1) substrates at 305 °C.](image)

7. DEPOSITION OF BISMUTH TITANATES

Thin films of bismuth titanates have earlier been prepared by numerous deposition methods such as rf-sputtering [98], ECR-plasma sputtering [99], pulsed laser deposition [100], molecular beam epitaxy (MBE) [101,102], laser MBE [103], sol-gel processing [104], spin-coating and pyrolysis [105] and CVD [106-114]. The only report of adsorption controlled layer by layer growth of the ferroelectric Bi_4Ti_3O_12 phase was made by reactive MBE in high vacuum (2x10^{-5} Torr) and at relatively high temperatures, 600-660 °C [101,102]. There are, however, no reports on deposition of bismuth titanates or any other bismuth based oxide by ALD.

7.1. By CVD

In conventional CVD of bismuth titanates and bismuth based oxides, the most common bismuth precursor has been triphenyl bismuth, Bi(C₆H₅)₃ [106-110]. However, there are reports on the use of triorthotolyl-bismuth, Bi(α-C₇H₇)₃ [111-113] and bismuth chloride, BiCl₃ [114] as precursors for deposition of Bi₄Ti₃O₁₂, but no report exists prior to these studies on the use of BiI₃. Worth mentioning is that also Bi-(t-OC(CH₃)₃)₃ and Bi(CH₃)₃ have been used as precursors in CVD of SrBi₂Ta₂O₉ [115,116]. The most common titanium precursor in CVD studies of bismuth titanates has been titanium isopropoxide, Ti(OCH(CH₃)₂)₄ [106-108,111-113] but the use of titanium ethoxide, Ti(OCH₂CH₃)₄ [109] and titanium chloride, TiCl₄ [114] has also been reported. In the present thesis the two metal iodides, BiI₃ and TiI₄ were used as metal precursors to deposit Bi₄Ti₃O₁₂ thin films on two different substrate materials, single crystalline MgO(0 0 1) (VII) and Pt-coated silicon (VIII).

7.1.1. MgO(0 0 1) substrates

![XRD patterns from Bi₄Ti₃O₁₂ films deposited at 600 °C and 700 °C.](image)

Using deposition temperatures of 600 °C and 700 °C phase pure Bi₄Ti₃O₁₂ films could be deposited. The Bi₄Ti₃O₁₂ films grow with a strong c-axis orientation and almost only 0 0 l reflections with l = 2n were present at both deposition temperatures (Fig. 7.1). However, the number of visible reflections from other orientations was larger and the corresponding
intensities were stronger for the films deposited at 600 ºC. Also the rocking curve FWHM values for the 0 0 l reflections increased with decreasing temperature and was found to be 1.9º and 1.0º for the films grown on MgO(0 0 1) substrates at 600 ºC and 700 ºC, respectively.

The ϕ-scan for the Bi₄Ti₃O₁₂ 1 1 21 reflection is shown in Fig. 7.2. It should be noted that the ϕ-scan for the MgO 2 0 4 reflection has been normalised to be located at 0º, but is not included in the figure. It can be seen that the ϕ-scan contains two sets of four peaks, one with stronger intensities at 0, 90, 180 and 270º and one with much weaker intensities at 45, 135, 225 and 315º. This implies that two orientations co-exist. For the peaks with stronger intensities, the [1 1 0] direction of Bi₄Ti₃O₁₂ is aligned with the a-axis of MgO, i.e. the two lattices are rotated 45º. The in-plane orientational relationship is thus [1 0 0]MgO//[1 1 0]Bi₄Ti₃O₁₂. For the peaks with weaker intensities, the a-axis of the Bi₄Ti₃O₁₂ film is aligned with the a-axis of the MgO substrate i.e. the two lattices are rotated 0º, corresponding to the in-plane orientational relationship [1 0 0]MgO//[1 0 0]Bi₄Ti₃O₁₂. It is interesting to note that the peaks corresponding to the [1 0 0]MgO//[1 1 0]Bi₄Ti₃O₁₂ orientation have a much stronger intensity than the peaks corresponding to the [1 0 0]MgO//[1 0 0]Bi₄Ti₃O₁₂ orientation. This agrees well with the fact that the first orientation exhibits a much lower value for the lattice mismatch (9%) than the second orientation (29%). The obtained in-plane orientational relationship is in good agreement with previous studies of epitaxial bismuth titanate films on MgO(0 0 1) substrates [117,118].

