Metastable YAlN and ScAlN thin films: growth and characterization

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Abstract

Sc$_x$Al$_{1-x}$N and Y$_x$Al$_{1-x}$N thin films were deposited in a ultra high vacuum system using reactive magnetron co-sputtering from elemental Al, Sc and Y targets in Ar/N$_2$. Their mechanical, electrical, optical, and piezoelectrical properties were investigated with the help of transmission electron microscopy, x-ray diffraction, ellipsometry, I-V and C-V measurements, and two different techniques for piezoelectric characterization: piezoresponse force microscopy and double beam interferometry. Compared to AlN, improved electromechanical coupling and increase in piezoelectric response was found in Sc$_x$Al$_{1-x}$N/TiN/Al$_2$O$_3$ structures with Sc content up to x=0.2. Microstructure of the films had a stronger influence on piezoelectric properties than the crystalline quality, which affected the leakage currents. Y$_x$Al$_{1-x}$N thin films show a formation of solid solution up to x=0.22. Lattice constants obtained experimentally are in good agreement with theoretical predictions obtained through first principle (ab initio) calculations using density-functional formalism. The mixing enthalpy for wurtzite, cubic, and layered hexagonal phases of the Y$_x$Al$_{1-x}$N system was also calculated.
Preface

The work presented in this Licentiate Thesis is a part of my PhD studies in the Thin Film Physics Group at Linköping University. The aim of my research is to gain new knowledge in synthesis and characterization of novel wurtzite AlN-based materials with enhanced piezoelectric and other application-significant properties. My research was financially supported by Linköping University, the Swedish Research Council, European Research Council, and Swedish Foundation for Strategic Research.
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My family and friends, and most of all – my sambo Martin, for your love and for making me smile every day.
Included papers

Paper 1

*Increased Electromechanical Coupling in w-Sc$_x$Al$_{1-x}$N*

Gunilla Wingqvist, Ferenc Tasnádi, Agnė Žukauskaitė, Jens Birch, Hans Arwin, and Lars Hultman


Paper 2

*Microstructure and Dielectric Properties of Piezoelectric Magnetron Sputtered w-Sc$_x$Al$_{1-x}$N Thin Films*

Agnė Žukauskaitė, Gunilla Wingqvist, Justinas Pališaitis, Jens Jensen, Per O. Å. Persson, Ramin Matloub, Paul Muralt, Yunseok Kim, Jens Birch, Lars Hultman

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Paper 3

*Y$_x$Al$_{1-x}$N Thin Films*

Agnė Žukauskaitė, Christopher Tholander, Justinas Pališaitis, Per O. Å. Persson, Vanya Darakchieva, Nebiha Ben Sedrine, Ferenc Tasnádi, Björn Alling, Jens Birch, Lars Hultman

*Manuscript in final preparation*
Related papers

Paper 4

Wurtzite Structure Sc$_{1-x}$Al$_x$N Solid Solution Films Grown by Reactive Magnetron Sputter Epitaxy: Structural Characterization and First-Principles Calculations

Carina Höglund, Jens Birch, Björn Alling, Javier Bareño, Zsolt Czigány, Per O.A. Persson, Gunilla Wingqvist, Agnė Žukauskaitė, Lars Hultman


Paper 5

Anomalously High Thermoelectric Power Factor in Epitaxial ScN Thin Films

Sit Kerdsongpanya, Ngo Van Nong, Nini Pryds, Agnė Žukauskaitė, Jens Jensen, Jens Birch, Jun Lu, Lars Hultman, Gunilla Wingqvist, Per Eklund

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1 Introduction

The ability to change surface properties by putting a thin coating on top of a material is not new. Already more than 1000 years ago ceramic glaze was used to decorate pottery as well as make it water-tight. Today, thin films can be found in many different corners of our everyday life. Some of them are used to prolong the lifetime of a cutting tool, others for decorative or optical purposes and many other applications are also possible. But while a lot of thin films can be considered a passive layer, there is also a wide spectrum of functional thin films that, not only change surface properties, but can actively interact with the environment.

An example of a functional property of a thin film is piezoelectricity. It enables a conversion between electrical and mechanical energy and is key to manufacturing of transducers and frequency filters – components of a standard mobile phone. This technology is based on a simple resonator – a piece of piezoelectric material between two electrodes. In thickness mode, a bulk acoustic wave (BAW) is reflecting between the electrode plates [1]. The resonance frequency is inversely proportional to the thickness of the piezoelectric material, so for high-frequency applications (for example telecommunications) thin films are needed. Such devices are called thin film bulk acoustic wave resonators (TFBAR). In the most common ladder filter configuration, several TFBARs with different resonant frequencies are connected in series. AlN is a well established material for such devices [2] because of its high electrical quality factor Q – allowing narrow and sharp frequency bands, as well as its compatibility with the manufacturing processes such as different material synthesis methods and photolithography.

The main focus of my research is functional AlN-based thin films. Alloying AlN with ScN has been shown to enhance the piezoelectric response [3]. The Sc<sub>x</sub>Al<sub>1-x</sub>N system is relatively unexplored, and a large portion of phase-stability and structural investigations in the full concentration range were performed here, in the Thin Film Physics division at IFM, Linköping University by Dr. Carina Höglund [4-7]. The next step – focusing on the dielectric properties and the
relationship between the microstructure and the piezoelectric response of AlN-rich ScAlN is presented in this thesis.

Sc$_x$Al$_{1-x}$N was a starting point and it opened doors to a completely new material system: Y$_x$Al$_{1-x}$N. Comparison between these two alloys gives a possibility to improve our understanding of film growth mechanisms in metastable materials.

1.1 Piezoelectricity

The phenomenon of piezoelectricity was discovered by Pierre and Jacques Curie in 1880. They noticed that some crystals start developing opposite charges on their surfaces when pressure is applied. According to Cady in Ref. [8] (published in 1946), the definition of piezoelectricity is: “electric polarization produced by mechanical strain in crystals belonging to certain classes, the polarization being proportional to the strain and changing sign with it”. This is the so called direct piezoelectric effect, while a converse effect is when the material is mechanically strained by an applied electric field. These two piezoelectric phenomena are interchangeable, so neither the direct nor the converse effect is more fundamental and the naming convention is historical [9]. Mathematically the relationships can be expressed as follows:

\[ P_i = e_{ij} \cdot S_{jk} \text{ (direct),} \]

\[ S_{ij} = d_{ijk} \cdot P_k \text{ (converse),} \]

where \( P \) is the polarization, \( S \) – the strain tensor, \( e_{ij} \) and \( d_{ij} \) are the piezoelectric coefficients, their units are pm/V or C/N. The first index \( (i) \) indicates the direction of the dielectric displacement, and the second index \( (j) \) – the mechanical deformation: if 3 corresponds to the polar axis, 1 and 2 would then refer to the orthogonal axes in the plane normal to 3 [10]. For example, \( d_{33} \) would mean that both electric field and mechanical deformation are observed along the same polar axis.

Piezoelectric materials are a sub-class of dielectrics. By definition, a dielectric material is an insulating material that does not conduct electric current, because unlike metals, a dielectric has no free (or loosely bound) electrons. Even so, electrical and optical properties of a dielectric material can be influenced by
applying an external electric field, causing polarization. This means that the charges inside the material will separate, but the displacement will be finite. The induced polarization $P$ will be parallel, and the displacement $D$ will be proportional to the electric field $E$:

$$P = \varepsilon_0 \cdot \chi_e \cdot E,$$

$$D = \varepsilon \cdot E,$$

where $\chi_e$ is called the electric susceptibility, $\varepsilon = \varepsilon_0 \cdot (1 + \chi_e)$ is the electric permittivity, $\varepsilon_0 = 8.85 \cdot 10^{-12} \, F \, m$ is permittivity of free space, and $\varepsilon/\varepsilon_0 = 1 + \chi_e$ is called the dielectric constant, or relative electric permittivity. A relative dielectric constant $\varepsilon_r = \varepsilon/\varepsilon_0$ is a material-dependent property and is further discussed in Section 5.3.2.

