Thin Film Synthesis of Nickel Containing Compounds

ERIK LINDAHL
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Abstract

Most electrical, magnetic or optical devices are today based on several, usually extremely thin layers of different materials. In this thesis chemical synthesis processes have been developed for growth of less stable and metastable layers, and even multilayers, of nickel containing compounds.

A chemical vapor deposition (CVD) method for deposition of metastable Ni₃N has been developed. The deposition process employs ammonia as nitrogen precursor. An atomic layer deposition (ALD) process for deposition of both polycrystalline and epitaxial NiO and using low oxygen activity, has also been developed. Both deposition processes utilizes bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (Ni(thd)₂) as the metal precursor. The Ni₃N deposition proceeds via surface reactions. The growth rate is very sensitive to the partial pressure of ammonia, why adsorbed –NH₂ species are believed to be of importance for the film growth. Similar reactions can be expected between the metal precursor and H₂O. For ALD of NiO a large excess of water was needed.

For the multilayered structures of Ni₃N/NiO, growth processes, working at low activities of oxygen and hydrogen, are needed to avoid oxidation or reduction of the underlying layer. Chemical vapor growth methods such as CVD and ALD are often suffering from using high activities of hydrogen or oxygen to deposit metals and oxides. An alternative deposition pathway for metal deposition, without any hydrogen in the vapor, has been demonstrated. The metal has been formed by decomposition of the metastable nitride Ni₃N in a post-annealing process. Ni₃N decomposes via different mechanisms, depending on environment in the annealing process. The different mechanisms result in different degrees of ordering in the resulting Ni films. From the knowledge gained about the chemical growth of NiO and Ni₃N as well as the decomposition of Ni₃N, well-defined multilayer structures have been produced in different combinations of NiO, Ni₃N and Ni.

Keywords: Chemical Vapor Deposition, CVD, Atomic Layer Deposition, ALD, Nickel nitride, Nickel oxide, Nickel, Epitaxy, multilayer, Thin film

Erik Lindahl, Department of Materials Chemistry, Inorganic Chemistry, Box 538, Uppsala University, SE-75121 Uppsala, Sweden

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:


III Atomic layer deposition of NiO by the Ni(thd)$_2$/H$_2$O precursor combination. E. Lindahl, M. Ottosson, J.-O. Carlsson, *Chemical Vapor Deposition*, 15, (2009), (7-9) 186-191

IV Epitaxial NiO (100) and NiO (111) films grown by atomic layer deposition, E. Lindahl, J. Lu, M. Ottosson, J.-O. Carlsson, *Journal of Crystal Growth*, 311, (2009), (16), 4082-4088


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My contributions

Planning and performing film depositions in [I]-[V]. Film characterization and evaluation of data, except for the TEM analysis in [III] and the magnetic measurements in the thesis, operation of the SEM in [I][II][V] and operation of the XPS in [I]-[V]. Main author of the papers.
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## Abbreviations

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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<tr>
<td>cp</td>
<td>Cyclopentadienyl</td>
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<tr>
<td>FWHM</td>
<td>Full With at Half Maximum</td>
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<tr>
<td>Gi-XRD</td>
<td>Grazing incidence X-Ray Diffraction</td>
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<tr>
<td>In plane</td>
<td>The planes orthogonal to the surface</td>
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<td>Out of plane</td>
<td>The planes in parallel to the surface</td>
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<td>QMS</td>
<td>Quadropole Mass Spectrometer</td>
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<tr>
<td>RMS</td>
<td>Root Mean Square</td>
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<tr>
<td>RSM</td>
<td>Reciprocal Space Map</td>
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<tr>
<td>SQUID</td>
<td>Superconducting Quantum Interface Device</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<td>UHV</td>
<td>Ultra High Vacuum</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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<td>XRF</td>
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<td>XRR</td>
<td>X-Ray Reflectivity</td>
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1. Introduction