In Fig. 7.3 the morphologies of the Bi₄Ti₃O₁₂ films deposited at 600 ºC and 700 ºC are shown. In the side-view AFM micrographs (Fig. 7.3A-B), it can be seen that the film deposited at 600
°C grows with a much rougher surface with a higher concentration of outgrowths than the film deposited at 700 °C. The outgrowths are thus most likely connected with the presence of other growth directions than [0 0 1]. From the plane-view AFM micrograph of the film deposited at 700 °C (Fig. 7.3D), it can also be seen that the crystals grow with one main orientation.

Fig. 7.3. AFM micrographs of Bi$_4$Ti$_3$O$_{12}$ films deposited at A, C) 600 °C and B, D) 700 °C.

7.1.2. Pt/Ti/SiO$_2$/Si substrates

The deposition temperature were again kept at 600 °C or 700 °C but the deposition process was started with a nucleation step at 400 °C for 15 minutes prior to the actual film growth. This was made to promote c-axis oriented growth. The use of a nucleation layer has previously been demonstrated to give Bi$_4$Ti$_3$O$_{12}$ films with good electrical properties [108,111-113].

The total gas pressure in the CVD reactor was found to be a critical processing parameter for deposition on Pt-coated silicon substrates. Films were deposited at three different total pressures, 3.8, 10 and 16 Torr, corresponding to total gas flows velocities at the deposition zone of approximately 180, 70 and 40 cm/s, respectively. Despite the change in total pressure all three films grow with a strong c-axis orientation, but the relative intensity of the 1 1 7 reflection increased with decreasing pressure (see Fig.7.4). The rocking curve FWHM value for the 0 0 6 reflection increased with decreasing pressure and was found to be 2.6° at 16 Torr and almost twice as large, 4.6° at 3.8 Torr. Therefore, it can be concluded that the c-axis orientation is improved at elevated gas pressures.
Fig. 7.4. XRD patterns of Bi$_4$Ti$_3$O$_{12}$ films deposited on Pt-coated silicon substrates at 700 °C at three different total pressures, 3.8, 10, and 16 torr. Note the logarithmic intensity scale.

The morphology of these films was investigated by SEM (Fig. 7.5). It can be seen that the film deposited at the lowest total pressure has more randomly oriented crystals, while the films deposited at higher pressures show smoother surfaces with more oriented crystals.

Fig. 7.5. SEM micrographs of Bi$_4$Ti$_3$O$_{12}$ films deposited at 700 °C at three different total pressures A) 3.8 Torr, B) 10 Torr, and C) 16 Torr 3×mag. of a pinhole in the insert to Fig. C.

The most important difference in the observed morphology is that the number of pinholes was reduced when lowering the pressure. The more randomly oriented grains in the film deposited at 3.8 Torr show no pinholes (Fig. 7.5A), whereas the film deposited at 16 Torr shows a higher concentration of distinct pinholes (Fig. 7.5C), although it has a smoother surface.
Comparing these observations with the above mentioned narrowing of the rocking curve FWHM values at higher gas pressure, we infer that an improved $c$-axis orientation correlates with the formation of pinholes in Bi$_4$Ti$_3$O$_{12}$ films fabricated by this technique.

It was not possible to measure nonlinear dielectric properties, such as $C$-$V$ and $P$-$E$ hysteresis curves for the CVD films fabricated at high total gas pressures. This failure is probably connected with the increasing concentration of pinholes in these films. The formation of pinholes will result in getting short circuits between the Au top electrode and the Pt bottom electrode and making Bi$_4$Ti$_3$O$_{12}$ films grown at high gas pressure to be very leaky. Nevertheless, the full set of dielectric characterisation has been performed for the Bi$_4$Ti$_3$O$_{12}$ films prepared at 3.8 Torr. The dielectric test was performed at room temperature in frequency range 0.5 to 100 kHz (Fig. 7.6) and a weak frequency dispersion was revealed, less than 7%, of the dielectric permittivity $\varepsilon$. The frequency dependence of the dielectric permittivity is straightened in the logarithmic scale indicating a relaxor-type behaviour. The dielectric loss $\tan \delta$ decreased with increasing frequency and reached a value of 0.018 which did not exhibit any dispersion up to 1 MHz.

