Reactive Magnetron Sputter Deposition and Characterization of Thin Films from the Ti-Al-N and Sc-Al-N Systems

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This Thesis treats the growth and characterization of ternary transition metal nitride thin films. The aim is to probe deeper into the Ti-Al-N system and to explore the novel Sc-Al-N system. Thin films were epitaxially grown by reactive magnetron sputtering from elemental targets onto single-crystal substrates covered with a seed layer. Elastic recoil detection analysis and Rutherford backscattering spectroscopy were used for compositional analysis and depth profiling. Different x-ray diffraction techniques were employed, \textit{ex situ} using Cu radiation and \textit{in situ} during deposition using synchrotron radiation, to identify phases, to obtain information about texture, and to determine the thickness and roughness evolution of layers during and after growth. Transmission electron microscopy was used for overview and lattice imaging, and to obtain lattice structure information by electron diffraction. Film properties were determined using van der Pauw measurements of the electrical resistivity, and nanoindentation for the materials hardness and elastic modulus. The epitaxial M_{n+1}AX_{n} phase Ti_{2}AlN was synthesized by solid-state reaction during interdiffusion between sequentially deposited layers of (0001)-oriented AlN and Ti thin films. When annealing the sample, N and Al diffused into the Ti, forming Ti_{3}AlN at 400 °C and Ti_{2}AlN at 500 °C. The Ti_{2}AlN formation temperature is 175 °C lower than earlier reported results. Ti_{4}AlN_{3} thin films were, however, not possible to synthesize when depositing films with a Ti:Al:N ratios of 4:1:3. Substrate temperatures at 600 °C yielded an irregularly stacked Ti_{n+1}AlN_{n} layered structure because of the low mobility of Al adatoms. An increased temperature led, however, to an Al deficiency due to an out diffusion of Al atoms, and formation of Ti_{2}AlN phase and Ti_{1-x}Al_{x}N cubic solid solution. In the Sc-Al-N system the first ternary phase was discovered, namely the perovskite Sc_{3}AlN, with a unit cell of 4.40 Å. Its existence was supported by \textit{ab initio} calculations of the enthalpy showing that Sc_{3}AlN is thermodynamically stable with respect to the binaries. Sc_{3}AlN thin films were experimentally found to have a hardness of 14.2 GPa, an elastic modulus of 21 GPa, and a room temperature resistivity of 41.2 \( \mu \Omega \text{cm} \).
The work presented in this Licentiate Thesis is part of my PhD studies in the Thin Film Physics Division at Linköping University. The goal of my research is to increase the knowledge about functional ternary transition metal nitrides deposited as thin films by reactive magnetron sputtering. Model systems have been $M_{n+1}AX_n$ phases and perovskites in the Ti-Al-N and Sc-Al-N systems. Epitaxial growth has shown to be a useful synthesis route for the Ti$_2$AlN and Sc$_3$AlN phases. The work was supported by the Swedish Research Council (VR) and the Swedish Foundation for Strategic Research. Most of the simulations were carried out at the National Supercomputer Centre (NSC), using resources allocated by the Swedish National Infrastructure for Computing (SNIC).
INCLUDED PAPERS

PAPER 1

*Topotaxial Growth of Ti₂AlN by Solid State Reaction in AlN/Ti Multilayer Thin Films*


I took part in the planning, synthesis, *in situ* and *ex situ* annealing and characterization, and wrote the paper.

PAPER 2

*The Influence of Substrate Temperature and Al Mobility on the Microstructural Evolution of Magnetron Sputtered Ternary Ti-Al-N Thin Films*


Manuscript in final preparation

I took part in the planning, synthesis and characterization (except for XPS), and contributed to the writing of the paper.

PAPER 3

*Sc₃AlN – A New Perovskite*

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*European Journal of Inorganic Chemistry*, accepted for publication

I carried out the major part in the planning, synthesis and characterization, and wrote the paper.
RELATED PAPERS, NOT INCLUDED IN THE THESIS

Bonding Mechanism in the Nitrides Ti$_2$AlN and TiN: An Experimental and Theoretical Investigation
M. Magnuson, M. Mattesini, S. Li, C. Höglund, M. Beckers, L. Hultman, and O. Eriksson

A Solid Phase Reaction between TiC$_x$ Thin Films and Al$_2$O$_3$ Substrates
P. O. Å. Persson, J. Rosén, C. Höglund, D. R. McKenzie, and M. M. M. Bilek
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1. INTRODUCTION

Thin film technology is a fast growing field and the number of applications increases every day. Films are used as protective coatings on tools, as decorative coatings found everywhere around us, as UV-light protections on windows, as diffusion barriers and connectors for all types of micro components in the electronics industry, etc.

The Thin Film Physics Division at Linköping University has a long tradition of depositing and characterizing epitaxial, single-crystal binary nitrides, especially TiN and AlN. The films are grown by reactive magnetron sputtering. Nitrides are compounds belonging to the group of ceramics, meaning that they can be metallic, semiconducting or insulating with properties like high melting point, high hardness, and oxidation resistance.

It has become clear that there could be a possibility to have one type of coating for every demand. Simple binary phases are not enough and recent research has therefore focused on ternary and multinary coatings. Since the middle of the 90s the Thin film group has systematically explored the Ti-Al-N system as one of the first ternary nitride systems, using the knowledge about the binaries. Initially, the cubic solid solution of Ti$_{1-x}$Al$_x$N was studied and more recently, the interest turned to the so called Mn$_{1+x}$AX$_n$ phases including Ti$_2$AlN, which is part of this Thesis.

The thin film growth of Ti$_2$AlN, sometimes with inclusions of Ti$_3$AlN, is reported. When further exploring the Ti-Al-N system we set out to lower the deposition temperature for Ti$_2$AlN, which was 675 °C at that time for parallel basal plane growth. In Paper 1 a new way of depositing Ti$_2$AlN by solid state reaction in AlN/Ti multilayer thin films is reported, taking the necessary temperature down to 500 °C. The attempts to grow Ti$_4$AlN$_3$ as another phase in the Ti-Al-N system, however, encounter problems, as reported in Paper 2.

By curiosity we wanted to replace Ti by other elements. The rare earth metal Sc (next to Ti in the periodic table) was chosen due to its interesting properties as an alloying element to Al. Paper 3 presents the successful results with the first ternary phase in the Sc-Al-N system. Synthetic epitaxial growths together with theoretical calculations reveal that Sc$_3$AlN exists as a phase that is thermodynamically stable.

This Thesis starts with a description of the transition metal nitrides that are interesting for this work, including some theoretical considerations about the ternary Ti-Al-N and Sc-Al-N systems. Then a chapter about the nucleation and growth of thin films follows, including what role epitaxy, seed layers, and substrates play in this work. The films are characterized with ion beam analysis, x-ray diffraction, electron microscopy, resistivity and hardness measurements and a large part of this Thesis is used to describe these
techniques. After that, the three included Papers are summarized followed by a brief description about the ongoing research and what my plans are before my dissertation. After the list of references the included Papers are appended.
2. TRANSITION METAL NITRIDES

2.1 TERNARY NITRIDES

Structures of transition metal compounds with nitrogen have shown to form close-packed or nearly closed packed structures, where the non-metal atoms are inserted into interstitial sites of the metal lattice. The metallic structures can for example be fcc, bcc, hcp, or simple hexagonal. In 1931, Hägg formulated a few empirical rules for crystal structures of transition metal nitrides and carbides. One rule says that the structure is determined by the ratio between radius of the non-metal $r_X$ and the radius of the transition metal $r_{Me}$ according to

$$r = \frac{r_X}{r_{Me}}.$$ (2.1)

If $r$ is smaller than 0.59 the metal sublattice is expected to be simple (fcc, bcc, hcp, or simple hexagonal), while compounds with larger $r$ values have a more complex metal sublattice.