Transition metal nitrides are often associated with the stable nitrides formed by the metals in the far left of the periodic table of the elements (TiN, CrN, HfN and TaN etc.). These materials are used as wear resistant and decorative coatings, diffusion layers, electrical contacts etc and are thermally and chemically stable [1]. The stability of transition metal nitrides decreases to the right in the periodic table of the elements and when passing manganese the materials turn from stable to metastable compounds. Nickel for example, found to the right of the transition metals, forms metastable nitrides, and have been the focus in this thesis. The nickel nitride have some similarities with the other iron metals (Fe, Co), which all forms metastable nitrides, sharing the $M_3N$ composition and adopt the same $\varepsilon$-$Fe_3N$ type structure. The structure can be described by a distorted hexagonal closest packing of the metal where the nitrogen is ordered in octahedral interstices [2-4]. Except for the $Ni_3N$ composition also a $Ni_4N$ and a $Ni_8N$ composition is reported to be possible in the nickel nitrogen system [5]. Iron and cobalt nitrides are reported to have a larger diversity in compositions and the Fe nitrides can have compositions ranging from FeN to $Fe_{16}N_2$ [3, 6-8]. The cobalt nitrides show compositions from CoN to $Co_3N$ [4, 9, 10]. In general the iron metal nitrides are not very well characterized neither with respect to mechanical, electrical, nor magnetic properties. The data available in literature diverge somewhat especially for the magnetic properties. The divergent data is probably associated with the metastable nature of the materials which makes them difficult to synthesise without excess metal. Many of the $Co_xN$ phases are magnetic and much focus in literature have been on the magnetic properties [10, 11]. The $\varepsilon$-$Fe_3N$ nitrides are reported to be magnetic and the saturation magnetization is reported to decrease, when increasing the value of $x$ and disappears at room temperature at $x$ larger than 2.3 [12, 13]. There are also reports of very large magnetic moments in the $\alpha''$-$Fe_{16}N_2$ phase [14-17]. The nickel nitrides are probably the least studied of the iron metal nitrides. $Ni_3N$ is reported to be a metallic conductor but the magnetic properties are reported to be ferromagnetic by some and paramagnetic by others [18-22]. As mentioned above all the iron metal nitrides are metastable and decompose to the corresponding metal and nitrogen gas at elevated temperatures. The decomposition for $Ni_3N$ starts at about 300°C at inert conditions [11]. The decomposition temperature is also
atmosphere dependent and in hydrogen atmosphere, the decomposition proceeds via ammonia formation. The decomposition temperatures can be decreased to about 180°C for Ni$_3$N at 1 Torr H$_2$ [II]. Previous studies have shown a decomposition of Ni$_3$N to proceed via the ordered nickel nitrides Ni$_4$N and Ni$_8$N [5].

In nanotechnology in general and in the microelectronic industry, the dimensions of the materials layers are decreasing down to monolayer. Moreover, the shape of the substrates tends to increase in complexity. Growth of multilayer structures is also of importance in order to combine the properties of the individual layers into working devices. Chemical Vapor Deposition (CVD) and especially Atomic Layer Deposition (ALD) give possibilities to grow such layers [23]. One of the main drawbacks of these techniques is the lack of available metal deposition processes using low hydrogen activities [23,24]. The metastability of the M$_3$N materials can be employed for metallization at conditions where direct deposition of the metal by chemical vapor methods is not possible. For vapor growth deposition of nickel, normally either very toxic precursors like Ni(CO)$_4$ or high vapor pressures of hydrogen are used [24]. Sputtering or evaporation methods for direct deposition of nickel are simple but have some general drawbacks as will be pointed out later.

The easiest way of producing a bulk material of Ni$_3$N is by annealing of the metal or the metal oxide in an ammonia flow at atmospheric pressure at 380°C [25]. Thin film deposition of Ni$_3$N has so far been associated with techniques working far from equilibrium, e.g., ion implantation and sputtering [5,19,20,26-28].

Nickel nitride has been deposited by chemical vapor deposition as thin films in this thesis. Film growth kinetics as well as film decomposition have been studied [I,II]. The growth of Ni$_3$N is based on reactions between a metal-carrying precursor and ammonia. Similar reactions can be expected between the same metal-carrying precursor and adsorbed –OH groups on a substrate to form nickel oxide. Nickel oxide is a very well characterized material, which has been grown by almost every deposition method available. However, most of the vapor NiO deposition processes suffer from the requirements of high oxygen activities [29-31]. However, there are examples of processes, operating at low oxygen activities, for the production of amorphous NiO films [32] even though the largest interest is directed towards crystalline films. In this thesis a vapor growth process for deposition of both polycrystalline and epitaxial NiO films have been investigated [III,IV]. By using the same metal precursor for oxide and nitride growth, multilayer structures can be grown within the same deposition system without any large technical difficulties. The metastable nature of the Ni$_3$N and the low oxygen activities for NiO growth give the possibility to grow combinations of both Ni$_3$N/NiO structures as well as Ni/NiO structures. Ni/NiO layers are of interest for resistive switching, random access memories as well as in magnetic
read heads [33,34]. Multilayer growth can be associated with many problems such as formation of interlayers by diffusion across layer interfaces. When growing multilayers by chemical vapor growth techniques, there is an obvious risk of reduction of oxide layers by hydrogen or oxidation of metal layers by oxygen. The growth of NiO/Ni$_3$N and Ni/NiO structures has been studied in paper [V].
2. Method

2.1 Experimental

2.1.1. Deposition methods

Some general aspects of the most common deposition techniques, working either in vacuum or with flowing gases, are summarized below. Electrochemical and sol-gel techniques are left out.

Sputtering and evaporation techniques are based on highly reactive species (atoms or ions) reaching the surface of the substrate and reacting with other surface species to form the deposit. These methods are often regarded as physical methods. By controlling the flux of species towards the substrate surface and the process time, the amount and stoichiometry of the deposited material can be controlled. These techniques are standard techniques today in both industrial production and research. The main drawback with both the evaporation and sputtering techniques is that they are line-of-sight techniques, i.e., only the substrate surface, exposed to the flux of growth species, will be coated. For many applications uniform deposition in trenches or on complicated shaped surfaces is needed. For such applications the chemical vapor growth methods excels.