The ability of a material to have piezoelectric properties depends on its crystal structure while the actual extent of the piezoelectric effect is material-dependent. Out of 32 existing crystal classes 21 are non-centrosymmetric. All non-centrosymmetric crystal classes except the cubic class 432 have been identified as structures that would exhibit piezoelectric properties. 10 out of the remaining 20 are polar crystal classes, such as wurtzite, that demonstrate spontaneous polarization – a non-vanishing electric dipole moment resulting from the asymmetry in the unit cell [11]. Materials with such polar crystal structures also possess pyroelectric properties (becoming electrically charged when heated). Measuring the pyroelectric current is one of the ways to check if the material exhibits the spontaneous polarization. If the dipole moment can be reversed the material is called ferroelectric, one example is lead zirconate titanate Pb[Zr$_x$Ti$_{1-x}$]O$_3$, also known as PZT.

There are many different applications for piezoelectric materials and most of them can be divided into two groups: sensors and actuators. In the sensor applications, usually the direct piezoelectric effect is used for force, pressure, or strain detection. The converse piezoelectric effect is more useful for actuators – generation of surface or bulk acoustic waves (SAW, BAW) as well as resonant sensors where the resonant frequency of the material is changing when it interacts with the environment, for example – biological and chemical sensing applications.
Wurtzite AlN belongs to one of the above mentioned 10 polar crystal classes that exhibit spontaneous polarization. Compared to other group III nitrides it has the highest piezoelectric response: $e_{33} = 1.46 \, C/m^2$ [12] and $d_{33} = 5.1 - 6.72 \, pm/V$ [13-15].
This thesis is focused on ternary nitrides where group IIIA nitride AlN is alloyed with group IIIB nitrides ScN and YN (group numbering according to CAS nomenclature). In this chapter both binary nitrides used in alloying and resulting ternary nitrides are presented. A short section on TiN, used as a seed layer and a bottom electrode in Paper 1 and Paper 2, is included as well.

2.1 Sc-Al-N

2.1.1 AlN

Aluminium nitride in its wurtzite phase (Fig. 2.1) is a wide band gap (6.2 eV [16]) dielectric material. As a product of reaction between molten aluminum and nitrogen, AlN was discovered by F. Briegler and A. Geuther in 1862, and first synthesized by J.W. Mallets in 1877 [17]. Research into physical properties of AlN started in the late 1950s, especially in the field of insulating refracting materials. In those days, the main synthesis method was pressure or reactive sintering, resulting in a porous material. Low density issues were eventually solved by additives and the material quality improved tremendously. High-quality AlN with possibilities for electronic applications emerged in 1990s, and, to my knowledge, reactively sputtered AlN was first reported by J. Duchêne in 1971 [18]. It is known for its high temperature stability, and good mechanical properties. Moreover, its high acoustic velocity and dielectric qualities made it a popular choice in electroacoustic and optoelectronic applications [19].

Wurtzite AlN consists of two hexagonal close-packed lattices – one with Al, and another with N atoms that are displaced one from another vertically (see Fig. 2.1). Each Al atom is bonded tetrahedrally to four N atoms and vice versa. Such structure can be described by three parameters: lattice constant $c$, which is the height of the cell, lattice constant $a$, which is the edge length of the base, and $u$, which is the bond length between cation and anion (Al and N atoms) expressed in units of $c$. There is no inversion symmetry along the c-axis, and all group IIIA
nitrides (AlN, InN, and GaN) experience the spontaneous polarization described in Chapter 1. The bond length ratio is a very important and material specific parameter as it is related to the polarization strength. In the case of an ideal wurtzite crystal structure, $u = 0.375$. The theoretically predicted “real” AlN has $u = 0.382$ [20], experimentally obtained lattice constants found in literature are $a = 3.11 \text{ Å}$ and $c = 4.98 \text{ Å}$ [21]. As it was mentioned in the introduction, the piezoelectric coefficient $d_{33}$ for AlN is in the range of 5.1-6.72 pm/V – the highest value among group IIIA nitrides [22].

![Figure 2.1. Wurtzite structure of AlN.](image)

Since each atomic layer consists of only one type of atoms, the synthesized material can be terminated with either Al or N, so called Al-face or N-face. The growth polarity determines the direction of the previously mentioned spontaneous polarization. Different approaches and possible explanations on how to control the polarity, such as substrate and seed layer choice [23], growth parameters [24], or doping of the interface [25] are of great interest. Also, though this thesis is concentrated on polar (c-axis oriented) AlN based materials to promote the piezoelectric properties, there are applications such as light emitting diodes (LED), where the built-in polarization is limiting the recombination rate and thus the efficiency. There, a non-polar orientation of the material, for example with the growth direction perpendicular to c-axis, is preferred [26]. Another potential application for tilted AlN thin films is biosensors, where measurements are performed in liquid, so the shear mode wave propagation has to be promoted [27].

Under special conditions, zinc-blende structure AlN is possible, and at high pressures and temperatures AlN can also be synthesized in a cubic phase, for
example as epitaxial films onto Si substrates [28] or stabilized in a TiN/AlN superlattice [29].

In my research, the w-AlN films served mostly as a starting point for optimizing growth parameters and as reference samples during the characterization. Different aspects of using reactive magnetron sputtering for growth of AlN and related materials are discussed more in detail in Section 3.3.

2.1.2 ScN

Scandium is a group IIIB element and usually is considered to be a transition metal. In its most stable form, ScN has a cubic, rock-salt (NaCl) structure, shown in Fig. 2.2 (a), but recently a theoretical study showed an existence of metastable nearly fivefold coordinated layered hexagonal phase (h-ScN) [30], Fig. 2.2 (b). Cubic ScN has many properties common for all transition metal nitrides, such as high hardness and high-temperature stability. It is also a wide band gap semiconductor (2-2.4 eV according to Ref. [31]), and even thermoelectric properties were demonstrated experimentally [32].

![Figure 2.2. Cubic (a) and layered hexagonal (b) structures of ScN.](image)

2.1.3 Sc<sub>x</sub>Al<sub>1-x</sub>N

The main drawback of AlN that limits the scope of applications is its rather low piezoelectric response (as compared to more conventional piezoelectric materials such as PZT) and electromechanical coupling coefficient $k_{33}^2$. For these reasons, there is a growing interest in finding ways to improve this material, and one way do to that is by alloying and creating new, ternary, nitride materials. In 2009 Akiyama et al. in Ref. [3] reported a 400% increase in piezoelectric response by alloying AlN with ScN. Later, a theoretical study showed this increase to be an
intrinsic effect [33] caused by the aforementioned metastable fivefold layered hexagonal h-ScN phase which weakens the internal resistance against changing c/a ratio. In *Paper 1* it is shown that $k_t^2$ increases from 7% for AlN up to 10% for Sc$_{0.2}$Al$_{0.8}$N. Other research groups were successful in manufacturing and testing TFBAR structures with up to x=0.12 [34] and x=0.15 [35].

According to calculations in Ref. [5], alloying results in positive mixing enthalpies, which means that there is an internal driving force towards phase separation in this material, this is also seen experimentally. I show in *Paper 2*, however, that the phase separation can be reduced by decreasing the growth temperature from 800 down to 400 °C. Additionally, an increase in piezoelectric response up to 180% in Sc$_{0.2}$Al$_{0.8}$N as compared to AlN is demonstrated, thus confirming previously reported results from Ref. [3].

### 2.2 Y-Al-N

#### 2.2.1 YN

Yttrium belongs to the group IIIB, same as scandium, though according to different literature sources, its properties are closer to lanthanides than to transition metals. It is a highly reactive element.