The temperature dependencies of the dielectric permittivity $\varepsilon$ and $\tan \delta$, showed in Fig. 7.7, are characteristic for a ferroelectric phase. Both $\varepsilon$ and $\tan \delta$ exhibit a bump at 340 °C and both quantities increase with temperature towards the ferroelectric-to-paraelectric phase transition (in bulk Bi$_4$Ti$_3$O$_{12}$ ceramics at $T_c = 675$ °C). In the measured temperature range 85-411 K, $\varepsilon$ (1 kHz) experiences 33 % variation around the mean value of 200.3.
Fig. 7.7. Temperature dependencies of the dielectric permittivity and the loss $\tan \delta$ in the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film grown at 700 °C and 3.8 Torr.

Fig. 7.8 shows ferroelectric hysteresis $P$-$E$ polarisation loops traced at various temperatures. Measurements at room temperature yield the remanent polarisation $P_r = 5.3 \ µC/cm^2$, induced polarisation of $14.9 \ µC/cm^2$ at 560 kV/cm, and coercive field as high as 150 kV/cm.

Fig. 7.9 demonstrates the electric field dependence of the dielectric permittivity $\varepsilon$. The measurement was carried out at a frequency of 100 kHz. $C$-$V$ characteristic is non-linear with
a hysteretic behaviour. A tuneability as high as 51 % was achieved, since $\varepsilon$ could be decreased to 51 % of the maximum value by applying a bias voltage of 10.5 V (electric field strength of 350 kV/cm). This performance in combination with sufficient low $\tan \delta \sim 0.018$ promises wide variety of electrically tuneable device applications. Measurements of $I$-$V$ characteristics yielded at room temperature a resistivity of $2 \times 10^9 \Omega\text{cm}$ and a leakage current of about $3 \times 10^{-5}$ A/cm$^2$ at 100 kV/cm.

![Dielectric permittivity vs Electric field](image)

**Fig. 7.9.** Capacitance-voltage (C-V) characteristic.

### 7.2. By ALD

In the attempts to develop an ALD process for deposition of bismuth titanates the first choice of precursors was the metal iodides. However, these experiments were unfortunately never successful. Additional experiments were therefore performed with metal chlorides, both exclusively and in combinations with metal iodides but also these experiments failed. The most successful experiments were achieved using the metalorganic precursors triphenyl bismuth and titanium isopropoxide combined with water.

The influence of the Bi:Ti precursor pulsing ratio was initially investigated at a growth temperature of 260 °C (Fig. 7.10). The film thickness increased linearly with the number of Bi(C$_6$H$_5$)$_3$ pulses up to a precursor pulsing ratio of 8:4, while above this ratio the linearity was lost.
The intersection of the linear region of the plot with the y-axis would give the film thickness for a pure binary TiO₂ film deposited by 1600 cycles. The thickness of this film would be about 37 nm, corresponding to a growth rate of about 0.23 Å/metal cycle. The calculated growth rates per metal precursor pulse were found to be constant at this value up to pulsing ratios of 8:4, while for higher pulsing ratios this value dropped. This was not expected since the total growth rate of the ternary film should depend on the growth rates of the two constituent binary oxides and in the initial experiments the binary Bi₂O₃ film was found to grow with extremely low rate, if at all. From this it can then be concluded that the growth rate is constant for deposition of bismuth oxide as well as titanium oxide at low precursor pulse ratios and that TiO₂ apparently enhances the reactivity of Bi(C₆H₅)₃. The decrease in growth rate at higher Bi:Ti pulse ratios could be explained by the decreasing effect of the as-deposited TiO₂ underlayer. Most likely, some catalytic effect of the previously formed TiOₓ surface is responsible for the enhanced reactivity of the Bi(C₆H₅)₃ precursor. The TiOₓ surface might thus provide a higher density of reactive surface sites for bismuth atoms, thereby increasing the effective deposition rate of BiO₃. Furthermore, in the films with higher Bi:Ti precursor pulsing ratio, a part of the bismuth oxide deposition cycles is carried out on the as-formed bismuth oxide overlayers. The catalytic effect of the TiOₓ surface is thus suppressed and the overall film growth rate is reduced.
The film composition was investigated for two different temperatures, 260 and 300 °C. The EDX Bi:Ti ratio values of the films deposited at 300 °C were all higher than the corresponding values of the films deposited at 260 °C (Fig. 7.11). The bismuth content increased with the number of the Bi(C₆H₅)₃ pulses, but the Bi:Ti ratio in the films never exceeded 0.61, according to the EDX measurements. The Bi:Ti ratio was investigated as a function of deposition temperature in the range 200-325 °C, at a constant Bi:Ti precursor pulsing ratio of 16:4. A maximum value of the Bi:Ti ratio was obtained at 300 °C.