Chemical Vapor Deposition (CVD) is a deposition technique, which is widely spread in industry today for fabrication of a diversity of different materials. The technique is based on heterogeneous chemical reactions between gaseous molecular or atomic precursors, simultaneously delivered to the substrate to form a deposit.

The kinetics of the deposition process is dependent on deposition temperature, partial pressure ratios of the precursors and the linear gas flow velocity over the substrate surface. Since the materials growth is based on chemical surface reactions and all surfaces are exposed to the process gas, the step coverage is higher in CVD than when using the physical methods. Additionally, selective growth can be achieved on desired substrate areas depending on differences in nucleation behavior and in the rate limiting chemical reactions on different substrate areas. Depending on the linear gas flow velocity, temperature and precursor partial pressures the growth process can occur under different controls. Mass transport control is achieved at low flow rates where the growth is limited by the diffusion of precursors through a stagnant gas layer close to the substrate. Such a growth process has nor-
mally low activation energy. A process limited by the kinetics of the chemical surface reactions is often desired for good step coverage and good uniformity. Such a control is associated with high activation energy of the reaction. The precursor partial pressures do in CVD also affect the growth rate. The effect of partial pressure on the growth rate depends on the reaction order and must be evaluated for the reaction in question. For surface reactions, reaction orders of 0-1 are expected. In an ideal CVD process, a linear relationship between film thickness and deposition time is obtained. However the shape of the curve in Fig. 1 which will be further discussed below can be administered also to CVD processes.

An example of a process, similar to CVD of nickel, can be found as far back as 1885, when L. Mond described a transport reaction where nickel powder was exposed to CO (g) to form Ni(CO)4. By heating the flow of Ni(CO)4 and leading the gas through a glass tube, a nickel mirror was deposited on the glass wall [35]. However, the process has the drawback of the high toxicity of Ni(CO)4. In this thesis CVD has been used for growth of Ni3N films.

Atomic Layer Deposition (ALD) is a rather new technique and was developed by T. Suntola in the early 70th. He is regarded as the inventor of the technique [36]. ALD resembles the CVD technique in the sense that they are both based on heterogeneous reactions between a gas phase and adsorbed atomic or molecular species on a substrate surface. However, in ALD the reactants are pulsed sequentially and separated in time [37]. Both epitaxial [IV] and polycrystalline NiO films [III] have been grown by the ALD technique in this work.

An ALD pulsing sequence for growth of binary materials follows below:

- Precursor 1
- Purge 1
- Precursor 2
- Purge 2

The growth proceeds via in time separated reactions: During the precursor 1 pulse, a saturated adsorption layer of precursor 1 is formed, which means that at maximum one monolayer of precursor 1 is formed. Excess of precursor 1 and eventual reaction products are purged away during the purge 1 pulse. Precursor 2 reacts with the already adsorbed precursor 1 species to form the desired material and the surface is saturated by precursor 2. Reaction products and excess of precursor 2 is purged away during purge 2 pulse. By repeating the pulsing sequence above, the film is built up by at most one monolayer at each cycle. This makes the deposition process slow but because of the sequential self saturated growth, excellent control of the film thickness is obtained also on complicated surface structures and in deep trenches. As mentioned above, the growth is at maximum one monolayer film at each cycle but normally less since the limit is determined by the ad-
sorption of one monolayer of precursor molecules and not by a monolayer of film. Since the growth is self-saturating, the precursor partial pressures and linear gas flow velocities have ideally no effect on the growth, i.e., the film growth is only affected by the deposition temperature and the substrate surface [37]. The amount of deposited material as a function of deposition cycles is ideally linear. However, deviations from linearity might occur because of how the morphology evolves. If the surface area is increased by the growth, more adsorption sites are available and hence the growth will increase with the number of deposition cycles until the surface area is constant. During the initial growth, a slightly S-shaped curve can be formed. At first there are often nucleation problems. Once stable nuclei are formed, film on film growth occurs. The preferred film on film growth increases the surface area. As the film growth proceeds these initially formed grains will grow together, coalesce, to form a continuous film. The film surface area will then decrease and hence the growth/cycle decreases [38]. Normally after coalescence, the growth/cycle reaches a stable value due to the fact that a stable surface area is achieved. However, secondary nucleation might occur, leading to an increase in surface area, which means that the above-described scenario will repeat itself. A schematic drawing of how the S-shaped curve could look like can be found in Fig. 1.