Already in the 1960s, Nowotny and co-workers put an effort into the discovery and synthesis of transition metal phases and within a short time over 200 new carbides and nitrides were presented. Among them were several phases in which the metal sublattice was no longer close-packed or nearly close-packed, but the non-metal atoms occupy octahedral interstitial sites. The corresponding Nowotny octahedral phases have the general formula $Me_aM_bX_c$, where $Me$ is a transition metal, $M$ is a non-transition metal and $X$ is a non-metal. They included more than 40 $M_2AX$ phases (at that time known as $H$-phases), a few $M_3AX_2$ phases, and several (inverse) perovskites. Most of the phases were carbides. The nitrides remain less explored than the carbides, probably due to that it is more complicated to achieve the right stoichiometry.

This Thesis deals with ternary nitrides, especially $M_{n+1}AX_n$ phases, where $X = N$, and inverse perovskites, both of which are presented below.

2.1.1 MAX PHASES

$M_{n+1}AX_n$ ($n = 1, 2, 3$) phases (MAX phases) are a large family of ternary nitrides or carbides, where $M$ is an early transition metal, $A$ is an A-group element and $X$ is either $C$ or $N$. The crystal structure is hexagonal and consists of repeated twinned $M_{n+1}X_n$ slabs, which are interleaved with A-element monolayers. The unit cells for $M_2AX$ and $M_4AX_3$ are shown in Figure 1.
Figure 1: Unit cells of (a) $M_2AX$ and (b) $M_4AX_3$.

MAX phases exhibit typical ceramic properties, like high melting points and good thermal stability due to the strong covalent-ionic M-X bonds. The M-A bonding on the other hand is metallic, yielding properties such as good electrical and thermal conductivity. The alternation of strong and weak bonds leads to kink and shear band formation during mechanical deformation, hence to high ductility and ease of machinability.

The first magnetron sputtered deposited thin film MAX phase was Ti$_3$SiC$_2$ in 2001, around 40 years after the discovery of that MAX phase. Soon after, the first and up to now only reported nitride MAX phase deposited as a thin film was epitaxially grown Ti$_2$AlN, using reactive sputtering from either a compound 2Ti:Al target or elemental Ti and Al targets. It has been shown that the microstructure of Ti$_2$AlN is determined by the substrate temperature. Parallel basal plane growth requires temperatures of at least 675 °C, while lower values induce growth with the c-axis tilted 60° away from the substrate normal, accompanied by surface roughening.

Paper 1 presents a new way to decrease the synthesis temperature of Ti$_2$AlN, namely by depositing layers of AlN and Ti and annealing them afterwards to activate the corresponding solid-state reaction. Paper 2 explores the possibilities to synthesize the related second MAX phase nitride Ti$_4$AlN$_3$ as a thin film, an attempt that did not succeed due to several reasons mentioned later.
2.1.2 PEROVSKITE PHASES

The perovskites were described by Gustav Rose already in 1839. The first crystals came from the Ural Mountains and were named after the vice president A. von Perowski in Petersburg, who was very interested in mineralogy and donated parts from his large mineral collection for research. Perovskites comprise a large family of ternary phases where face-centered oxide atoms are added to a metallic body centered cubic unit cell, see Figure 2a.\textsuperscript{12} Since the 1940s research progressed incredibly and the perovskites have shown to have many extreme properties. The discovery of ferroelectricity in barium titanate\textsuperscript{13} was followed by a large family of ferroelectric and piezoelectric oxides. The first superconducting perovskite BaPb\textsubscript{0.8}Bi\textsubscript{0.2}O\textsubscript{3} with a transition temperature $T_C = 11$ K was discovered in 1974\textsuperscript{14} and nowadays there are perovskite-like phases with a $T_C$ up to 156 K at high pressures.\textsuperscript{15} Another property found in the 1990s was the colossal magnetoresistance (CMR)\textsuperscript{16}.

The perovskite reported in Paper 3 is of a type known as anti- or inverse perovskite, having a metallic face centered cubic structure with nitrogen atoms in body-centered position, see Figure 2b. For some of the known perovskites the radius ratio in Equation (2.1) is larger than 0.59 and it is therefore necessary to extend the Hågg rule to include these structures.\textsuperscript{6} This type of perovskites was discovered much later than the oxide perovskites and is not as explored. They are interesting though, due to the possibility to design them as insulators, semiconductors, or conductors depending on their electronic nature.\textsuperscript{17-18}

An inspiration to the work done in Paper 3 is the existence of perovskite Ti\textsubscript{3}AlN\textsuperscript{19} and Sc\textsubscript{3}InN\textsuperscript{20} which yield Sc\textsubscript{3}AlN by replacing Ti by Sc or In by Al, respectively.

![Figure 2: Unit cells of (a) a perovskite and (b) inverse perovskite.](image-url)
2.1.3 SCANDIUM

Scandium is a rare earth metal with element number 21 in the periodic table, next to titanium. It was discovered by Lars Fredrick Nilson from Sweden in 1879 in the minerals euxenite and gadolinite. Sc has a density of 2.985 g/cm$^3$ and a melting point of 1541 ºC.

Sc has mostly been used as an alloying element for Al, increasing its hardness and making it suitable for high temperature applications. In the former USSR, the development of Sc containing Al-alloys began in the 1980s, which originally were used in the nose cones of some USSR submarine-launched ballistic missiles, making them hard enough to pierce the Arctic ice cap without damage.

The reason why Sc has not yet been used in many applications is its high costs. The price of a 99.9% pure Sc ingot is ~131 US$ per 1 g. As long as there is no demand for Sc, there is no motivation for a larger production. With an increased demand, followed by a more large scale mining, the price could go down. The introduction of Sc-based perovskite nitrides may further promote the interest in the metal.

2.1.4 TERNARY PHASE DIAGRAMS OF THE Ti-Al-N AND Sc-Al-N SYSTEMS

For a ternary phase at a certain composition to be thermodynamically stable, it is required that the free energy of the ternary phase is lower than a combination of two or more of the binary phases or single elements at a given temperature. A first approximation for the free energy can be given by the enthalpy, simply neglecting the effect of temperature. Thus, first-principles Density functional Theory (DFT) enthalpy calculations can give a hint for if a phase might exist or not.

The Ti-Al-N system is quite well explored. The known binary phases are Ti$_3$Al, TiAl, TiAl$_2$, TiAl$_3$ and the nitrides Ti$_2$N, TiN and AlN. The ternary phases Ti$_2$AlN$^{23}$, Ti$_3$AlN$_2$ and Ti$_4$AlN$_3$ are all reported to exist together with a solid solution between TiN and AlN yielding Ti$_{1-x}$Al$_x$N (with 0 ≤ x ≤ 0.67). Ti$_3$AlN$_2$ does not exist in bulk form, but is predicted theoretically as a metastable phase. A ternary phase diagram for Ti-Al-N is given in Figure 3.
To further explore the transition metal ternary nitride field one can employ theoretical calculations to predict new phases. Of course theory is not always representative for what can be done experimentally, but it can inspire the search for phases that might have been overlooked or can be thermodynamically metastable.

Table 1 lists the known phases in the Ti-Al-N system and their ground state total energies $E_0^{29}$. The energies were calculated by the Projector Augmented Wave method as implemented in the Vienna Ab-initio Simulation Package, together with the Generalized Gradient Approximation for the exchange-correlation functional. To illustrate a way of thinking when predicting a phase, an example for the existence of Ti$_3$AlN is presented in a few steps.