YN can be synthesized in a cubic structure (same as Fig. 2.2 (a) for ScN), but contrary to ScN, forms oxide-hydroxides YOOH when exposed to moist air [36], hence a 5 nm thick capping layer of amorphous AlN is suggested by Gregoire *et al.* in Ref. [36]. Reported values for its direct band gap range from 1.5 eV [37] to 2.3 eV [38], and the indirect band gap of 0.498 eV was recently reported [39], in comparison to previously calculated theoretical values of 0.85 eV [40] and 0.54 eV [41]. Investigations of possible application for YN include buffer layer for GaN thin films [42], phase-stabilization of Cr-Al-Y-N coatings [43, 44], oxidation resistance of Ti-Al-N based coatings [45]. It was also demonstrated that AlN nanorods doped with Y possess ferromagnetic properties [46].
2.2.2 YxAl1-xN

Knowledge gained in alloying AlN with ScN was applied to grow ternary AlN-rich YxAl1-xN. Reactively sputtered YAIN thin films have not been reported before; previous investigations are limited to bulk YN-rich YAIN [47] and theoretical calculations of mixing enthalpies presented in relation to the Cr-Al-Y-N system [44]. The most similar material system investigated experimentally to this day is YxIn1-xN in Ref. [39].

Large volume difference between Al and Y means that mixing enthalpies for all investigated YxAl1-xN phases (cubic, layered hexagonal, wurtzite) are higher than those for ScAlN, as demonstrated in Paper 3. The calculations show that the wurtzite structure is the most favorable in the range 0<x<0.75. In comparison, ScxAl1-xN has the lowest mixing enthalpy for the wurtzite structure up to x=0.6 [5].

2.3 TiN

In order to do electrical and piezoelectric characterization of the ScAlN films a bottom electrode serving as a seed layer is needed. Reactively sputtered TiN ($d_{001} = 3.00 \text{ Å}$) thin films were chosen because of a rather good lattice match to AlN ($a = 3.11 \text{ Å}$) and good electrical conductivity. Epitaxial and smooth films with rocking curve full width half maximum values (FWHM) ≤0.05° were achieved by depositing films at $T_s=800 \text{ °C}$ in Ar/N$_2$ gas mixture with rather low nitrogen partial pressure. The crystalline quality was evaluated using X-ray diffraction (see Section 5.1.1); the surface roughness and topography of the films were investigated using atomic force microscopy (see Section 5.1.3) and scanning electron microscopy. The TiN films proved to be very sensitive to Al$_2$O$_3$ surface contaminations, so special precautions had to be taken during the substrate preparation.
3 Synthesis

Generally speaking, thin films are synthesized by first transferring source material into gas phase. While in gas phase, the material is transported towards the substrate where it condenses and forms a thin film. Deposition techniques are usually divided into physical vapor deposition (PVD) and chemical vapor deposition (CVD). In the first group, a solid to gas phase transformation is done through heating or sputtering, while in the second one the vapor is created and film is formed through chemical reactions [48]. In this thesis all material synthesis was performed by PVD processes.

3.1 Physical vapor deposition

Physical vapor deposition is a term that includes techniques for synthesizing thin films where source material is transformed into gas through a physical process. It can be done through heating (thermal evaporation), high power arc discharge (cathodic arc deposition), ablation of a target with a pulsed laser (pulsed laser deposition) or sputtering, where material is turned into vapor through ion bombardment of a target (the source) (sputter deposition).

All thin films discussed in this thesis were deposited using reactive DC magnetron sputter deposition, described more in detail in the next section. Thermal evaporation was used to deposit Cr/Au electrodes on top of the films for electrical characterization (Paper 1 and Paper 2).

3.2 Reactive DC magnetron sputtering

Sputtering is a PVD technique where a target is bombarded by ions. First reported by Grove in 1852 [49] it is now one of dominating processes in the vacuum coating industry. The main advantage of using this technique is operating away from the thermodynamic equilibrium conditions so the metastable materials or material phases can be synthesized and investigated.
The ions are generated in plasma, which ignites when gas is introduced into the vacuum chamber and a negative potential $U$ is applied to the target. This is possible because there are always some ionized gas atoms and free electrons available due to natural cosmic radiation. The ions are accelerated towards the target while more gas atoms are ionized through collisions with free electrons. When the ions collide with the target surface, target atoms are ejected (sputtered) and transported through the chamber towards the substrate. At the same time secondary electrons are produced, consequently ionizing more and more gas. The amount of these secondary electrons is directly related to the ionization rate. A set of permanent magnets can be placed behind the target to trap the secondary electrons close to the target surface, thus enhancing the sputtering process. Another advantage of such configuration is that lower gas pressure is needed for plasma ignition and maintaining of a stable process. The described film deposition method is called magnetron sputtering and it is one of the most common sputtering techniques used today. Trapping electrons with the help of a magnetron was first suggested by Penning in 1935 [49]. Based on the manner of how the negative potential is applied onto the target, different magnetron sputtering modes are possible, such as direct current (DC), pulsed DC, radio frequency (RF) and high power impulse magnetron sputtering (HIPIMS).

Figure 3.1. Magnetron sputtering process: (a) magnet configuration and species participating in the sputtering process, (b) schematics of a vacuum chamber. N and S represent magnetic polarity, “+” stands for the sputtering gas ion, “−” is a free electron, and “T” is the ejected target atom.
In Fig. 3.1 the magnet configuration and the main components of a magnetron sputter deposition chamber are depicted. The target is shown to have a so called erosion track where more material is sputtered due to higher density of magnetic field lines trapping more secondary electrons and attracting more gas ions (Fig. 3.1 (a)). Magnets can be arranged in different ways, for example, a large ring-shaped magnet and a small magnet in the middle, in other constructions the large ring is replaced by small magnets distributed in a circle. During the sputtering process the magnetrons heat up and have to be cooled (not shown in the figure), otherwise the magnets can overheat and lose their magnetic properties. Quite often the chamber walls are cooled as well to improve the vacuum level by cold-trapping residual gases. The schematic drawing in Fig. 3.1 (b) shows only one magnetron positioned directly in front of the substrate. In reality, deposition chambers are often equipped with two or more tilted magnetrons with the sample positioned in a common focal point, thus allowing co-sputtering from several targets. By changing the applied power (or voltage) the amount of sputtered material can be varied to obtain samples with different compositions. Samples from Paper 1 and Paper 2 were deposited in a deposition chamber with 3 magnetrons, and for samples presented in Paper 3 another deposition chamber, equipped with 4 magnetrons, was used. When using multiple magnetrons, substrate rotation becomes an essential condition to obtain homogeneous films.

The most common gas used in a sputtering process is argon. Due to its inertness it does not interact with sputtered atoms chemically allowing using it with any kind of target material. However, under some conditions, for example when bias voltage is applied onto the substrate or the distance between the target and the substrate is relatively short, it can be mechanically trapped in the resulting thin film and affect its morphology [50-52]. In addition to argon, reactive gases such as oxygen or nitrogen can be introduced into the chamber. They react with the sputtered atoms both on the target and on the film surface thus forming a compound material, for example, a nitride. Such process is called reactive magnetron sputtering. It was first introduced by Veszi in 1953 to deposit tantalum nitride thin films [49]. The main problem with reactive sputtering is target poisoning: reactive gas reacts with the target surface and forms an insulating
layer that charges up and shields the electric field thus reducing the sputtering rate dramatically. This phenomenon is more common when dealing with oxygen and is usually solved by using RF magnetron sputtering. In the case of nitrides reactive DC magnetron sputtering is possible using even pure nitrogen as process gas.

3.3 Growth of binary and ternary AlN-based thin films

There are three possible structures in a solid material: amorphous, polycrystalline, and crystalline. In an amorphous material atoms are arranged in a random fashion – long-range order is lacking and no periodicity in the structure is observed. Single-crystal material has the highest level of order, as there are no grain boundaries and the entire sample is one uninterrupted crystal lattice. Polycrystalline material is composed of crystallites of varying size and can have a preferred orientation (texture). In my research, the most common type of structure was a polycrystalline film with a single preferred orientation: a c-axis oriented wurtzite. With high enough amounts of Sc or Y the films had no preferred orientation and consisted of small, randomly oriented grains.