Fig. 1. Schematic drawing of an S-shaped curve for the film thickness or amount of deposited film as function of the number ALD cycles.
2.1.2. Selection of precursors

Growth rate and risk of contamination of the film are dependent on the used precursor in both CVD and ALD. However, the requirements on the precursor are a bit different for the two techniques. In general precursors can be gases, liquids or solids at normal conditions. Gases are easiest to handle since they can be easily delivered to the reactor via mass flow controllers. Liquids, with a high vapor pressure, are also convenient to handle and the amount of precursor is easily controlled either by the temperature of the container they are kept in or by reducing the flow from the container by a needle valve. Solid precursors are sublimated by heating the solid. The amount of sublimated material is affected by the surface area of the solid precursor. This may change as the deposition experiment proceeds due to increase in crystallite size and crust formation after prolonged heating. In ALD another problem with solid precursors, associated with the pulsing, can occur. The gas pulsing may transport precursor particles from the precursor container to the substrate.

In CVD a large and stable precursor feed to the deposition zone is important, i.e., high vapor pressures are needed to achieve high growth rates. Highly reactive reactants can in CVD lead to homogeneous gas phase reactions which in some cases may lead to particle formation and poor adhesion to the substrate. In ALD on the other hand more reactive reactants can be used, because of the separation of the precursors in the process steps. However, the requirement of vapor phase stability is much higher for the ALD precursors. If the precursor decomposes upon heating in the gas or on the substrate surface, saturation can not be achieved and hence the benefits of ALD can not be reached.

Frequently used precursors are metal halides which usually can be easily vaporized. However, precursors for nickel deposition can not be found in this group due to the very low vapor pressures which would lead to unrealistic sublimation and deposition temperatures.

Other precursor molecules used are based on the cyclopentadienyl ligands \((\text{Me(cp)}_x)\), which are stable when combined with metals such as iron. However, from the 18 valence electron rule regarding stability of metal organic compounds, the nickel analogs should be unstable. Nickel cyclopentadienyls have been used for both nickel CVD and nickel oxide ALD. For nickel oxide growth, high activities of oxygen are needed for growth of films of high purity. Oxygen precursors such as ozone, oxygen or hydrogen peroxide are most frequently used [39-41]. CVD using cyclopentadienyl and hydrogen are often associated with high carbon contents. By tuning of the experimental parameters, films containing 3-4 atomic% carbon can be obtained at 175°C and 760 Torr H\(_2\) pressures [42,43].

A class of molecules, which are frequently employed for both CVD and ALD, are the metal beta-diketonates. The base compound is bis(2,4-penta-
nedionato)Ni(II), normally referred to as the M(acac)x. A drawing of the Ni(acac)2 molecular structure can be found in Fig. 2. For nickel oxide deposition, the Ni(acac)2 have been employed previously. For ALD growth of NiO the reactivity towards water is reported to be low and both the growth per cycle as well as the crystallinity is reported to be enhanced by use of O2 [29,30]. To be able to deposit nitrides, metals or oxides on top of easily oxidized materials such as metals, it is of course very important to keep the oxygen activity as low as possible why water is a suitable oxygen source. The Ni(acac)2 is reported to form trimers to give six coordinated nickel [44]. The presence of trimers may affect the sublimation and the stability of the evaporation process. By inserting other substituents to the α-carbon, the properties of the compound can be changed. For example, if highly electronegative substituents such as fluorine is introduced, a bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionate)Ni(II) (Ni(hfac)2) is formed (also shown in Fig. 2). The bond to the metal will be weakened because of the higher electronegativity of fluorine and hence the reactivity will be increased. The Ni(hfac)2 has been used as a precursor for nickel CVD at large excess of hydrogen [45].

The drive for nickel to form six coordinated compounds is observed also for Ni(hfac)2, which easily form a hydrate, difficult to get rid of in lab. The existence of a hydrate is troublesome since if water is supplied together with the metal precursor, means that ALD conditions cannot be reached. Also in these studies films free of oxygen has been deposited the Ni(hfac)2 is not a suitable candidate. One way of avoiding six coordination of nickel is to insert bulky substituents to the ligand, which sterically makes six coordination less favorable. The bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (Ni(thd)2) has bulky tertbutyl groups as substituents (see Fig. 2). The Ni(thd)2 has a reasonably high vapor pressure at moderate temperatures (165°C) and is stable on oxide surfaces up to about 290°C and to about 260°C on nickel surfaces.

![Figure 2](image-url)Fig. 2. Metal β-diketonates from left to right Ni(acac)2, Ni(Hfac)2 and the one used for film growth in this thesis, Ni(thd)2

There are only a few nitrogen-carrying precursors available for growth of nitrides and ammonia is by far the most used. In principle hydrazine can be used but for practical and safety reasons it is in most applications not an
option. Ammonia forms NHₓ species on the surface when adsorbed and reactions with NHₓ can be expected to be similar to the reaction with surface – OH groups, formed upon water adsorption.