Table 1: Ground state total energies for known phases in the Ti-Al-N system.$^{29}$

<table>
<thead>
<tr>
<th>Element</th>
<th>Nitride $E_0$ [eV]</th>
<th>Intermetallic $E_0$ [eV]</th>
<th>Ternary $E_0$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>-7.7642</td>
<td>TiN -19.4492</td>
<td>Ti$_3$AlN -32.217</td>
</tr>
<tr>
<td>Al</td>
<td>-3.7392</td>
<td>h-AlN -14.8896</td>
<td>TiAlN -40.0166</td>
</tr>
<tr>
<td></td>
<td>Ti$_2$N -27.2897</td>
<td>TiAl -12.3093</td>
<td>Ti$_2$AlN -71.3145</td>
</tr>
<tr>
<td></td>
<td>TiAl$_3$ -20.5598</td>
<td>---</td>
<td>Ti$_3$AlN$_3$ -51.6736</td>
</tr>
</tbody>
</table>
Step 1: Check which of the nitrides is the most energetically stable:

\[
E(TiN) + E(Al) = -23.183 \text{ eV}
\]

\[
E(AlN) + E(Ti) = -22.652 \text{ eV}
\]

⇒ TiN and Al is more stable than AlN and Ti (N prefers to bond to Ti).

Step 2: Check if Ti₃AlN is more thermodynamically stable than compounds with the same global concentration (the two most probable cases):

\[
E(Ti₃AlN) - \frac{2E(TiN) + E(TiAl) + E(Ti₃Al)}{2} = -0.3376 \text{ eV}
\]

\[
E(Ti₃AlN) - E(AlN) - 3E(Ti) = -1.2486 \text{ eV}
\]

⇒ Ti₃AlN is more stable than a combination of other compounds.

The two last steps compare Ti₃AlN with other stable ternaries.

Step 3: Check if Ti₃AlN is more thermodynamically stable than Ti₂AlN and some compounds with the same global concentration (the two most probable cases):

\[
E(Ti₃AlN) - E(Ti₂AlN) - E(Ti) = -0.0466 \text{ eV}
\]

\[
E(Ti₃AlN) - \frac{E(TiN) + E(Ti₂AlN) + E(Ti₃Al)}{2} = -0.1086 \text{ eV}
\]

⇒ Ti₃AlN is more stable than Ti₂AlN with a combination of other compounds.

Step 4: Check if Ti₃AlN is more thermodynamically stable than Ti₃AlN₃ and some compounds with the same global concentration (the most probable case):

\[
E(Ti₃AlN) - \frac{2E(Ti₃AlN₃) + 3E(Ti₃Al) + E(TiAl)}{6} = -0.1183 \text{ eV}
\]

⇒ Ti₃AlN is more stable than Ti₃AlN₃ with a combination of other compounds.

These calculations agree with the fact that Ti₃AlN exists as a thermodynamically stable phase!

To check whether it is possible to synthesize Ti₃AlN₂, similar calculations can be performed. The most important step is to compare Ti₂AlN₂ with a mixture of Ti₂AlN₃ and Ti₂AlN.

\[
E(Ti₂AlN₂) - \frac{E(Ti₂AlN₃) + E(Ti₂AlN)}{2} = 0.0922 \text{ eV}
\]
A positive result shows that it is energetically more favorable to form a mixture of Ti$_4$AlN$_3$ and Ti$_2$AlN instead of Ti$_3$AlN$_2$. From this we conclude that Ti$_3$AlN$_2$ not is thermodynamically stable. However, it might still be metastable as predicted in Reference 27.

Only Ti$_2$AlN$^{1,2}$, sometimes with inclusions of Ti$_3$AlN$^3$, has been synthesized as thin films. *Paper 2* is about the attempts to synthesize Ti$_4$AlN$_3$ (known from bulk) as a thin film. It did not succeed, but it is a good example showing that things can well be predicted with calculations. Synthesis, however, may eventually not be feasible because of experimental conditions, like temperature (which affects the adatom mobility and thereby kinetics of the thin film growth).

The ternary Sc-Al-N system is much less explored than the Ti-Al-N system. A few binary phases exist, as the nitrides ScN and AlN and the intermetallics AlSc$_2$, AlSc, Al$_2$Sc and Al$_3$Sc.$^{25}$ Until now no ternary phases have been reported.

The research leading to *Paper 3* was intended to fill the empty area in the ternary Sc-Al-N phase diagram. In fact the perovskite Sc$_3$AlN is predicted to be thermodynamically stable at the global concentration of Sc:Al:N=3:1:1 according to enthalpy calculations analog to the ones above,

$$E(Sc_{3}AlN) - E(ScN) - E(AlSc_2) = -0.535 \text{ eV}, \text{ and}$$

$$E(Sc_{3}AlN) - E(AlN) - 3E(Sc) = -2.603 \text{ eV},$$

yielding negative values. The depositions of Sc$_3$AlN succeeded and all characterizations agree with the prediction. Further calculations also show that the calculated lattice parameter of 4.42 Å agrees with the experimentally observed of 4.40 Å.

A hypothetical MAX phase Sc$_2$AlN is, however, not thermodynamically stable according to the calculations. Correspondingly, thin film deposition experiments with a global concentration of approximately Sc:Al:N = 2:1:1 yields a phase mixture of Sc$_3$AlN, ScN, and Al$_3$Sc.
3. THIN FILM DEPOSITION AND GROWTH

3.1 REACTIVE MAGNETRON SPUTTER DEPOSITION

Physical vapor deposition (PVD) is a widely used technique for thin film synthesis, where the deposition material is vaporized and condensates on a substrate forming the film. The method involves only physical processes, like high temperature evaporation or sputtering and no chemical reactions like in chemical vapor deposition (CVD).

In this Thesis all films were grown by reactive magnetron sputter deposition, in a form that is described below. This technique has the advantage that it is possible to control the growth of pure and dense films, which are suited for materials characterization. To minimize the amount of impurities in the films it is necessary to have very good vacuum conditions in the deposition chamber. A schematic of a deposition chamber is shown in Figure 4. The special feature with this chamber, used for the depositions under high vacuum conditions in Paper 1 and 2, is that the growth can be followed and studied in situ with x-ray radiation from a synchrotron.

![Figure 4: A magnetron sputter deposition chamber with the possibility to do in situ x-ray diffraction measurements.](image)

One solid piece of material for each desired element in the film, a sputtering target, is mounted on a magnetron in the deposition chamber. N, which is part of all the films in my research here, is introduced into the chamber as a pure reactive gas. An inert gas, in this case Ar, is added as the working gas for the sputtering process in order to eject atoms from
the surface layer of the sputtering target. The negatively charged target (cathode) is
bombarded with the highly energetic gas and ejects atoms from its surface. The ejected
atoms, the inert and reactive gases form a plasma and the magnetron is used to confine the
plasma close to the target surface. The magnetic fields from the permanent magnets force
the electrons to gyrate close to the target and increase the probability for collisions
yielding a higher ionized plasma. The sputtered particles fill the chamber and condensate
on the chamber walls and substrate (anodes), forming a film. Depending on the power of
each magnetron, the substrate temperature and potential, and the nature of the substrate,
the film will contain one or more phases.

The films in Paper 3 were grown by magnetron sputter epitaxy (MSE), which is
defined as epitaxial growth by magnetron sputter deposition under the same stringent
vacuum and sample handling conditions as is the practice in molecular beam epitaxy
(MBE). The chamber used for these experiments did not have the possibility for in situ
x-ray measurements, but possibilities to rotate the sample, larger targets and ultra high
vacuum conditions.

3.2 NUCLEATION AND GROWTH

When the vapor atoms impinge on the substrate, adatoms assemble and nucleate to form
two or three dimensional islands on the substrate surface. The islands grow larger and
finally coalesce to form a film. How the coalescence will occur depends on the mobility of
atoms on the surface and the higher the mobility, the more liquid-like coalescence. The
growth continues and forms a closed network of islands. The empty areas slowly fill up,
leaving voids here and there.