It can be seen in Fig. 7.12 that the XRD patterns of the as-deposited films (deposition temperature = 260 °C) with higher Bi:Ti pulsing ratio contained the 0 1 2 reflection of metallic bismuth. The occurrence of metallic bismuth in the films was verified by XPS measurements. All films annealed at 500 °C in air for one hour were found to be amorphous (not included in Fig. 7.12). Obviously, the annealing temperature of 500 °C was sufficient to oxidise the metallic bismuth but insufficient for crystallisation. However, all the films annealed at 700 °C for one hour were crystalline and only the Bi₂Ti₂O₇ phase was detected by XRD (Fig. 7.12B). It can be seen that the peak intensities increased with the Bi:Ti precursor pulse ratio i.e., with an increased bismuth content in the film. The annealed Bi₂Ti₂O₇ films did not show any preferred orientation, since the observed peak intensities agree well with the corresponding peak intensities for a randomly oriented sample.
The dielectric behaviour was also studied. Stable permittivity values could be determined for films deposited at 260 °C and then annealed at 500 °C for 1 hour. These films were amorphous according to XRD and the peaks from metallic bismuth observed for the as-deposited films had disappeared. The Bi:Ti precursor pulsing ratios of the investigated films were 12:4 and 16:4, respectively and the corresponding EDX Bi:Ti ratios were 0.45 and 0.49. The obtained permittivity values were about 56 and 65 for the two samples. These values are in a good agreement with the reported permittivity value of 64 for Bi\(_2\)Ti\(_2\)O\(_7\) thin films deposited by MOCVD [110].

8. CONCLUDING REMARKS AND FUTURE OUTLOOK

In conclusion the present study of deposition of bismuth titanates, bismuth oxides and titanium oxides has resulted in the following results.

I) The precursor combination of BiI\(_3\) and O\(_2\) is suitable in CVD of bismuth oxides in the temperature range 500-750 °C. The phase content in the deposited films could be tuned by varying the oxygen/bismuth precursor ratio and by the deposition temperature. At suitable conditions the Bi\(_2\)O\(_{2.33}\) and the BiOI phases could be grown epitaxially on MgO(0 0 1) substrates.

II) ALD of bismuth oxide could never be realised. The use of the three bismuth precursors, BiI\(_3\), BiCl\(_3\) and Bi(C\(_6\)H\(_5\))\(_3\) gave no films or films with a high content of precursor residues i.e. chloride or carbon. Here new precursors have to be investigated in the future.
III) TiI₄ was found to be a good precursor for both CVD and ALD of titanium oxide. Epitaxial rutile films were deposited at as low temperature as 375 °C with ALD on two different cuts of α-Al₂O₃ substrates, while at the same deposition temperature epitaxial anatase films could be deposited on MgO(0 0 1) substrates. In addition to the substrate influence on phase content, the film thickness was found to be critical. All thinner films deposited at 305 °C on MgO(0 0 1) substrates contained phase pure anatase while for thicker films the rutile phase started to appear in the films. A future challenge would be to utilise O₂ as oxygen precursor in combination with TiI₄ in ALD of TiO₂.