What kind of structure will form during the deposition process depends on a large number of factors. They can be 1) process specific, such as substrate temperature and bias, magnetron power and operating mode, gas pressure and composition, as well as vacuum quality; 2) substrate specific – surface morphology, composition, contaminations, crystal orientation; 3) film growth specific – type of material, lattice mismatch with the substrate or seed layer, surface mobility of adatoms, preferred nucleation sites and so on. It is not the scope of this thesis to explain all these factors, but to discuss general trends that are of importance when dealing with AlN, ScAlN, and YAlN thin films.

1) AlN:

When using reactive DC magnetron sputtering, the stoichiometric wurtzite AlN is not difficult to form, but the film orientation, crystalline and microstructural quality depends on the factors mentioned above. In general, piezoelectric and other application-significant properties of AlN, and other group
III-nitrides are very sensitive to oxygen contamination [53], so ultra high vacuum (UHV) is preferred together with using gas purifiers and high purity elemental targets. The substrates should be thoroughly cleaned and thermally degassed prior to the deposition.

In my work, the properties that were used as indicators of quality improvement were the increase of AlN 0002 peak intensity in X-ray diffraction θ/2θ scan (see Section 5.1.1), decrease of ω-FWHM value, and the decrease of the roughness observed in the atomic force microscopy (see Section 5.1.3). It is known that high ad-atom mobility is needed for epitaxial growth of the stable binary wurtzite phase [54]. At lower total gas pressures the sputtered species arrive at the substrate with higher energies. Additional energy is supplied by substrate heating. It is also known that high partial pressure of N₂ reduces the adatom mobility. This explains why the best results were obtained when the growth temperature was higher than 600 °C [55] and using Ar/N₂ mixture at relatively low pressures and low N₂ content as compared to the depositions at higher process pressures or depositions in pure N₂ that resulted in increased surface roughness. The samples discussed in Paper 1 and Paper 2 were deposited at a floating substrate potential, and in Paper 3 substrate dc bias of -30 V was applied.

Thin amorphous AlN capping layers (see YAlN) were deposited at 150 °C using no applied substrate bias and 10 mTorr N₂ process pressure, thus preventing crystallization.

2) ScAlN:

As mentioned in Section 2.1, alloying ScN with AlN results in positive mixing enthalpies. For this reason the ScₓAl₁₋ₓN films are considered to be metastable. The amount of Sc in the films is controlled by adjusting the relative applied target power. Total Al+Sc power was kept constant at 150 W. Growth experiments were performed at different temperatures, ranging from room temperature up to 800 °C. Films deposited at 400 °C proved to possess the best characteristics such as high crystalline quality and low leakage currents and for these reasons they are the main focus in Paper 1 and Paper 2. Based on the fact that films deposited at higher temperature showed indications of mass separation into ScN-rich and AlN-
rich domains, it is possible that the kinetic energy of incoming species is too high when $T_s \geq 600$ °C, resulting in an increased mobility on the film surface. The effect of an applied substrate bias in combination with lowering the growth temperature is yet to be investigated.

3) YAlN:

The experiments were performed in a UHV chamber equipped with 3” Al target and 2” Y target. The Y concentration was controlled in the same manner as Sc in the ScAlN films, but now the total Al+Y power was kept at 350 W. Yttrium has a much larger atomic volume and is known for poor stability in air, consequently new challenges and problems arise compared to growth of ScAlN. A thin layer of amorphous AlN was deposited on top of the films prior to exposing them to atmosphere for protection against oxidation. The time of flight elastic recoil detection analysis (ToF-E ERDA, see Section 5.2.2) results presented in Paper 3 proved it to be effective. However, the elemental target itself contained a lot of impurities such as O, F, Cr, and possibly W which are transferred into the films. It has been previously reported that even during the growth of pure YN yttrium acts as a getter for residual gases [42]. This resulted in a substantial amount of oxygen (up to 1-2 at.%) and fluorine inside the present films increase with the Y concentration.

The growth experiments led me to conclude that the crystalline quality of the $Y_xAl_{1-x}N$ films improved with temperature, which is an opposite trend from the one observed in $Sc_xAl_{1-x}N$. 
4 Modeling

Our theoretical understanding of materials is constantly improving. At the same time, computers get cheaper and more powerful, while experimental resources become more expensive. For this reason, theoretical calculations and modeling are often used in a search for new stable phases, predicting materials with enhanced properties, as well as to explain the formation of metastable thin films and the driving forces inside them.

Ternary nitrides are not an exception. All theoretical results discussed in this thesis are based on first principle (ab initio) calculations within density-functional theory (DFT) using the Vienna Ab Initio Simulation Package (VASP), which utilizes the Projected Augmented Wave (PAW) method, together with the General Gradient Approximation (GGA) pseudopotential. The calculations are done in an iterative fashion where, after initial setting up of a structure, energy minimization and structure relaxation are performed, optimizing the parameters at every cycle until desired accuracy is achieved. In order to accurately model the randomness of pseudobinary $A_xB_{1-x}C$ alloys the special quasi-random structure method (SQS) is used [56]. In ternary Sc$_x$Al$_{1-x}$N and Y$_x$Al$_{1-x}$N it results in the ordered nitrogen sublattice, while in the metal sublattice the Al and Y or Sc atoms are distributed in a structure that best reproduces the short-range ordering of a random alloy, but keeping the typical bond length – a rather realistic representation of such material system. The drawback of using SQS is that supercells have to be relatively big (for example 128 atoms) to obtain reliable results, which increases the calculation time. For binary alloys such as AlN, ScN or YN, the modeled cells can be much smaller as no randomization is needed.

Theoretical calculations can be based on empirical data. However, the experimental outcome can be influenced by many different factors, thus affecting the reliability and accuracy of such modeling. When ab initio calculations are utilized, no experimental data is needed as a starting point. Instead, one starts with the Schrödinger’s equation. As it is not possible to directly solve it for more than two particles, certain approximations have to be used. One of the most
common approaches is the DFT formalism where the properties of a system can be
described by electron density functionals [57] – considering the nuclei to be
immobile and using only the average number of electrons at a point in space to
calculate all other properties. For developing this method, a Nobel Prize in
Chemistry was awarded to W. Kohn in 1998.

Ab initio calculations are often used for Ti-Al-N and other related systems.
Sc$_x$Al$_{1-x}$N has also received quite a lot of attention. Results from mixing enthalpy
calculations for a cubic, hexagonal and wurtzite structures as well as lattice
constants are presented and described in detail in Ref. [5, 7, 58]. Y$_x$Al$_{1-x}$N results
from collaboration with Theoretical Physics division are presented in Paper 3. The
accuracy of theoretical calculations depends on correct selection of exchange
correlation functional and pseudopotentials. In the case of Paper 3, the GGA
approximation was used and resulted in a slight overestimation for predicted
lattice constants.

4.1 Phase stability predictions

Sc$_x$Al$_{1-x}$N and Y$_x$Al$_{1-x}$N are called metastable materials because their mixing
enthalpy $\Delta H_{\text{mix}}$ (increase in the total energy of the system) is $>0$ and higher than
for the binary AlN, ScN and YN in their ground-state structures (wurtzite AlN,
cubic ScN and cubic YN). Reactive sputtering allows synthesizing different alloys
away from the thermodynamic equilibrium, so even metastable phases can be
obtained. A metastable material also means that there is an internal driving force
towards phase separation into domains with different crystal structures or
compositions, e.g., into AlN-rich and ScN-rich or YN-rich domains, which can be
controlled by adjusting the deposition parameters such as growth temperature
(Paper 2).