There are three different initial growth modes observed, illustrated in Figure 5. These
are:

- **3D-island growth**: Clusters of atoms nucleate on the substrate and grow in three
dimensions to form islands. This happens when the deposited atoms are stronger
bonded to each other than to the substrate.

- **2D-layer growth**: The growth is in two dimensions, filling up one atomic layer before
the next layer starts to form.

- **Stranski-Krastanov growth**: This is a combination of layer and island growth, which
starts with the formation of a few layers and continues with island formation.
Figure 5: Basic modes of thin film growth with (a) island growth, (b) layer growth, and (c) Stranski-Krastanov growth.

The models mentioned above are just a simplification and do not fully explain how a structure like a MAX phase forms. Growth of this relatively complicated structure requires a high mobility of the adatoms. It seems that the attempts to grow Ti$_4$AlN$_3$ in Paper 2 did not succeed because the structure requires 4 layers of Ti and 3 layers of N between every Al layer (see Figure 1), and the temperature was too low for a high enough mobility to achieve the correct partitioning and positioning of the different atoms over the depth of a unit cell. An increase in temperature, however, led to Al diffusion out of the film and to a phase mixture of Ti$_2$AlN and Ti$_{1-x}$Al$_x$N.

3.3 EPITAXY

Epitaxial thin film growth means that the film which is grown is influenced by the structurally-ordered fashion of the material that it is deposited on. Epitaxy arises when the system lowers its interfacial energy to align the lattice of the film with that of the substrate. There are two types of epitaxy, homoepitaxy where the film and the substrate are of the same material, and heteroepitaxy where the film and substrate are composed of different materials like in this Thesis. In homoepitaxy there will be no strain between the film and the substrate because their lattice parameters are perfectly matched. But in most of the cases of heteroepitaxy the lattices are not matched. Hence, the deposited film can either be strained to match the substrate coherently or relaxed by introducing dislocations where possible in a semi- or incoherent manner.\textsuperscript{35}
All films in this Thesis are epitaxially grown on lattice-matched seed layers and substrates. Growth on amorphous or non-lattice-matched substrates typically yields incoherent polycrystalline or amorphous films.

3.4 TOPOTAXY

*Paper 1* is about topotaxial growth of Ti$_2$AlN thin films from multilayers. While epitaxy is a lattice match in two dimensions of one material deposited on another, topotaxial growth is when the growth occurs within the solid state in two or three lattice matched dimensions. An example of topotaxy is when Ti$_2$AlN is formed by solid state reaction between AlN and Ti in a diffusion couple. After depositing epitaxial layers of AlN(0001) and Ti(0001) they were annealed and diffusion of N and Al into Ti yielded Ti$_2$AlN(0001). In Figure 6 are transmission electron microscopy images from such a sample before and after annealing together with a sketch of the thicknesses of each layer. It can be seen that the individual layer thicknesses changed during the solid state reaction when Ti$_2$AlN formed and higher resolution images (not shown) confirmed that the layers between AlN in Figure 6b indeed were Ti$_2$AlN. This way of depositing Ti$_2$AlN lowered the deposition temperature for basal plane growth by 175 °C.

![Figure 6: Cross-sectional transmission electron microscopy image of the AlN / Ti multilayers (a) before and (b) after annealing, together with sketches of the individual layer thicknesses.](image)

3.5 THE SUBSTRATES AND ROLE OF SEED LAYERS

The main substrate materials that I have used are single-crystal MgO(111) or Al$_2$O$_3$(0001). The motivation for these is that the growth of high quality epitaxial films of MAX phase or perovskite material requires a template. A good template is given if the lattice mismatch between the film and the substrate is small, which is the case for these materials. Another important requirement is that the substrate must be stable at temperatures up to ~1000 °C to avoid interdiffusion between the substrate and film. The advantage of Al$_2$O$_3$ is that the (0001) surface can be polished very smooth, while the (111) surface of MgO in
comparison is rough. MgO, however, has the advantage of the smallest lattice mismatch to the films deposited in this Thesis. The nominal in plane lattice mismatch between Ti$_2$AlN(0001) and the substrates MgO(111) and Al$_2$O$_3$(0001) are 0.3% and 11.5%, respectively.

Unfortunately, both MgO and Al$_2$O$_3$ have shown not to be stable enough when judged on a nanometer level for film-substrate reactions. Even at rather low temperatures (690 °C and 900 °C for MgO and Al$_2$O$_3$, respectively) interdiffusion is observed between the substrates and films.\textsuperscript{36-37} To avoid such reactions, a so called seed or buffer layer is deposited on the substrate before growing the actual film on top. The seed layers here were the nitrides AlN in \textit{Paper 1}, Ti$_2$AlN in \textit{Paper 2}, and ScN in \textit{Paper 3}. The motivation for the choice is that they contain the same material as the films and have a good lattice match to them.
4. ANALYSIS TECHNIQUES FOR THIN FILMS

4.1 ION BEAM ANALYSIS TECHNIQUES

Ion beam analysis is used for determination of the concentration of specific elements in a sample. Thickness, compositional gradients and depth positions of different elements can also be determined.

Ion beam analysis consists of mainly four techniques, which are illustrated in Figure 7. Rutherford backscattering spectroscopy (RBS) and elastic recoil detection analysis (ERDA) are based on elastic scattering of incoming ions. The ions lose a specific amount of energy and in RBS the energies of the scattered incoming ions are detected, while in ERDA the energy of the target atoms (as a function of energy) are detected. RBS is suitable for depth profiling and analysis of thin films (up to ~500 nm) containing medium to heavy elements on light substrates. ERDA is good for depth profiling and analysis of elements with a mass smaller than the mass of the incoming heavy ions. Nuclear reaction analysis (NRA) makes use of that the incoming beam excites the nuclei, which will return to their ground state accompanied by the emission of γ-rays or particles. NRA is used for depth profiling of light elements, like H, in heavier substrates. In particle induced x-ray emission (PIXE) the target atoms are excited by the incoming beam and when they return to their ground state element characteristic x-rays are emitted. PIXE is used for determination of trace elements in a matrix of light elements.38-39

All the mentioned techniques are nondestructive, fast, quantitative, have a high sensitivity and no sample preparation or material specific reference samples are needed. Disadvantages are the needs for an accelerator and special detectors, and that the evaluation might be lengthy.

Figure 7: Schematic figure showing the difference between (a) RBS, (b) ERDA, (c) NRA, and (d) PIXE.
4.1.1 ION-SOLID INTERACTION

ERDA and RBS are the techniques usually used for thin film analysis of samples like the ones in this Thesis. They are both based on the elastic scattering that occurs when an incoming light ion (RBS) or heavy ion (ERDA) primary beam hits a sample, see Figure 8. In both cases classical two-particle scattering theory is valid, which means that the momentum and the energy must be conserved during a collision. The incoming atom of mass $m_0$, energy $E_0$ and velocity $v_0$ hits a sample atom of mass $m_2$ that is scattered with the angle $\varphi$ and obtains the energy $E_2$ and velocity $v_2$. The incoming atom is scattered with the angle $\theta$ and has energy $E_1$ and velocity $v_1$ after the collision. It is a sufficient approximation to assume that all the scattering processes are binary and completely elastic.\textsuperscript{39-40}

![Collision kinematics: Classical two-particle scattering when an atom with mass $m_0$ collides with an atom of mass $m_2$.]