The selection of the oxygen source for oxide deposition is in general based on the reactivity of the selected metal precursor. In literature there are several examples of the need for adsorbed -OH groups to make the β-diketonate precursors reactive on the surface [46,47]. In this study, the focus has been, as mentioned above, to use precursors with low oxygen activities, and therefore water has been used. The reaction between molecular hydrogen and β-diketonate precursors have been reported to be very slow on insulating oxide surfaces but to proceed at an acceptable rate on metallic surfaces [48]. The nucleation rate for deposition of copper and copper nitride using β-diketonate precursors have been shown to increase if water is added to the process. Adding water as a third reactant is not possible in the case of nickel due to the higher affinity towards oxygen for nickel compared to copper, which leads to nickel oxide formation [49]. With the knowledge of the reactions between β-diketonate and –OH groups, similar reactions can be expected between -NHₓ and the metal β-diketonate for growth of Ni₃N which is easily converted to the metal by subsequent annealing.

2.1.2. ALD/CVD deposition system.

The films in this study have all been deposited in the same deposition system. The system is a five zone furnace hot wall system built in-house. The reactor is a 60 mm silica tube. The Ni(thd)₂ was sublimated in the first two furnace zones and was delivered to the reaction zone by Ar gas. To avoid mixing of the reactant gases, all the precursors are delivered to the reaction zone in separated tubes and mixed in the reaction zone in a TiN coated substrate block. For short purging times, a small back flow was applied to the water and metal precursor tubes during the purging pulses. Reaction between water and metal precursor was avoided by loading the metal precursor directly from an inert atmosphere in a glove box, attached to the system.

2.1.3. Film characterisation methods

The deposited films have been analysed by a diversity of different analysis techniques. Some of the methods are briefly commented below. In both ALD and CVD research the measurement of thickness is central to determine growth/cycle in ALD or growth rates in CVD. However, films of equal thickness, deposited at different conditions, do not necessarily have to have the same density, i.e., the amount of deposited material may not be the same. In this study normally both thickness measurements by x-ray reflectivity (XRR) and measurement of the amount of deposited material / unit area by
x-ray fluorescence (XRF) have been used as complementary techniques. In XRF the integrated area of the Ni\(\alpha\) peak is proportional to the amount of deposited nickel. The XRR technique requires smooth film surfaces to get the thickness information while XRF can be used regardless of the surface roughness. If a series of films with different known thicknesses from XRR and with similar density is measured, a plot of the thickness as a function of XRF signal can be made and hence thickness can be determined. By interpolation or extrapolation of the data a thickness can be attributed also to rough and thin non-conformal films, with the error of ascribing the same film density as for the films in the standard curve. In this thesis the XRF signal is presented as a calculated thickness to give a more physical meaning to the otherwise arbitrary values also for deposits which have not coalesced.

Impurity levels were measured by XPS. The sensitivity of the XPS system for impurities such as carbon is in the 1\% range. The XPS technique is very surface sensitive and to get some depth information, the surface was sputter cleaned by argon ions before analysis. When sputtering the surface, preferential sputtering effects may cause problems. For NiO, metallic states are introduced due to the preferential sputtering of oxygen [50]. The preferential sputtering is, however, much worse for the nickel nitride where the nitrogen is easily sputtered. For determination of chemical composition, sensitivity factors for the elements are used. However, the sensitivity factors are matrix dependent why known standards are needed to get absolute film composition values. In this thesis only standard sensitivity factors are used meaning that the composition values given are approximate. However, the trends are still valid.

In x-ray diffraction (XRD), when \(\theta-2\theta\) scans are employed, one should be aware of the fact that only the planes in parallel with the surface are measured. Since only surface parallel planes are measured \(\theta-2\theta\) scans give information on preferred growth directions, i.e., texture. Due to the experimental set-up, low intensities are obtained for thin polycrystalline films. To increase the intensity, grazing incidence x-ray diffraction (Gi-XRD) has been used to determine the crystallographic phase of polycrystalline films. In Gi-XRD, the incidence angle is kept constant at a low angle (in this work up to 1\(^\circ\)) and the detector is scanned in \(2\theta\). The Gi-XRD technique increases the intensity for thin layers because the diffraction volume is increased, compared to a \(\theta-2\theta\) scan. By changing the incidence angle the depth of information can be changed. This has been used for polycrystalline two-phase films and multilayers. If the interfaces between the layers are distinct and smooth the intensity from the top layer should have its intensity maxima as the incidence angle is at the angle of total reflection for this layer. The layer closest to the substrate should ideally not give any diffraction until the incidence angle is larger than the total reflection angle for the top layer. For real layers normally some scattering occurs at the interfaces why some intensity is observed from the bottom layer also for incidence angles just below
the total reflection angle. By plotting the intensity as a function of the incidence angle for the two phases it is possible to decide which phase is placed on top of the other (or if they are mixed) [51]. Gi-XRD can also be used to decide if an epitaxial film has a non-ordered part since an epitaxial film will not give any diffraction from a Gi-XRD measurement. The drawback with Gi-XRD is that basically all planes in a polycrystalline film will scatter, why texture information is in principle lost.

Epitaxial films have been characterized by pole figures, rocking curves and RSM. More information on thin film diffraction methods can be found in text books like ref [51].