Using ab initio calculations mixing enthalpies vs. elemental concentrations in
the alloy can be obtained for different crystal structures. An example is presented
in Fig. 4.1 (adapted from Paper 3), where comparison between Sc$_x$Al$_{1-x}$N and
Y$_x$Al$_{1-x}$N mixing enthalpies is presented. This graph tells us several things. First of
all, as expected, all investigated structures have positive $\Delta H_{\text{mix}}$. Second, the
wurtzite structure should dominate when $x<0.75$, and afterwards the cubic structure would be more preferred. We can also see that the layered hexagonal structure is never the lowest in mixing enthalpy. These observations give a hint on what to expect when trying to produce $Y_xAl_{1-x}N$ thin films in the deposition chamber. An initial experimental study, presented in Paper 3, shows that while at low Y concentrations the film is c-axis oriented wurtzite with some epitaxial relationship to the substrate, already at $x=0.22$ the material becomes highly polycrystalline and without any preferred orientation.

Figure 4.1. Mixing enthalpies for wurtzite, layered hexagonal and cubic $Y_xAl_{1-x}N$.

4.2 Expected properties

Apart from the preferred material phase and its stability, other physical properties of the materials can also be acquired from the theoretical calculations. In the scope of this thesis lattice constants and piezoelectric coefficients are of interest. Experimental and theoretically predicted lattice constants values of Sc$_x$Al$_{1-x}$N were presented by C. Höglund et al. in Ref. [5]. A similar study for $Y_xAl_{1-x}N$ can be found in Paper 3. Calculations of the piezoelectric response $d_{33}$ for Sc$_x$Al$_{1-x}$N are based on values from Ref. [33], a comparison with experimental data is presented in Paper 2 (see Sections 5.3.3 and 5.3.4).
5 Characterization

5.1 Structural and mechanical properties

5.1.1 X-ray diffraction

When x-rays interact with a solid material, electrons around the atom start to oscillate with the same frequency as the incoming beam. In the case of a crystalline material where the atoms are arranged in a periodic manner the constructive interference of x-rays leaving the sample in certain angles will form a diffraction pattern [59]. Bragg’s law is used to define relationship between angle \( \theta \) of incident (and diffracted) beam and the atomic plane spacing \( d \) (Fig. 5.1 (a)):

\[
n \cdot \lambda = 2 \cdot d_{hkl} \cdot \sin \theta, \tag{5.1}
\]

where \( \lambda \) is the x-ray wavelength, \( hkl \) are Miller indices defining an atomic plane and \( n \) is an integer. For a hexagonal (wurtzite) crystal system, the following equation is valid:

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + l^2}{a^2} \right), \tag{5.2}
\]

where \( a \) and \( c \) are lattice constants. A similar equation is available for cubic crystal as well:

\[
\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}. \tag{5.3}
\]

Because the wavelength of x-rays is comparable to spacings between atoms, the beams leaving at angles fulfilling Bragg’s law are of high intensity and are easy to detect. They are called Bragg reflections. This is the physical principle of the X-ray diffraction (XRD) – a non-destructive and versatile measurement technique used to evaluate crystalline materials. It can be used to determine phase of the material, crystal orientation, lattice constants, grain size, thickness and other properties as well as for estimation of crystalline quality.

In this thesis different XRD techniques were employed to determine 1) crystal orientation of thin films and crystalline quality, 2) phase and epitaxial
relationship between substrate and the film, 3) lattice constants, and 4) film thickness:

1) One of the most common techniques is the $\theta/2\theta$ x-ray diffraction measurement, where $\theta_{in}=\theta_{out}$ and are continuously changed to record Bragg reflections from atomic planes oriented parallel to the sample surface (Fig. 5.1 (b)). An example of such scan is Fig. 2 in Paper 1 where XRD was used to characterize AlN and ScAlN thin films. The position of the peaks can be used to determine the crystal orientation and for lattice constant calculations. At the same time, the intensity of the peaks in the XRD spectra is used to evaluate quality of the films. Narrow XRD peaks indicate a material with high crystalline quality. To get a quantitative estimation of the quality, from a rocking curve measurement around the selected peak position a full width half maximum (FWHM) value can be calculated.

![Figure 5.1. Principles of x-ray diffraction: (a) Bragg's law, (b) schematics of a Bragg-Brentano diffractometer.](image)

2) $\theta/2\theta$ measurement is limited to diffraction from atomic planes parallel to the sample surface, therefore, in some cases, other techniques have to be used to obtain information about the structure of the samples. To determine phase, preferred orientation or epitaxial relationship between the substrate and the film pole figures can be recorded. The measurement is performed at a fixed $2\theta$ value and the angular orientation of the sample is changed through changing azimuth angle $\phi$ and tilt angle $\psi$. 

20
3) Peak positions in $\theta/2\theta$ scans can be used to extract the lattice constants. But if the film is c-axis oriented, only the $c$ parameter will be quantified. To obtain in-plane lattice constant, so called asymmetric XRD scans (where incoming beam angle is not the same as the reflected one) have to be performed to obtain reflections from inclined planes. In the case of AlN, the $105$ reflection is used quite often.

Figure 5.2. An XRR scan of AlN film. Using the eq. (5.4) the thickness was determined to be ~320 Å, while fitting the data in WinGixa software resulted in $t=306$ Å.

4) X-ray reflectivity (XRR) measurements can be used to determine the thickness of deposited films in the thickness range of 0.1 to 100 nm [60]. When working with ternary alloys the growth rate varies for different concentrations and different process pressures. The thickness measurements are very important in the electrical and optical characterization, where the film thickness is used for the calculations of relative dielectric constant $\varepsilon_r$ (Section 5.3.2), or band gap determination (Section 5.3.1) so for accurate results and comparison it is best to have the same thicknesses for all samples in question. Though this measurement can be carried out with the same experimental setup as $\theta/2\theta$ measurements, this is not a diffraction technique, but instead is based on change in refractive index when x-rays pass from air into a solid material at $\theta$ values in range of 0.5° to ~5°. There are several different approximations, valid for low angles [21] is:

$$\Delta\theta = \frac{\lambda}{n\cdot t}, \quad (5.4)$$
where $\lambda$ is the wavelength of x-rays, $\Delta \theta = \theta_{m+n} - \theta_m$ is the angle difference between peak positions of the fringes in radians, $n$ is the number of fringes between $\theta_{m+n}$ and $\theta_m$, and $t$ is the thickness of the film. An example of an XRR scan is shown in Fig 5.2. For more accurate results, other methods are recommended, such as plotting $\sin^2 \theta$ against $n^2$ from a modified Bragg law:

$$n \cdot \lambda = 2 \cdot t \cdot \sin \theta \sqrt{1 + \frac{\eta^2 - 1}{\sin^2 \theta}},$$

(5.5)

where $n$ is a number of a peak, and $\eta$ is a complex refractive index of the film. The slope of the plotted line is equal to the film thickness $t$. As the XRR data can be influenced by density and surface roughness of the films, it is also recommended to use fitting software, such as WinGixa, for additional accuracy and information about the material. In my experience, the difference between manual calculation and simulation is larger for thicker films.

Of course, in nature, the crystal structure of a thin film is seldom perfect. There are many different factors, for example grain size or defects that can influence the height, the shape and the width of the peaks. Strain and stress in the film affect the crystal lattice constants and XRD peak positions change. In the case of thickness measurements, surface roughness and density of the film also contributes to the end result.

### 5.1.2 Transmission electron microscopy

The idea of a transmission electron microscope (TEM) was first proposed and the term was first used in 1932 by Knoll and Ruska, who later received a Nobel Prize [61]. The main motivation was to improve the resolution which in the ordinary visible-light microscopes was until then limited by the wavelength of visible light to 300 nm. The theoretical resolution limit for TEM using, for example, 100 keV electrons is 4 pm [61]. In reality, the resolution is limited by imperfect electron lenses and other instrument-related issues and is of the order of 1 Å. Depending on the operation mode, TEM makes it possible to obtain bright field (BF), dark field (DF), or atomic-resolution images (high resolution TEM, (HRTEM)), diffraction patterns from nanometer-scale regions (selected area
electron diffraction (SAED) pattern), and spectroscopic information (scanning TEM or (S)TEM coupled with energy dispersive X-ray spectroscopy or EDX). All these data are especially important when dealing with metastable phases and piezoelectric materials, where microstructure and crystalline quality have influence on other properties.