The momentum conservation of the collision can be described with

\[ m_0 v_0 = m_0 v_\cos \theta + m_2 v_2 \cos \varphi, \quad \text{and} \quad 0 = m_2 v_2 \sin \varphi - m_0 v_\sin \theta. \]  

The energy is also conserved, yielding

\[ E_0 = E_1 + E_2, \quad \text{and} \]

\[ \frac{1}{2} m_0 v_0^2 = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2. \]

These formulas can be used for deriving the kinematic factor $K$ in RBS, which is the energy fraction of the incoming ion after a collision. The fraction $1-K$ is the energy transferred to the target atom.\textsuperscript{39} $K$ is given by
\[
K_{\text{proj}} = \frac{E_x}{E_0} = \left[ \frac{\sqrt{m_2^2 - m_2^2 \sin^2(\theta) + m_0 \cos(\theta)}}{m_0 + m_2} \right]^2, \text{ where } \frac{m_2}{m_1} \geq 1. \quad (4.5)
\]

The kinematic factor \( k \) for the recoil atoms in ERDA can be derived in a similar way, yielding

\[
k_{\text{recoil}} = \frac{E_x}{E_0} = \frac{4 m_0 m_2}{(m_0 + m_2)^2} \cos^2(\phi). \quad (4.6)
\]

4.1.2 RUTHERFORD BACKSCATTERING SPECTROSCOPY

RBS is a method which is widely used for composition analysis and profiling of thin films to a depth of \(~500 \text{ nm}\). Light protons, usually \( \text{He}^+ \) or \( \text{H}^+ \), are elastically backscattered from the target atoms in the sample. Elements with the mass from Be to U can be detected, but the possibility to quantify an element is dependent on the combination of elements in film and substrate. In Figure 9 a typical RBS setup together with the definition of angles and energies is shown.

![Figure 9: A typical RBS setup.](image)

The ions with highest energy have been backscattered by the heaviest element on the film surface. The energy is given by

\[
E_i = K_{\text{proj}} E_0. \quad (4.7)
\]

The energy from an ion scattered by an atom deeper in the film also loses energy by interaction with electrons before and after scattering. This energy can be calculated by

\[
E_2 = K_{\text{proj}} (E_0 - \Delta E_{\text{in}}) - \Delta E_{\text{out}}, \quad (4.8)
\]
where $\Delta E_{in}$ and $\Delta E_{out}$ denote the energies that the incoming ions loose when traveling in and out a depth $t$ of the sample, respectively, see Figure 9. These calculations are usually not trivial since $\Delta E$ depends on the element and its energy-specific stopping power.\(^\text{39}\)

While the kinetic factor determines the energy, the backscattering yield of an element determines its detected intensity or signal height in the full spectrum. A relative height of a spectrum, $\sigma_{rel}$, can be calculated for a known atomic number of element $x$. If the atomic number of the heaviest element in the film $Z_{\text{max}}$ is known, then

$$\sigma_{rel} = \left( \frac{Z_x}{Z_{\text{max}}} \right)^2 . \quad (4.9)$$

With more than one element in the film the backscattering yield $Y_{rel,x}$ scales with the amount of each element ($x_{rel}$ between 0 and 1) as

$$Y_{rel,x} = \sigma_{rel} x_{rel}. \quad (4.10)$$

A typical RBS spectrum (2.0 MeV He$^+$ beam, $\alpha = 6^\circ$, $\beta = 7^\circ$, $\theta = 167^\circ$) is presented in Figure 10. It stems from a Sc$_{0.46}$Al$_{0.32}$N$_{0.22}$ film and ScN seed layer on an MgO substrate. The edge 1 arises from Sc at the surface of Sc-Al-N because Sc is the heaviest element in the film. The deeper in the film the ions are scattered by Sc, the lower is the energy they have. The spectrum goes to 2 where the interface to ScN can be seen. A higher Sc signal at 3 indicates that ScN has a higher Sc-concentration than Sc-Al-N. Edge 4 and 5 originate from the Al at the film surface and interface to ScN, respectively, depending on that Al is the second heaviest element in the film. Due to that Mg from the substrate is heavier than N in the ScAlN film and ScN seed layer, their signals are overlapping and the Mg from the interface is seen at 6 while the N appears at 7.

The evaluation of the RBS spectrum was usually done with the SIMNRA software. After energy calibration for the surface edge of some atoms of different mass in the surface layer the film spectrum can be simulated. This can be more or less time consuming depending on the atomic distribution in the film.

The simulated spectrum deviates from the measured one at low energies, see 8 in Figure 10, because multiple scattering occurs and the simulation program SIMNRA uses a binary collision approximation, as was introduced in Figure 8.
Figure 10: A RBS spectrum from a Sc-Al-N film on MgO capped with a ScN seed layer.

As can be seen in Figure 10, the simulated thickness of the film in ion beam analysis is given by an area density. If the gravimetric density \( \rho \) is known (often the bulk density is more or less correct), however, the thickness \( t \) in meters can be calculated by inserting the thickness given in atoms/cm\(^2\) as \( x \), the relative mass \( M \), and Avogadro’s number \( N_a \) into

\[
t = \frac{x \times M}{\rho \times N_a} \tag{4.11}
\]

To achieve a better separation of elements in e.g. multilayers the angle or the mass of the incoming beam can be increased, usually resulting in a lower count rate and noisier spectrum.

I have used the RBS technique regularly in my research. All the rate calibrations in Paper 3 leading to right stoichiometry for Sc\(_3\)AlN were done with RBS. In Paper 1 RBS was used to confirm that the as-deposited AlN and Ti layers were stoichiometric and without intermixing. It was also used to see that annealing led to interdiffusion between the layers and intermixing of Ti, Al and N. In Paper 2 RBS was used to check for the stoichiometry change when depositing with the same parameters at different substrate temperatures. With the substrates used in the different Papers it has always been necessary to calibrate the absolute spectrum height according to the substrate, an estimation of the N content as 100 at.% minus all the heavy elements. This presupposes a low C and O content, which always showed to be correct when cross-checking the results in this Thesis with ERDA.
4.1.3 CHANNELING RBS

In channeling RBS the incoming ion beam is aligned along a crystal axis of the sample so that atoms in deeper layers of the sample are shadowed by each other from the beam. This can, for example, be applied for measurements of very thin amorphous or defected crystals on single-crystal substrates where the light elements overlap with the substrate. The alignment of the crystal will lower the intensity coming from the substrate and thereby increase the intensity detected from the film. Channeling RBS can also be used for thick epitaxial layers to check for the amount of impurities or lattice disorders.\textsuperscript{39,40}

Channeling RBS has not been used particularly here, but might be a good suggestion to use for future measurements on single-crystal samples.

4.1.4 ELASTIC RECOIL DETECTION ANALYSIS

The possibility to measure light elements with RBS is limited and it is not possible to detect H. Instead, a forward scattering technique like ERDA can be used. With ERDA it is also possible to quantify the amount of light elements in a film on a heavy substrate. All elements lighter than the incoming beam can be detected, in a depth range of up to \(~1\ \mu m\) for the 40 MeV iodine beam used for experiments in this Thesis. In comparison to RBS, where the incoming ions are backscattered, the incoming heavy ions knock out lighter target ions which are detected as a function of energy and mass.

Most of the theory in RBS is also valid for ERDA. The major difference is the way recoil atoms are detected and identified. A detection setup that simultaneously obtains information from both the mass of the recoil atom and its energy is needed. A common type is the time-of-flight energy (ToF-E) setup, which distinguishes between atoms (mass \(m\)) of the same energy \(E\) due to their different velocities \(v\) according to energy conservation

\[
E = \frac{1}{2}mv^2. \tag{4.12}
\]

By measuring the time \(t\) it takes for an atom to move between two foils with a distance \(L\), the mass \(m\) is achieved with

\[
m = \frac{2Et^2}{L}. \tag{4.13}
\]

Opposite to RBS, heavier recoil atoms have a lower energy, but as in RBS the energy decreases the deeper in the sample the recoils come from.
The evaluation of an ERDA spectrum requires, like RBS, a few samples with known surface elements for calibration. First the time-of-flight for different masses is calibrated, where the surface edge is specified for each element. Then the energy is calibrated with the same elements.