Surface morphologies have been studied by Atomic Force Microscopy (AFM) for low surface roughness on insulating substrates where Scanning Electron Microscopy (SEM) gives charging effects. The AFM is very sensitive for low roughness samples. However, the lateral resolution is limited by the tip size.
3. Results

3.1 Precursor stability.

As mentioned earlier the chemical stability of the ALD precursor is of great importance. In this context stability means that it is possible to let a flow of the precursor over the substrate surface without gaining any deposit. However, since most surfaces are more or less catalytic, the stability differs on different surfaces. Fig. 3 shows the amount of deposited material measured by XRF and calculated as a growth of NiO/pulse·s after alternate pulsing of argon and the metal precursor. It is observed that the decomposition of Ni(thd)$_2$ on Ni surfaces is highly enhanced compared to the decomposition on NiO and SiO$_2$ surfaces. The data suggest that ALD deposition by using Ni(thd)$_2$ is possible up to 275°C on SiO$_2$ and NiO. ALD deposition on nickel surfaces on the other hand is restricted to temperatures below 260°C. The solid product from decomposition of Ni(thd)$_2$ (the deposit) is a by carbon slightly contaminated metallic nickel film which makes the decomposition highly autocatalytic. The decomposition on the NiO surface reduces the oxide which further increases the decomposition since a metallic surface is obtained. The reduction of the oxide indicates that reducing reaction products are formed upon the decomposition of the metal precursor. For comparison the decomposition of Ni(hfac)$_2$ is shown. The Ni(hfac)$_2$ is not a suitable precursor for ALD deposition of nickel compounds because it leaves a deposit after alternate Ni(hfac)$_2$/argon pulsing already at 200°C.

The Ni(hfac)$_2$ decomposition curve as a function of temperature have a different shape compared to the Ni(thd)$_2$ decomposition because of a lower precursor partial pressure used in the experiments. Also the Ni(hfac)$_2$ precursor reacts with its own hydrate water, forming an oxygen rich deposit. In the Ni(thd)$_2$ experiments, 1500 cycles of alternating 1.5s Ni(thd)$_2$ and 8s Ar purges were used, while in the Ni(hfac)$_2$ experiments, 250 cycles of 8s Ni(hfac)$_2$ and 8s purge were used.
Fig. 3. Stability of Ni(thd)$_2$ on SiO$_2$, NiO and Ni surface. The decomposition of Ni(hfac)$_2$ precursor on a SiO$_2$ surface is also displayed.

The other compound discussed earlier in this text, Ni(acac)$_2$, is reasonably stable on SiO$_2$ surfaces and should according to literature give an “amorphous black” deposit from ALD deposition in combination with water [29]. Growth experiments with water as oxygen source at 250°C gave a grayish deposit of low crystallinity, containing carbon impurities in the 10% range. Based on the stability on both NiO and Ni surfaces in combination with the possibilities to get a hydrate free precursor material, the Ni(thd)$_2$ precursor was chosen and was used throughout this work.

3.2 Growth of nickel nitride.

Pulsing of ammonia and Ni(thd)$_2$ in an ALD process yielded a deposit of metallic luster. The growth/cycle does not exceed 0.1Å/cycle on SiO$_2$ surfaces which is too low for a feasible deposition process. Switching the process to CVD mode by introducing ammonia and Ni(thd)$_2$ simultaneously, a growth rate of about 0.1-1.1 nm/minute is obtained. At the applied deposition temperatures, polycrystalline Ni$_3$N films are obtained. A typical diffractogram is displayed in Fig. 4.
Fig. 4 X-ray diffractogram from a Ni$_3$N film deposited at 275°C.

Two linear fits can be made to the natural logarithm of the deposition rate plotted as a function of the reciprocal absolute deposition temperature. At the lower temperatures (205-230°C) the high calculated activation energy indicates a growth process being under surface kinetics control, Fig. 5. When the deposition temperature exceeds 240°C, the activation energy is decreased, indicating a different growth mechanism. When the growth temperature is further increased above 275°C, the linearity in the Arrhenius’ plot is lost. At the higher temperatures the impurities of carbon and oxygen increase to 5 % at 290°C.

Fig. 5. A, displays the Arrhenius’ plot for the growth of Ni$_3$N. B, C, D display the microstructure obtained at 230°C, 250°C and 290°C, respectively. Scale bar is 100 nm in all images.
The obtained microstructures are displayed in Fig. 5. The films grown at temperatures up to 275°C are dense and uniform. However, when the deposition temperature is increased to above 275°C, a microstructure containing rod-like grains is observed. This microstructure is associated with a preferred film on film growth in combination with a mass transport controlled growth, which is evident from the decrease in growth rate when the linear flow velocity is decreased. By measuring the growth rate as a function of the partial pressures of the different precursors the reaction order can be obtained. At 230°C the logarithm of growth rate as a function of the logarithm of the precursor partial pressure shows two linear regions to give reaction orders of 3 or 1.3, which is not normally associated with surface reactions. These two regions can be explained by nucleation problems on the substrate surface where the nucleation problems are decreasing with higher precursor partial pressures. At 250°C a total reaction order of 1 is obtained, which is expected for a surface reaction. It is also observed that the growth rate is independent of the Ni(thd)₂ supply but dependent on the NH₃ partial pressure.