The principle of operation of the TEM is based on electrons accelerated by typically 200 kV potential and then focused using multiple electromagnetic lenses onto a very thin “electron-transparent” sample. When electrons travel through the sample, they can be transmitted or scattered. The transmitted and scattered electrons are focused again and projected onto a screen where an image is formed (Fig. 5.3). The scattered electrons can be used to obtain additional information about the sample, for example chemical composition.

![Figure 5.3. A schematic drawing of a basic TEM.](image)

Though supplying us with a lot of valuable information, TEM also has its drawbacks – complicated and destructive sample preparation, small sampling volume and the interpretation of results is not trivial.

In Figure 5.4 examples of images obtained with different operation modes are shown. By inserting an objective aperture or a selected area aperture (Fig 5.3) and by adjusting the strength of the intermediate lens one can switch between imaging and diffraction modes:
1) In the BF imaging mode, only the central transmitted beam is selected with the objective aperture, and the contrast is formed by mass-thickness and diffraction. Darker areas represent higher crystallinity, thicker sample and higher concentration of heavier atoms (Fig. 5.4 (a)).

2) In the DF mode the aperture is displaced so the central beam is blocked and the off-axis scattered (diffracted) beams can pass through. This way the most intensity comes from grains that have most defects or that are most misaligned, while voids and highly crystalline grains become dark (Fig. 5.4 (b)).

Figure 5.4. Images obtained using different operation modes of TEM: a) bright field and b) dark field overview images of Sc$_{0.2}$Al$_{0.8}$N ($T_s=800 \, ^\circ$C), c) high resolution image of AlN with $[2 \overline{1} 0]$ zone axis, d) selected area diffraction pattern of a Sc$_{0.2}$Al$_{0.8}$N ($T_s=400 \, ^\circ$C), with Al$_2$O$_3$ substrate, TiN seed layer and film diffraction spots marked.
3) Lattice resolved images can be obtained as a result of the phase contrast present at high magnification in HRTEM mode (Fig. 5.4 (c)). HRTEM micrographs are used for analysis of the crystal structure, grain boundaries, interfaces, stacking faults and other defects. The interpretation of phase contrast images is challenging since not only the sample structure, but also imaging conditions (defocus, astigmatism) affect the final image. An example of HRTEM image analysis can be found in Paper 2.

4) If instead of the objective aperture a selected area aperture is inserted and the strength of the intermediate lens is adjusted, a SAED pattern is projected onto the screen. In this mode it is possible to move the beam around the sample to obtain a diffraction pattern from different areas – if one wants to exclude diffraction spots from the substrate, for example. In Fig. 5.4 (d) a pattern with spots originating from the substrate, seed layer and film is shown. Spot broadening indicates degradation in crystalline quality, and for a random polycrystalline material the diffraction pattern would consist of rings instead. More indexed SAED patterns and descriptions of different features can be found in Paper 2.

5) STEM is a rather different TEM technique in the sense that a very narrow probe-like beam is used and the sample is scanned point by point. The high angle annular dark field (HAADF) detector can be used together with STEM to obtain information only from electrons scattered in certain angles. The intensity in HDAADF-STEM images depends on the atomic mass and the sample thickness. When STEM is combined with EDX, an elemental map of sample areas can be obtained, for example see Figure 5 in Paper 2.

5.1.3 Atomic force microscopy

Atomic force microscopy (AFM) is a scanning probe microscopy (SPM) technique used for topography analysis. It was developed in 1986 as a collaboration between Stanford University and IBM by Binning, Quate, and Gerber. In AFM the sample surface (or rather the adsorbed fluid layer) is probed
with a sharp tip located on an end of a cantilever. The cantilever is bent or deflected by forces between the sample and the tip. The deflections are measured by a 2D photodetector using a reflected laser beam. The information is then used by special software to generate a topographic 3D map of the sample surface. Depending on the distance between the tip and the sample, operation modes can be divided into three groups: a) contact mode, b) intermittent (tapping) mode, and c) non-contact mode. In my studies, tapping mode AFM was used for analysis of surface roughness, while piezoresponse force microscopy (PFM, see Section 5.3.3) was performed in contact mode.

In tapping mode the cantilever is oscillated at its resonance frequency, which is material as well as cantilever-dimension dependent. The amplitude can range from 20 nm up to 100 nm, and at each swing the tip lightly taps the sample surface. A feedback loop ensures a constant amplitude mode.

An example is shown in Fig. 5.5. In Paper 2, where test series with an alternative seed layer – ZrN, providing a better lattice match for ScAlN samples with higher Sc content were carried out. The expected improvement in crystalline quality was not observed, one of possible reasons could be a different surface topography.

![Figure 5.5. Surface topography of different seed layers: a) ZrN, b) TiN.](image)

The main advantages of the tapping mode AFM are lower damage possibility for both the sample and the tip as compared to contact mode, as well as better accuracy for large scan sizes as compared to non-contact mode [62].
5.2 Chemical composition

5.2.1 Rutherford backscattering spectrometry

Rutherford Backscattering Spectrometry (RBS) is a quantitative technique used for composition analysis of thin films, especially useful when dealing with heavy elements. RBS is based on a backscattering phenomenon when a light ion, for example He\(^+\), is elastically backscattered from heavier atoms in the sample. Depending on the atomic mass of the encountered atom and how deep in the sample it is located, the incoming ion (also known as projectile) would lose a certain amount of energy:

\[
E_1 = E_0 \cdot K_{\text{proj}},
\]

(5.6)

where \(E_0\) is the energy of the incoming ion, \(E_1\) – of the backscattered ion, and \(K_{\text{proj}}\) is so called kinematic factor that depends on atomic mass of incoming ion and atom of the sample it backscatters from:

\[
K_{\text{proj}} = \sqrt{\left[\frac{M_2^2 - M_1^2 \cdot \sin^2(\theta) + M_1 \cdot \cos(\theta)}{M_1 + M_2}\right]^2} = \left(\frac{M_2 - M_1}{M_2 + M_1}\right)^2
\]

(5.7)

if \(\theta=180^\circ\), which is a preferred position for the detector, although in practice the value of \(\theta\) is closer to 170\(^\circ\). \(K_{\text{proj}}\) is always less than 1.

The maximum sampling depth that can be reached with this method is \(~500\) nm. The energy of backscattered ions is measured with an energy sensitive detector.

Figure 5.6. Rutherford Backscattering Spectroscopy: a) measurement geometry, b) experimental (black dots) and simulated (grey line) results.
detector, used to record a spectrum with number of counts per energy channel. The recorded data is then compared to a simulated back-scattered spectrum in a special computer program, for example SIMNRA. An example of the (a) measurement geometry with incident ions of 2 MeV He⁺ along with a (b) RBS spectrum for a ScAlN/TiN/Al₂O₃ sample is shown in Fig. 5.6. A solid line represents the simulated data and the scatter – experimental results. From the intensity of the peaks the composition of this particular sample was found to be Sc₀.22Al₀.78N with a Ti₀.46N₀.51 seed layer.

Despite the fact that mass resolution is better for lighter elements, usually signals from light elements overlap with the substrate and become difficult to analyze. In practice, RBS is therefore employed mostly for the analysis of heavy target elements deposited on lighter substrates and other techniques should be used in combination with RBS to obtain more detailed information.

5.2.2 Elastic recoil detection analysis

When working with group III materials, contaminants such as oxygen have a strong influence on piezoelectric and electrical properties of the films [53]. Time of flight energy elastic recoil detection analysis (ToF-E ERDA) is another ion-beam based characterization technique used for determining the chemical composition of thin films. The main advantage with this technique is its sensitivity to light elements, as well as the ability to produce a depth profile.