ERDA was used in Paper 3 due to that the films were too thick to be measured with RBS. The depth profile in the paper illustrates nicely how evenly distributed the elements were in the film and how low the H, C, and O impurity levels were.

4.2 X-RAY DIFFRACTION

X-rays have a wavelength in the same order of magnitude as the lattice constants in crystals. They are therefore suited for characterization of materials’ crystal structures. It is a popular technique, which does not require sample preparation (more than a clean surface), is non-destructive, and without need for lengthy evaluations.

The x-rays used for this Thesis are either generated in an x-ray Cu-tube or in a synchrotron with a far greater intensity. In a Cu-tube electrically charged particles are accelerated onto a Cu-plate from where the x-rays are emitted. With a Ni-filter only the Cu $k_{\alpha}$-radiation is filtered out, giving a wavelength of 1.54 Å. The synchrotron radiation is produced by accelerated electrons that move along a curved line within a deflecting magnetic field. A radiation range from microwaves to hard x-rays is produced, yielding a possibility to choose wavelengths for measurements.\(^{41}\)

When x-rays are scattered by a periodic crystal they will interfere constructively and thereby give rise to intensity peaks. The requirements for constructive interference are given in Bragg’s law,

$$n\lambda = 2d\sin \theta,$$

where \(n\) is an integer number of the wave length \(\lambda\), \(d\) is the lattice plane distance and \(\theta\) the scattering angle.

Bragg’s law says that the pathway difference between two atomic layers is \(2d\sin \theta\), yielding an intensity maximum for an integer number of wavelengths, see also Figure 11.\(^{42}\)
The way the x-rays will be scattered is dependent on the structure factor and multiplicity of the crystal planes, yielding different intensities for the diffracted beam. If randomly oriented crystallites in the sample are smaller than 2-5 nm they may not be possible to detect due to a severe peak broadening and the structure is then called x-ray amorphous. The user should consider using another technique, like transmission electron microscopy, to solve the problem of crystallinity.

The most common use of x-ray diffraction (XRD) is for phase-, texture, and stress analysis of polycrystalline materials. In the present work the substrates are single-crystals and the films are epitaxial. The interesting information gained with this technique for known material systems is which phases a film consists of, thickness, roughness, and texture. If a film consists of an unknown phase, like in Paper 3, XRD is an important technique to gain information about lattice parameter, crystal structure, and texture. For the in situ XRD work in Paper 1 and 2, the x-rays are also used for determination of the thickness, phase, and roughness evolution during film growth and in annealing studies. A schematic view over the tilting possibilities of the samples in the diffractometers used in this work is shown in Figure 12.
4.2.1 X-RAY DIFFRACTION

In a so called symmetric $\theta$–$2\theta$ diffraction scan only the specular reflections originating from lattice planes parallel to the sample surface are revealed. In this Thesis the position of the peaks is used to identify the phases and the texture in the studied films. The full width at half maximum (FWHM) of a peak is an indication for the grain size in the film.

In some crystal structures diffraction on planes with Miller indices $hkl$ gives destructive interference and no peak intensity. This was used in Paper 3, where the perovskite $\text{Sc}_3\text{AlN}$ (with no forbidden peaks) can be distinguished from the face centered cubic (fcc) structured $\text{ScN}$ and $\text{MgO}$ (with peak intensity only for all $hkl$ being even or odd). For this, non-specular $\omega$–$2\theta$ scans were made around all $hkl$. The setup for such scans is asymmetric and a tilt in $\phi$ and $\Psi$ is necessary. It yielded intensity from all phases at fcc crystal lattice points and peaks only from $\text{Sc}_3\text{AlN}$ at the other lattice points. The intensities from the perovskite peaks were very low, but their relative heights agreed with the structure factor.

4.2.2 POLE FIGURES

Pole figures can be used to find out more about the preferred orientation, or texture, in a film. Before recording a pole figure the exact position in $\theta$ and $2\theta$ for the expected peak needs to be determined. During measurement the sample is scanned in both $\Psi$ (0 - 90°) and $\phi$ (0 - 360°), revealing a view over all orientations yielding peaks at the set 2$\theta$ angle. A measurement like this gives the symmetry of the crystal and is used as a help to point out a certain crystal structure.

4.2.3 X-RAY REFLECTIVITY

X-ray reflectivity (XRR) measurements are $\theta$–$2\theta$ diffraction scans at low angles, based on the reflections of x-rays at surfaces and interfaces. These measurements are mostly used for thickness determination, but also to check for roughness of the film.

The thickness can be determined by the modified Bragg’s law, which takes into account the grazing incidence angle $\theta$.

$$n\lambda = 2D \sin \theta \sqrt{1 + \frac{\eta^2 - 1}{\sin^2 \theta}}, \quad (4.15)$$

where $D$ is the thickness and $\eta$ is the complex refractive index of the film.

By plotting $n^2$ against $\sin^2 \theta$ the slope of the linear curve can be used for determination of the thickness. When depositing the different layers in Paper 1 an XRR scan was taken
after each deposition. Every added layer added a significant reflectivity curve, which overlapped with the previous. An evaluation of an irregular multilayer structure like this requires computer simulations. Depending on the shape of the decrease of the curve at increasing $\theta$ angles a conclusion about the roughness can be drawn.

### 4.2.4 TIME-RESOLVED X-RAY INTERFERENCE

Time-resolved x-ray interference data are recorded to follow the thickness and roughness evolution during growth. The intensity oscillations originate from the constructive and destructive interference that occurs due to the difference in the path ways for the x-ray beams that are scattered at the substrate and film surface. When the film thickness $D$ is such that the pathway difference is an integer number of wave lengths, the beam will interfere constructively, according to Bragg’s law.

In Figure 13 the time-resolved x-ray interference graph from Paper 1 is redrawn. A roughening of the film surface, compared to the extremely smooth $\text{Al}_2\text{O}_3(0001)$, leads to a steep decrease in the oscillation maxima, as seen in Layer 1. The decay at fixed angles is linked to a decreasing intensity in the corresponding x-ray reflectivity scan.

In addition, the x-ray beams are scattered at monolayers on the film surface to interfere constructively and destructively. A decay as in Layer 3 in Figure 13 is a typical roughening on the monolayer scale, where the oscillation intensity decreases symmetrically, and the later part of Layer 2 is a typical smoothening. This phenomenon is only observable for very smooth layers, like during layer-by-layer growth, where the surface roughness is only a few monolayers.

In Paper 1 each AlN layer roughened the surface due to the relatively low adatom mobility on the AlN(0001) surface at a growth temperature of 200 °C. Each Ti layer smoothened the surface again, due to weak bonding on the Ti(0001) surface implying a high adatom mobility.

![Figure 13](image-url)
4.3 TRANSMISSION ELECTRON MICROSCOPY

The wavelength of visible light limits the image resolution in light microscopes, which was the main reason for developing electron microscopes that use the wave nature of highly energetic electrons instead of light. For materials science and especially thin film research this has been revolutionary due to that it is possible to image samples with a resolution of <1 Å, which means that it is possible to image the atomic arrangement in a material. What limits the resolution is not the wavelength any more, but apertures, aberration in the lenses, and the inelastic scattering process in the samples.

A TEM consists in principle of an electron gun emitting an electron beam, two or more electromagnetic lenses condensing the beam on the sample, an imaging lens system collecting the transmitted and scattered beams, and lenses projecting the image on a screen or into a CCD camera.

There are different mechanisms that yield contrast in a TEM image. Mass-thickness contrast arises when electrons are elastically and incoherently scattered by atoms in the sample. The scattering is dependent on the atomic mass, the density, and the thickness of the sample. The higher the mass and density of the material and the thicker the sample, the more scattering will occur. Mass-thickness contrast is in this Thesis used for images taken at lower magnification. Diffraction contrast occurs due to that the electrons are coherently scattered at certain Bragg angles in crystalline materials. This requires an alignment of the sample (or the electron beam) along certain crystal zone axes. Alignment onto exact zone axes is also used for high resolution imaging as described below.