The nucleation problems can be seen in the SEM images in Fig. 6 with the separated grains initially. Despite the relatively long deposition time of 7.5 minutes at 230°C, a low nucleation density on the surface is observed (Fig. 6A). It can also be observed for 15 minutes deposition, that the number of Ni₃N nuclei has hardly increased (Fig. 6B). This means that the Ni₃N growth proceeds at the already formed grains rather than on the substrate surface, forming new nuclei. At 250°C the initial nucleus density is higher (Fig. 6D). However, also here growth is preferred on already formed grains. Coalescence is reached faster, though, and a film on film growth is obtained.

![Fig. 6. Evolution of morphology as a function of deposition time. A-C are deposited at 230°C and D-F at 250°C. Scale bar is 100 nm](image-url)
The differences in the initial nucleation behavior can also be seen in the plot of the amount of deposited material as a function of the deposition time which shows that at 230°C the initial growth rate is lower compared to what is observed when film on film growth is possible. The growth rate as a function of deposition time is almost a straight line at 250°C, which shows that the nucleation problem is smaller at this temperature, Fig. 7.

Fig. 7. Amount of deposited Ni$_3$N, calculated from XRF data, as a function of deposition time for the deposition temperatures 230°C and 250°C, respectively.

The as-deposited nickel nitride films are metallic conductors as observed in Fig. 8, where the film resistance is a linear function of the absolute temperature which is what is expected for a metallic conductor and is in line with what has previously reported [52].

Fig. 8. Film resistance as a function of temperature.
Films of 100 nm in thickness were also characterized with respect to magnetic properties by SQUID measurements. The data show a weak ferromagnetic moment and a Curie temperature over 350 K (Fig. 9). A hysteresis of 500 Oe is also observed. The magnetic moments recorded can possibly be due to nickel inclusions or stochiometry differences within the film. Even though no nickel phase have been detected by XRD the magnetic measurements are far more sensitive.

![Fig. 9. SQUID data from a 100 nm thick Ni$_3$N film.](image)

### 3.3 Decomposition of nickel nitride.

As mentioned previously the nickel nitride is metastable and decomposes to nickel metal and nitrogen gas at elevated temperatures. The nitride is also possible to decompose at lower temperatures in a hydrogen atmosphere where the nickel nitride decomposes to NH$_3$ and nickel metal. The decomposition was studied with respect to the structural changes by in-situ XRD. The films were heated in either inert atmosphere at 300°C or in 1 Torr hydrogen at 180°C. The XRD measurements were carried out by performing a number of 0-20 scans at a constant temperature, meaning that the structural changes were studied as a function of time at in beforehand chosen temperature. The experiments were interrupted when no changes could be observed in the diffractograms. A number of 150 nm thick Ni$_3$N films were deposited on SrTiO$_3$ (00l) (STO) substrates. The STO substrate has a mismatch with the Ni$_3$N film of about 15.4 % in the [00l] direction and about 9 % for a cube on
cube growth for the resulting nickel metal. The mismatch is small enough to expect a somewhat textured film. The texture increases the intensity for the planes in parallel to the surface, resulting in high intensities in XRD even for relative thin samples. The mismatch is, however, large enough to give some peak separation in 2θ, which makes in-situ XRD possible. The film decomposition was also studied in UHV, where the N\textsubscript{2} (g) emission was studied as a function of time with a mass spectrometer. Films of the same thickness were also deposited on non-etched Si (100) substrates. These polycrystalline films were decomposed at the same conditions in UHV as reference samples to get rid of eventual orientation effects. Also partly decomposed polycrystalline films were studied by Gi-XRD with varying incidence angles to determine the localization of the different phases.

Previous studies of the decomposition of Ni\textsubscript{3}N samples obtained from ion implantation have suggested decomposition via nitrides with lower nitrogen content, such as Ni\textsubscript{4}N and Ni\textsubscript{8}N [5]. The Ni\textsubscript{4}N and Ni\textsubscript{8}N phases were investigated by electron diffraction in a transmission electron microscope with the possibilities of heating the samples inside the microscope [5]. The Ni\textsubscript{8}N structure is easiest described as a slightly enlarged cubic Ni structure with a unit cell being twice the size of a nickel unit cell. This means that the Ni\textsubscript{8}N will be very hard to distinguish from Ni since the Ni\textsubscript{8}N (222) will overlap with the Ni (111) etc.

3.3.1 Ordering of as-deposited films.

The films grown on STO (001) substrates show preferred (001) and (111) growth orientations but several other surface parallel orientations can also be observed in the 0-2θ scan in Fig. 10.