![Figure 5.7. A typical ERDA depth profile of Sc₃Al₃₋ₓN/TiN/Al₂O₃ structure studied in Paper 2.](image-url)

Figure 5.7. A typical ERDA depth profile of Sc₃Al₃₋ₓN/TiN/Al₂O₃ structure studied in Paper 2.
Similarly to RBS, the sample is irradiated with an ion beam, but in the case of ERDA, the ions are heavier than the target elements in the sample, for example $^{127}$I$^{9+}$ and have much higher energy (10-100 MeV). Another difference is that while in RBS the back-scattered ions are detected, in ERDA the target atoms are kicked out by heavier ions and leave the sample in the forward direction ($0°<θ<90°$). By combining time of flight information together with the energy measurement the mass of the recoiled atom is measured and depth profiling is acquired [63].

For the same sample as in section 5.2.1, the composition inside the film was found to be Sc$_{0.21}$Al$_{0.77}$N$_{0.988}$ (F$_{0.002}$O$_{0.034}$C$_{0.0034}$), see Figure 5.7.

As mentioned in section 3.3, the elemental Y target contained unexpectedly high amounts of O and F. With help of ERDA it was possible to quantify the amounts in the grown films and a linear dependence on Y magnetron power suggests that the Y target was the main origin of the contamination.

5.3 Optical, electrical, and piezoelectrical properties

5.3.1 Ellipsometry

Ellipsometry is a non-destructive optical technique used to investigate dielectric material properties [64]. This technique is based on measuring a change in light polarization when it is reflecting from a surface. The name “ellipsometry” comes from analysis of the general polarization state of the reflected light wave, which is elliptic. In my research spectroscopic ellipsometry (SE) was employed for determination of high frequency dielectric constants of Sc$_x$Al$_{1-x}$N (Paper 1) as well as for band gap determination of Y$_3$Al$_{1.8}$N (Paper 3).

In SE the sample is irradiated by a light source with a known polarization and measured over a specific energy (wavelength) range. The change of polarization in the reflection is observed and expressed through two variables: amplitude Ψ and phase Δ. Depending on what material properties are analyzed, Ψ and Δ can be recorded as functions of wavelength or angle of incidence, or both, as in the case of Paper 3. A drawback of ellipsometry is that it is an indirect technique, which means that in order to determine sample properties calculations and fitting procedures for these two variables have to be performed and compared.
to the experimental data. In the case of a thin film an optical structure model has to be built including all components: substrate, seed layer, film, capping layer, and so on. To obtain reliable results the thicknesses of all layers have to be known and well defined.

### 5.3.2 Electrical characterization

Electrical characterization is a very important part of investigation of a potentially piezoelectric material. Dielectric constant, electromechanical coupling coefficient, leakage currents, and losses (dissipation) can be evaluated using current-voltage (I-V) and capacitance-voltage (C-V) measurements.

Au/Cr/Sc$_x$Al$_{1-x}$N/TiN/Al$_2$O$_3$ structures, as shown in Fig. 5.8, were used to determine how alloying affects the dielectric properties of the films as compared to pure AlN.

![Figure 5.8. A schematic layout of structures with a 100 nm thick TiN bottom electrode and a Au/Cr top electrode, 600 µm in diameter, used in the electrical characterization.](image)

C-V measurements are performed by applying a DC bias voltage onto the structure while making the measurements with an AC signal. The DC voltage is increased stepwise, the AC sweep is performed at each step and the capacitance $C$ is measured. Usually such measurements are performed at an AC frequency in the range of 10 kHz – 10 MHz. In measurements for Paper 1 and Paper 2 the DC voltage was changed from -5 V to 5 V by 1 V steps with AC amplitude of 100 mV at 1 MHz. Sometimes it is of interest to repeat the measurement at different frequencies to ensure the stability of a device.

For a perfect dielectric material, the result of such measurement would be a straight horizontal line – constant capacitance at each step of voltage, though in
reality usually there is a slight slope. From the C-V measurement, the relative dielectric constant $\varepsilon_r = \varepsilon / \varepsilon_0$ can be extracted:

$$C = \frac{\varepsilon_r \cdot A}{d} = \frac{\varepsilon_0 \cdot \varepsilon_r \cdot A}{d},$$

(5.8)

where $A$ is the area of the capacitor and $d$ is the thickness of a dielectric material between the plates (electrodes). In the case of structures shown in Fig. 5.8, the capacitor area was defined by the size of top electrode. The resulting dielectric constants are presented in Paper 1.

As mentioned above, another material property that can be obtained from such measurements is electromechanical coupling $k_t^2$. It is the ratio between electrical energy converted to mechanical energy and input electrical energy, or mechanical energy converted to electric energy and input mechanical energy [10], so in effect it is an efficiency of energy conversion in a piezoelectric material. Typical values found in literature for AlN are $\sim 7\%$. Using the following equation, where $e_{33}$ is the piezoelectric constant, $C_{33}$ is stiffness, and $\varepsilon_{33}$ is the dielectric constant of the material

$$k_t^2 = \frac{100 \cdot e_{33}^2}{C_{33} \cdot \varepsilon_{33}},$$

(5.9)

the electromechanical coupling for Sc$_x$Al$_{1-x}$N films was shown to increase up to $10\%$ with $x=0.2$ (Paper 1).

If a current is measured as a function of applied voltage, a current-voltage (I-V) characteristic can be obtained. For a good dielectric (insulating) material, a resulting plot should be a horizontal line at $I=0$ meaning that there was no current flowing between the electrodes. In reality the line is slightly tilted. This measurement can be used to determine if there are any leakage currents, then the current should increase with every step of the voltage. Such measurements were performed on the structures shown in Fig. 5.8 and the results are presented in Paper 2, Figure 6. In those Sc$_x$Al$_{1-x}$N samples the leakage current was increasing with increasing Sc concentration as well as with increasing growth temperature.
5.3.3 Piezoresponse force microscopy

Piezoresponse force microscopy (PFM) is another SPM technique. In general, it is rather similar to AFM (Section 5.1.3). The main difference is that in PFM the converse piezoelectric effect is used; an electric field is applied across the sample through a conductive tip. This causes an expansion or contraction of the material leading to surface vibrations. This way, instead of topography, a piezoresponse map is formed. These measurements are carried out in contact mode. The phase contrast of maximum 180° can be obtained if two domains are oriented normal to the sample surface but with the opposite polarity. Figure 5.9 is an example of such mapping done in two different samples. The polarity distribution of the (a) AlN sample seems to be rather uniform, while (b) ScAlN sample shows several distinctive areas where the phase is different than film average (bright and dark spots). It was later discovered that this particular ScAlN sample had oxygen content of >1 at.%, Data in the literature shows oxygen contamination usually has a detrimental effect on piezoelectric response and can cause a sudden change in polarity [53], which could explain the presence of such areas.

![Figure 5.9. Phase images obtained by PFM: a) AlN, b) ScAlN with elevated oxygen content.](image)

While this technique is very useful for verification of uniform polarization in the sample, the extraction of actual piezoelectric constants is complicated because there is always system-inherent background level present, as well as an electrostatic contribution from the surface charges. Also, the output signal is
usually rather noisy. If an AC modulation voltage $V = V_0 \cdot \cos \omega t$ is applied and the surface displacement $\Delta Z$ is measured through a standard lock-in amplifier set up, for the extraction of effective piezoelectric response $d_{33, eff}$ a following expression can be used:

$$\Delta Z = \Delta Z_0 \cdot \cos(\omega t + \varphi).$$

(5.10)

Here, $\Delta Z_0 = d_{33, eff} \cdot V_0$ is the amplitude and $\varphi$ is the phase difference between the voltage and the piezoresponse [65]. A more detailed review of this technique and recommended experimental parameters can be found in Ref. [66]. Piezoelectric response values in comparison to theoretical calculations and results obtained from double beam interferometry (DBI) technique (Section 5.3.4) are presented in Paper 2, Figure 7.

### 5.3.4 Other ways to determine the piezoelectric response

Besides the PFM, described in the previous section, there are many techniques to characterize a piezoelectric material. According to IEEE Standard on Piezoelectricity [67], none of them is considered to be a standard procedure because the choice is subject to various considerations, such as shape and size of the samples, and available instrumentation. Below, I discuss 1) principles for calculating the piezoelectric coefficient if other material properties are known and the techniques called 2) double beam interferometry (DBI), 3) piezometer, and 4) a new application for nanoindentation.