IV) By combining the BiI₃ and the TiI₄ precursors in CVD, epitaxial Bi₄Ti₃O₁₂ films were deposited on MgO(0 0 1) substrates at 700 °C. The main in-plane orientational relationship was found to be [1 0 0]MgO//[1 1 0]Bi₄Ti₃O₁₂. The total gas pressure was found to be the critical processing parameter to grow films with good ferroelectric properties on Pt-coated silicon. Bi₄Ti₃O₁₂ films deposited at 700 °C and with a total gas pressure of 3.8 Torr exhibited the best dielectric performance. A dielectric constant (ε) of around 200 and a dielectric loss (tan δ) of 0.018 at 100 kHz were measured, while the remnant polarisation (Pᵣ) and the coercive filed (Eₑ) were found to be 5.3 μC/cm² and 150 kV/cm, respectively. The utilisation of titanium iodide and bismuth iodide as precursors for CVD of bismuth titanate is thus looking promising for future thin films applications where the deposition temperature can be allowed to exceed 500 °C. Below this temperature iodine might be incorporated in the deposited films.

V) The best Bi-Ti-O films deposited by ALD were deposited using bismuth triphenyl as bismuth precursor. However, the bismuth/titanium ratios in the films never exceed 0.61, which is a much too low value for formation of the ferroelectric Bi₄Ti₃O₁₂ phase. To get more successful ALD depositions of bismuth titanates and bismuth based oxides new bismuth precursors have to be tried. A possible alternative might be to use bismuth precursors already containing bismuth-oxygen bonds, since only metallic bismuth could be deposited by the triphenyl bismuth process.
9. ACKNOWLEDGEMENTS

First of all I would like to express my sincere gratitude to my supervisor Doc. Anders Hårsta. You have always been very helpful, encouraging and supportive during these years. For me you have been an excellent supervisor and I hope that I’ll still be invited to the annual barbecues in the years to come.

I also want to thank Prof. Jan-Otto Carlsson for giving me the opportunity to dig deeper into the fields of thin films and inorganic chemistry.

Two people who have strongly influenced the path of my PhD studies are Prof. Markku Leskelä and Doc. Mikko Ritala. These guys, the hottest of THE HOT GUYS, introduced me to the fascinating field of ALD. Wherever we have met you always brought great science and great fun. It has been a pleasure working with you. Hyvää Soumi!

Now is the time to thank one of my colleagues, Dr. Kaupo Kukli who have become a great friend. We have did some great work in the name of the God of Bismuth, may he always be with you. I also want to thank Mr Jaan Aarik for letting me come and work in the lab in Tartu. Hästi Eesti!!!

I want to thank Prof. Alex Grishin and Dr. Sergey Khartsev. In a time of need these guys truly helped me out for which I’m very grateful.

I want to thank Kina and Jonas in the so-called “oxide group” I know that you will be successful in your work finishing your PhDs. Jonas keep collecting!!

I would like to thank Gunilla, Barbro and Ulrika who have always been very helpful with administrative work and daily problems. I also want to thank Torvald, Nisse, Anders, Janne and Kerstin (glasblåserskan), your skills have always been highly appreciated.

I would like to thank the Mårtenssons for being the greatest friends/neighbours/colleagues. You made life inside and outside work more joyful.
I want to thank my roommates during the years, Ping and Paulos. I also would like to thank Kajsa, Kina and Sofia for trying real hard to make the time after work more fun for all the PhD students. I also want to thank the rest of the people at department past and present. Lasse for always being extremely generous. And to Kenneth I only say “Then you found a job and……”. Dr. Lars Norin is acknowledged for proof reading the thesis. I also want to thank the rest of the people at Ångström who have helped me during the years.

There are some people outside the walls of Inorganic Chemistry that have made the years in Uppsala something to remember, Katherine, Lars J., Kalle, Krille-bus, Fredrik and Johan to mention some.

I would like to thank my brothers Johan and Peter and my parents Bodil and Georg for being supportive during these years. I also want to thank the rest of my family Sandra, the Vennströms, Ann-Sofie, Gunnar and Simba. I know you all have tried hard to understand what I have been doing during these years.

Finally, I want to thank Marie for your love and support. Your contribution to the realisation of this thesis can not be measured.