4.3.1 HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY

In high-resolution TEM (HRTEM) it is possible to image the lattice of a material. To achieve high quality images it requires an accurate alignment, both of the beam and the sample. The objective lens, however, suffers from spherical aberration, chromatic aberration and astigmatism. The FEI TITAN microscope at Forschungszentrum Dresden-Rossendorf used in Paper 3 has a corrector for spherical aberration making it possible to get images with an even higher resolution than the ones achieved in the FEI Tecnai G² TF 20 UT at Linköping University used for all other images.

4.3.2 ELECTRON DIFFRACTION

In the electron diffraction mode, like in XRD, the reciprocal space is imaged and therefore electron diffraction is also a useful tool for getting lattice structure information. To limit the information to come from a certain area of the sample, like from a small area or single
grain, an aperture can be inserted in the image plane, called selected area electron diffraction (SAED).

SAED was used in Paper 3 to test that the phase was indeed a perovskite and that the film was a single-crystal. Both bright and weak spots were observed which agreed with the structure factor of a perovskite. Agreement was found on both accounts.

4.3.3 SAMPLE PREPARATION

A TEM sample has to be thin enough to transmit the electron beam and still keep intensity while containing the materials structure of interest. A thin sample also minimizes the risk that any two grains overlap over the depth or that the electrons are multiple scattered. This requires a careful sample preparation. The samples in this Thesis are all cross-sectional samples, meaning that the whole thickness of a film can be studied, including any microstructural evolution. A sample is prepared by gluing two samples with the films against each other into a Ti-grid, grinding it down to ~50 µm thickness followed by ion etching until there is a hole in the center. The extremely thin area next to the hole is used for imaging.

4.4 ELECTRICAL CHARACTERIZATION

Following structural and compositional characterization, the next task for a new material like Sc$_3$AlN in Paper 3 is to measure its physical properties. Here, resistivity measurements were performed to find out whether it is conducting like the binary intermetallics or semiconducting like ScN and AlN. Since it is a perovskite and some of them are reported to be superconducting, even at temperatures of up to 120 K, we also measured the temperature-dependent resistivity, from room temperature down to a few Kelvin. A van der Pauw setup at the University of Illinois at Urbana, IL, was used instead of the four point probe that usually is used for resistivity measurements.

4.4.1 VAN DER PAUW RESISTIVITY MEASUREMENTS

The advantage with van der Pauw resistivity measurements is that the measurement can be done on a sample with arbitrary shape. Four small Pt-contacts were milled into half of the thickness of the film, preferably in a square ~5 mm apart, by focused ion beam, see Figure 14. On top of each contact a wire bonding was evaporated. A current was sent from contact $a$ to $c$ and the voltage was measured between $b$ and $d$ and the resistance $R$ was calculated. To get better statistics also a measurement with a current from $a$ to $b$ and a voltage from $c$ to $d$ should be done.
The sheet resistance $R_s$ is given by

$$R_s = \frac{\pi \bar{R}}{\ln 2}.$$  \hspace{1cm} (4.16)

The resistivity $\rho$ is then calculated by measuring the film thickness $D$ and using

$$\rho = D \times R_s.$$ \hspace{1cm} (4.17)

For the temperature-dependent resistivity measurements, the sample was cooled down to 4 K and the resistivity was continuously measured while the temperature increased to room temperature. Initial results indicate that as-deposited Sc$_3$AlN(111) films are not superconducting above 4 K.

4.5 MECHANICAL CHARACTERIZATION

4.5.1 NANOINDENTATION

Nanoindentation experiments are useful to find out about the mechanical properties of a thin film. During a measurement a sharp diamond tip is pressed into the surface of the material with a controlled load. By recording the displacement of the indenter during loading and unloading, see Figure 15, and employing the evaluation method developed by Oliver and Pharr\textsuperscript{49}, the hardness and reduced elastic modulus can be determined.
The reduced modulus $E_r$ is given by the slope of the initial gradient when unloading ($S = dP/\,dh$), the contact area $A$ and the equation

$$E_r = \frac{1}{2} \sqrt{\frac{\pi}{A} \left( \frac{dP}{dh} \right)}.$$  \hspace{1cm} (4.18)

The elastic modulus $E_i$ and Poission’s ratio $\nu_i$ from the indenter have to be taken into account and the elastic modulus of the sample $E$ can be calculated by

$$\frac{1}{E} = \frac{1 - \nu^2}{E_i} + \frac{1 - \nu_i^2}{E_i}.$$ \hspace{1cm} (4.19)

In this Thesis nanoindentation was used in Paper 3 to get a first hint about the mechanical properties of the new phase Sc$_3$AlN. The results yielded a hardness of 14.2 GPa and an elastic modulus of 249 GPa. This is lower than the reported hardness and elastic modulus of ScN, being 21 GPa and 356 GPa, respectively, and in the same range as for Ti$_3$AlC with values of 11 GPa and 240 GPa, respectively.
5. SUMMARY OF RESULTS

PAPER 1:

Topotaxial Growth of Ti$_2$AlN by Solid State Reaction in AlN/Ti Multilayer Thin Films

It has been an ambition to lower the substrate temperature for depositing MAX phase thin films. Until this paper was published, the lowest temperature for parallel basal plane growth of Ti$_2$AlN was 675 °C. These films had been grown by reactive magnetron sputtering from two elemental targets.

This paper presented a new way to form Ti$_2$AlN at the much lower temperature of 500 °C. The experiments were carried out at the European Synchrotron Radiation Facility (ESRF) allowing x-ray scattering analysis in situ during depositions and annealing.

Sequential layers of wurtzite-AlN and α-Ti were deposited by (reactive) magnetron sputtering from elemental Ti and Al targets onto Al$_2$O$_3$(0001) at 200°C. An x-ray diffraction scan after each deposition showed that the films were heteroepitaxially (0001) oriented. During deposition, oscillations of time resolved x-ray interference scans were recorded. The decrease in the amplitude of the AlN oscillations indicated that the surface roughened, which is explained by the low adatom mobility on the AlN surface. On the contrary the amplitude of the Ti oscillations increased due to the high adatom mobility on the Ti surface, resulting in a surface smoothening. Ex situ Rutherford backscattering spectroscopy showed that the layers were stoichiometric to within 2 at.% and that there was no intermixing of the individual AlN and Ti layers.

After deposition of the layers, the sample was annealed and an x-ray diffraction scan was recorded every 30 minutes. At a temperature of 400 °C it was seen that perovskite Ti$_3$AlN formed within 5 minutes and the reaction was completed after 30 minutes. At 500 °C the MAX phase Ti$_2$AlN formed within 5 minutes, after 30 minutes the perovskite vanished and after 1 hour the phase transformation to Ti$_2$AlN was completed with some residual AlN.

The paper suggests a sequence of steps for diffusion and phase transformation of the diffusion couples as illustrated in Figure 16. Ti is highly reactive at a temperature of 400 °C and has a large solid solubility in the α phase. Therefore N interstitially diffuses into Ti, followed by substitutional diffusion of Al forming Ti$_3$AlN. The decomposition
rate of AlN and the Al diffusivity were amplified at 500 °C. This made it possible to add Al and N to Ti$_3$AlN, reorganize the crystal structure, and formed Ti$_2$AlN.