1) If the electromechanical coupling $k_T^2$, elastic coefficient $s_{33}^E$ and dielectric constant $\varepsilon_r$ are known, the piezoelectric response $d_{33}$ (applied electric field and the resulting strain along the c axis) can be calculated from the following equation:

$$d_{33} = k_T \sqrt{\varepsilon_0 \cdot \varepsilon_r \cdot s_{33}^E}.$$

(5.11)

Using eq. 5.11 does not include any non-linearity that occurs in some piezoelectric materials, and it is not valid in conditions close to the resonance frequency.

In the case of a thin film “clamped” onto a stiff substrate, for example sapphire, another expression is be used if piezoelectric constant $e_{33}$ and elastic stiffness $c_{33}^E$ are known:
where \( d_{33,f} \) is the so called clamped piezoelectric response. Eq. 5.12 was used to calculate a theoretical piezoelectric response of \( \text{Sc}_x\text{Al}_{1-x}\text{N} \) thin films in Paper 2, where values of \( e_{33} \) and \( c_{33}^E \) were taken from Ref. [33].

2) Another technique used in Paper 2 was the DBI. The main requirement from the sample preparation point of view is that both sides of the sample have to be reflective. With this requirement in mind, several structures, shown in Fig. 5.8, were deposited onto double-side polished sapphire substrates. Using this method a laser beam is split in two and guided towards back and front sides of the sample. When an electric field is applied between the top and bottom electrodes the mechanical displacement of the film is recorded through interference between a reference beam and the beams reflected from the sample. A more detailed description of the experimental set up can be found in Ref. [68].

3) A piezometer, where a sample is clamped and subjected to low frequency force while the electrical signal is recorded was used to characterize \( \text{Sc}_x\text{Al}_{1-x}\text{N} \) thin films by Akiyama et al. in Ref. [3]. Such piezometers are sometimes called “Berlincourt” piezometers or simply \( d_{33} \)imeters and were initially developed for bulk ceramic materials. Ref. [69] gives more details on the experimental set-up and suggested modifications for characterization of thin films.

4) New techniques are also emerging and development of new applications using already available equipment is of strong interest. One example could be nanoindentation – a common technique for determination of hardness and other mechanical material properties. Recently it was proposed to use nanoindentation to extract the piezoelectric response of thin films by applying a voltage through a conductive indenter tip across the sample to mechanically deform it and record the deformation with the same tip. The measurement of a direct piezoelectric effect is also possible by indenting the film and measuring the generated voltage as a function of load.
Other techniques are available too; in some of them free-standing membranes or cantilever structures are required. Most of these methods were developed for characterizing bulk ferroelectric materials like PZT, where the piezoelectric response is reasonably stronger than in the AlN as well as sample dimensions are much larger, so there can be issues with the sensitivity or producing thick enough samples. Common to the above, the main issue in piezoelectric characterization is that the extracted values of piezoelectric response using different techniques are diverse even for the same sample and a direct comparison is not feasible. A discussion on this issue and a suggested solution, in the case of Sc$_x$Al$_{1-x}$N, to compare values normalized to AlN are presented in Paper 2.
6 Current research and future plans

The field of alloying group IIIA and IIIB nitrides to obtain novel materials with improved properties relevant to electroacoustic and optoelectronic applications is wide and relatively unexplored. There is much to be done and I’m happy to be a part of it.

ScAlN was a starting point for my research. Here, looking at previously published work and my results presented in Paper 1 and Paper 2, it is clear that piezoelectric response is increasing with addition of Sc. However, phase instabilities and microstructural degradation cause additional problems compared to when dealing with binary nitrides such as AlN. An alternative approach to solid solution could be depositing AlN/ScN multilayers. The effect of applying a substrate dc bias in combination with lowering deposition temperature is also of interest. Additionally, a study of optical properties of ScAlN, similar to one presented in Paper 3 for YAlN, is planned.

Based on YAlN results presented in Paper 3 we see that the growth mechanism and phase instabilities are different compared to ScAlN. Additional studies to fully understand the differences are needed. Based on theoretical prediction, a strong increase in piezoelectric response is not expected, but other possible applications such as band gap tuning have to be investigated. As a side-track, a study on amorphous AlN, where the crystallization is hindered by alloying with low amounts of YN, would be very interesting.
7 Summary of included papers

Paper 1

Wurtzite Sc\textsubscript{x}Al\textsubscript{1-x}N thin films with x=0.1, 0.2, and 0.3 were deposited using reactive magnetron sputtering from two elemental targets onto Al\textsubscript{2}O\textsubscript{3}(0001) substrates with TiN(111) seed layers serving as bottom electrodes. The films were investigated from a structural and electrical point of view and compared to reference AlN samples. While the best crystalline quality of AlN was achieved at substrate temperature T\textsubscript{s}=800 °C, Sc-containing films deposited at the same temperature had high leakage currents and could not be used for the electrical characterization. For this reason, only ScAlN samples deposited at 400 °C were analyzed. XRD confirmed epitaxial growth for all Sc concentrations and lattice constants for x=0.1 and 0.2 were shown to match previously published theoretical values. However, the XRD response was too low to get accurate results for x=0.3. Au/Cr/ScAlN/TiN structures were used for electrical characterization and from the capacitance (C) the relative dielectric constant \( \varepsilon_r \) was extracted. These values, together with stiffness \( C_{33} \) and piezoelectric constant \( e_{33} \) found in literature were used to calculate the electromechanical coupling coefficient \( k_t^2 \) and an increase from 7% for AlN up to 10% for Sc\textsubscript{0.2}Al\textsubscript{0.8}N was obtained. High frequency dielectric constants \( \varepsilon_\parallel \) and \( \varepsilon_\perp \) were obtained by ellipsometry and compared to density-functional perturbation theory results.

Paper 2

Wurtzite Sc\textsubscript{x}Al\textsubscript{1-x}N thin films with x=0, 0.1, 0.2, and 0.3 were deposited using reactive magnetron sputtering from two elemental targets onto Al\textsubscript{2}O\textsubscript{3}(0001) substrates with TiN(111) seed layers serving as bottom electrodes at T\textsubscript{s}=400, 600, and 800 °C. XRD and TEM together with EDX mapping were used for evaluation of microstructure and crystalline quality of the films. I show that an increase in substrate temperature results in a degraded crystalline quality, while the
microstructure of the films is more sensitive to the increase of Sc concentration. Sc-containing samples deposited at 800 °C show signs of mass separation into AlN-rich and ScN-rich domains, which is more pronounced in samples with x=0.3. Electric characterization of the films show high leakage currents in samples with Tₙ>400 °C and piezoelectric characterization shows an increase in piezoelectric response by up to 180% for Sc₀.₂Al₀.₈N independently of growth temperature. Normalized results match well with experimental and theoretical values found in literature.

**Paper 3**

YₓAl₁₋ₓN thin films with x=0, 0.04, 0.13, and 0.22 were deposited using reactive magnetron sputtering from two elemental targets onto Al₂O₃(0001) and Si(100) substrates. Mixing enthalpy calculations showed wurtzite to be a preferred phase up to x=0.75, although energies for all phases are much higher than in the case of ScₓAl₁₋ₓN. TEM was used to perform a structural analysis showing a polycrystalline film and columnar growth. STEM and EDX mapping show no elemental segregation. XRD was used to measure lattice constants, comparisons with theoretical predictions show a good match indicating a solid solution. In general, the crystalline quality of the films is degrading with addition of Y. Increasing the growth temperature has a positive effect due to improved mobility of Y atoms, commonly considered as an element with a slow diffusion rate. Solid solution is confirmed by optical characterization, the direct band gap decreases down to 4.9 eV (as compared to 6.2 for pure AlN) for x=0.22.
8 References