The Ångström Consortium for Thin Film Processing, the Swedish Institute, the Royal Swedish Academy of Sciences and ESF ALENET are acknowledged for financial support

Uppsala, November 2000

Hot guys of the world unite and take over!!!
10. REFERENCES

107. L. A. Wills and B. W. Wessels, in Chemical Vapor Deposition, Eleventh Int. Conf., 
319 (1994).
(1996).
Ferroelectr., 18, 183 (1997).
117. H. Masumoto and T. Hirai, J. de Physique IV(C5) supplément au J. de Phys. II, 5, 671 
123. S. Andersson, B. Collen, G. Kruuse, U. Kuylenstierna, A. Magneli, H. Pestmalis and 
### 11. APPENDIX

Lattice parameters and space groups.

<table>
<thead>
<tr>
<th>Phase</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β-angle</th>
<th>Space group</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Bi₂O₃</td>
<td>5.848</td>
<td>8.166</td>
<td>7.510</td>
<td>113°</td>
<td>P2₁⁄c</td>
<td>35</td>
</tr>
<tr>
<td>β-Bi₂O₃</td>
<td>7.742</td>
<td></td>
<td>5.631</td>
<td></td>
<td>P 42₁⁄c</td>
<td>38,39</td>
</tr>
<tr>
<td>δ-Bi₂O₃</td>
<td>5.525</td>
<td></td>
<td></td>
<td></td>
<td>Pn₃m</td>
<td>36,37</td>
</tr>
<tr>
<td>γ-Bi₂O₃</td>
<td>10.268</td>
<td></td>
<td></td>
<td></td>
<td>I₂3</td>
<td>40-42</td>
</tr>
<tr>
<td>Bi₂O₂.₃₃</td>
<td>3.850</td>
<td></td>
<td>35.10</td>
<td></td>
<td>I₄/mmm</td>
<td>48</td>
</tr>
<tr>
<td>BiOI</td>
<td>3.994</td>
<td></td>
<td>9.949</td>
<td></td>
<td>P₄/mmm</td>
<td>119</td>
</tr>
<tr>
<td>β-Bi₅O₇I</td>
<td>18.387</td>
<td>4.2497</td>
<td>13.254</td>
<td>108.1°</td>
<td>C2/m</td>
<td>120</td>
</tr>
<tr>
<td>α-Bi₅O₇I</td>
<td>16.267</td>
<td>5.356</td>
<td>11.503</td>
<td></td>
<td>C</td>
<td>121</td>
</tr>
<tr>
<td>Rutile (TiO₂)</td>
<td>4.5933</td>
<td>2.9592</td>
<td></td>
<td></td>
<td>P₄₂/mmm</td>
<td>122-124</td>
</tr>
<tr>
<td>Anatase (TiO₂)</td>
<td>3.7852</td>
<td>9.5139</td>
<td></td>
<td></td>
<td>I₄₁/amd</td>
<td>122,123,125</td>
</tr>
<tr>
<td>Bi₄Ti₅O₁₂</td>
<td>5.450</td>
<td>5.4059</td>
<td>32.832</td>
<td>90,0°*</td>
<td>B1α1</td>
<td>54,62,66,67</td>
</tr>
<tr>
<td>Bi₅Ti₂O₇</td>
<td>20.68</td>
<td></td>
<td></td>
<td></td>
<td>Fd₃m</td>
<td>126</td>
</tr>
<tr>
<td>Bi₁₂TiO₂₀</td>
<td>10.1739</td>
<td></td>
<td></td>
<td></td>
<td>I₂3</td>
<td>127</td>
</tr>
<tr>
<td>MgO</td>
<td>4.213</td>
<td></td>
<td></td>
<td></td>
<td>Fm₃m</td>
<td>128</td>
</tr>
<tr>
<td>SrTiO₃</td>
<td>3.905</td>
<td></td>
<td></td>
<td></td>
<td>Pm₃m</td>
<td>129</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>4.758</td>
<td>12.991</td>
<td></td>
<td></td>
<td>R 3c</td>
<td>130</td>
</tr>
</tbody>
</table>

*The structure at RT thus appear to be orthorhombic but optical studies have shown the phase to be monoclinic.