Figure 16: Suggestion for diffusion steps for formation of Ti$_2$AlN during solid state reactions between AlN / Ti multilayers.
PAPER 2:

The Influence of Substrate Temperature and Al Mobility on the Microstructural Evolution of Magnetron Sputtered Ternary Ti-Al-N Thin Films

Until now Ti₂AlN is the only MAX phase nitride reported as a thin film, but another MAX phase, Ti₄AlN₃, is known from the bulk. The aim of this paper was to explore the synthesis of Ti₄AlN₃ by thin film deposition. The influence of the substrate temperature was studied particularly, as it affects the Al mobility which, in turn, determines the composition, texture, and morphology during growth.

Ti-Al-N films, both with Ti:Al:N ratios of 2:1:1 and 4:1:3, were deposited onto Al₂O₃(0001) substrates in a deposition chamber mounted to a goniometer at the European Synchrotron Radiation Facility (ESRF) allowing to obtain phase and structural information from the sample with x-ray scattering in situ during deposition.

θ–2θ scans were taken after each deposition step to check for phase changes and preferred crystallographic orientations. Deposition of 4TiAl3N at 675 ºC directly onto the substrate or with a Ti₂AlN seed layer yielded a phase mixture of Ti₂AlN and Ti₁₋ₓAlₓN with x close to 0. At a temperature of 725 ºC the Ti₁₋ₓAlₓN peak intensity increased. When lowering the temperature to 600 ºC peaks showed up, which could be attributed to high order Ti₄AlN₃000l or tilted basal plane peaks.

Rutherford backscattering spectroscopy results showed that depositions at 600 ºC yielded Ti:Al:N ratios of 4:1:3, while higher temperatures gave an Al loss and O uptake. The Al loss was not observed in Ti₂AlN though. Therefore, it seemed that Ti₂AlN was more stable than Ti₄AlN₃ at temperatures above 600 ºC at the deposition conditions used in this study.

Cross sectional transmission electron micrographs showed that the film deposited at 675 ºC consisted of both Ti₂AlN and Ti₁₋ₓAlₓN. The film deposited at 600 ºC, however, had sections with pronounced hillock formations between smooth sections. Both sections showed a layered structure with repeated twinning as in Mn+1AXn, but without the periodicity of Ti₄AlN₃. The Fourier transformations of the images correspondingly showed streaks instead of individual spots, representing different Ti₄₋ₓAlₓNₙ stacking sequences.

X-ray photoelectron spectroscopy sputter depth profiles were obtained for N(1s), Ti(2p), Al(2p) in the above mentioned samples and three reference samples (TiN, Ti₀.67Al₀.33N, and Ti₂AlN). The N(1s) spectra all showed a peak originating from Ti-N bonds in the samples and the Ti(2p) showed the corresponding typical nitride doublet peaks. The Al(2p) signal differed though significantly between the Ti₁₋ₓAlₓN, with Al-N bonds, and Ti₂AlN and 4TiAl3N, with binding energies close to Al-Al bonds. This confirmed the above finding that the 4TiAl3N film contained mirror planes of Al as in a MAX phase, but without the periodical stacking.
In conclusion, Ti₄AlN₃ did not form by the present deposition processing. At temperatures above 600 ºC, Al was lost to the vacuum and there was not enough left to form stoichiometric Ti₄AlN₃. Lower temperatures prevented Al loss, but the Al adatom mobility was too small for growth of the periodic layers forming Ti₄AlN₃. Instead competing film-forming reactions lead to Ti₂AlN, and intergrown Tiₙ₊₁AlNₙ structures.
PAPER 3:

Sc$_3$AlN – A New Perovskite

Sc is a transition metal, next to Ti in the periodic table. Even though there has been much research going on regarding ternary nitrides with Ti, the corresponding phase diagram for the Sc-Al-N system has been empty. The aim with this work has been to explore that ternary phase diagram. A first ternary Sc-Al-N phase was found in the perovskite Sc$_3$AlN deposited as a single-crystal film at 650 °C.

Reactive magnetron sputtering from 2 targets under ultra high vacuum conditions was used to epitaxially grow Sc$_3$AlN(111) with ScN(111) seed layers onto MgO(111) substrates. With elastic recoil detection analysis it was determined that the composition ratios of Sc:Al:N were 3:1:1 and that the impurity level was close to the detection limit.

X-ray diffraction was used for phase information. Pole figures and $\theta$-$2\theta$ scans supported that the film and seed layer had exclusively grown in the 111-direction, showed a cube-on-cube epitaxy, and revealed the lattice parameter of 4.40 Å. By non-specular $\omega$-$2\theta$ scans it was possible to distinguish the fcc-crystals ScN and MgO from the perovskite Sc$_3$AlN, detecting additional reciprocal lattice points unique for a perovskite.

Cross sectional transmission electron microscopy was employed both to obtain information about the crystal quality and more information about the phase. An overview image showed that the layers were clearly distinguishable and the selected area electron diffraction patterns from the film showed that it was a single-crystal and contained the characteristic perovskite reflections (like in x-ray diffraction). The film was also imaged in high resolution in a Cs-corrected microscope. Imaging of the Sc$_3$AlN film along its [210]-zone axis revealed a layered structure, which agreed with the Sc-N and Sc-Al layers projected in that direction of a perovskite.

As an evidence for the assumptions for the phase being a perovskite, density functional theory calculations were performed. Both the lattice parameter and the prediction that a perovskite Sc$_3$AlN should be thermodynamically stable agreed with the experiments.

When deviating from Sc:Al:N = 3:1:1 composition towards higher Al and N contents initial results showed that the perovskite is a line compound in equilibrium with ScN and Al$_3$Sc.

Nanoindentation experiments yielded a hardness of 14.2 GPa and an elastic modulus of 21 GPa. Resistivity measurements yield a room temperature resistivity of 41.2 $\mu$Ωcm.

The new phase fills the empty gap in the ternary Sc-Al-N phase diagram, which now can be drawn like in Figure 17.
Figure 17: The PVD ternary phase diagram at 650 °C as determined in Paper 3.
6. ONGOING AND FUTURE RESEARCH

The scope of my PhD studies remains to learn more about ternary transition metal nitride thin film synthesis. I have shown here that there are pronounced differences between the Ti-Al-N system and the Sc-Al-N system. Basically there is likely no Sc$_2$AlN MAX phase, whereas Ti$_2$AlN can be readily formed. Moreover, initial diffusion experiments of AlN and Sc analogue to the ones in Paper 1 do not yield a ternary phase, but a few binary ones.

The newly found Sc$_3$AlN perovskite formed by reactive co-sputtering of Sc and Al will be further explored according to its structure and properties. It is also interesting to see the effect of temperature and compositional variations, or what happens if we vary the substrate orientation or even use an amorphous substrate.

In the Thin Film Group there has been quite some work going on regarding the solid solution Ti$_{1-x}$Al$_x$N – What about a solid solution between ScN and AlN, which maybe could be age hardened like it is successfully done in Ti$_{1-x}$Al$_x$N and Al-alloys containing Sc? Also studies of the effects of Sc doping into Ti$_2$AlN and Ti doping into Sc$_3$AlN are the subject of my initial studies.

Now that we have seen that there are still interesting ternary phases left to explore I will continue to do that. It could both be interesting to compare the differences in properties when exchanging Al to another A-group element and to move on with other transition metals instead of Ti or Sc. Together with the help from theoreticians I am sure we will better understand the mechanisms for why phases form or not.

One problem which always shows up when doing reactive sputtering with low N contents is that low N partial pressures is very difficult to regulate practically. A small deposition parameter change yields another stoichiometry in the film and results that are not comparable to each other. Constant calibration with ion beam analysis measurements is therefore required, an equipment that unfortunately not is available in Linköping, making it a lengthy procedure.

It might appear easy just to tune the deposition parameters and design the phase you want to have. If it would only be that easy! The day when I feel that I have understood all the competing mechanisms in reactive sputtering of ternary nitrides – that day I think it is time to do something else.
7. REFERENCES


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