![Fig. 10. 0-2θ diffractogram of the as-deposited Ni\textsubscript{3}N film. The main orientations are identified as (001) and (111).](image-url)
The films show an in-plane ordering with several in-plane orientations in the pole figure. The main orientations are identified as Ni$_3$N (001)[100]/STO (001)[110] with a two fold rotation. Also a weaker orientation, rotated 90°, is observed, i.e., Ni$_3$N (001)[100]/STO (001)[100]. However, several other orientations are also observed such as the Ni$_3$N (111)[011]/STO (001)[100]. The out-of-plane ordering of the Ni$_3$N layer is measured by rocking curve broadenings, which are in the 5.5° range for both the Ni$_3$N (111) and Ni$_3$N (002) orientations, indicating a low ordering.

3.3.4 *In-situ* studies of Ni$_3$N decomposition.

The film decomposition in inert atmospheres was measured by *in-situ* XRD at 760 Torr He pressure and at a constant temperature of 300°C. The measurement was performed by making one scan between 40-56° in 2θ with a scan time of 300 s. After a delay time of 300 s another scan was made. The procedure was repeated until no changes were observed in the diffractograms. The result can be observed in Fig. 11. What is evident from the diffractograms is that the cell parameters are initially increasing. It can also be observed that the cell parameter increase is larger for the (001) orientation, compared to the (111) orientation. An expansion of cell parameters due to a higher mobility of the nitrogen atoms within the structure would give uniformly larger cell parameters, why the increased cell parameters are most probably due to strain effects within the film. Furthermore, no intermediate phases can be observed and the decomposition appears to be direct from the nitride to the metal. The direct decomposition to Ni from Ni$_3$N is in contradiction to what has been observed previously [5]. The Ni$_4$N phase should be observed with a peak at 2θ = 48.9°. If the Ni$_4$N phase is formed it must have a low degree of ordering and is therefore not observed in the out of plane XRD.

![Fig. 11. Decomposition of Ni$_3$N at 300°C and 760 Torr He as observed by *in-situ* XRD. The time between the start of each scan is 300 s.](image-url)
The same experiment was also carried out in UHV but instead of measuring the phase change, the out-gassing of nitrogen from the film was measured by a mass spectrometer. To make sure of what contributions to the mass number 28 (nitrogen) originates from the film, a blank substrate was measured. The result from the blank is inserted in Fig. 12 and shows very low values. When heating the Ni$_3$N film, a rapid initial N$_2$ evolution is observed, indicating an initial fast film decomposition. By continuous heating the N$_2$ signal is slowly decreasing (Fig. 12). The high initial decomposition is believed to originate from the surface. After reaching a maximum the nitrogen signal decreases as a function of time which is expected for a process controlled by diffusion. After about 100 minutes an increase in the decomposition rate is observed as a second peak in the nitrogen emission signal. After the second peak, the N$_2$ signal is again decreasing. The N$_2$ emission curve has the same shape for films deposited on non-etched Si (100) substrates, indicating that the shape of the curve is not affected by the ordering of the films. The second emission peak can either be due to morphological changes like smaller grain size, formation of a porous structure or cracks within the film which makes the diffusion length shorter within the solid structure and hence a higher N$_2$ out-gassing rate. The other explanation is that a second decomposition process is becoming dominant. Although the N$_2$ emission is high initially, the Ni (002) peak is hardly observable until after 40 min, i.e., the material is loosing N$_2$. However, the structure is changing only slowly. The data indicate a decreasing N content within the film with conservation of the structure. When the N content is low enough, the hexagonal structure is not favourable any longer and a faster decomposition to the cubic structure is observed and hence the second peak in the N$_2$ (g) emission curve is obtained. However, one should be aware of that in XRD only the ordered parts are measured, why decomposition yielding low ordered intermediates is easily missed.

Fig. 12. The N$_2$ emission from a 150 nm thick Ni$_3$N film during annealing at 300°C under UHV conditions.
By changing the decomposition atmosphere from inert to 1 Torr H₂ gas the Ni₃N decomposition proceeds already at 180°C. *In-situ* XRD shows a different decomposition compared to what was observed for the inert atmosphere. The Ni₃N cell parameters are constantly decreasing with time and the Ni (002) peak can be observed as a broad peak after about 30 minutes where the Ni₃N peaks are of about half its original intensity, Fig. 13. A constantly decreasing cell parameter is what is expected for a material with a variable stoichiometry. The data indicate not only a different mechanism for the decomposition but also a lower ordering of the formed nickel compared to the high temperature conditions.

![In-situ XRD from a 150 nm thick Ni₃N film deposited on a STO (001) substrate. The time between the start of each scan is 330 s.](image)

**3.3.5 Gi-XRD study of the decomposition of polycrystalline films.**

By depositing polycrystalline films on non etched Si (100) substrates and partly decompose them, also less ordered intermediate phases can be observed by Gi-XRD. Just as for the *in-situ* studies no intermediate phases were detected which is in contradiction to what is reported earlier [5]. From the Gi-XRD measurements it is also possible to receive indications of where the two phases Ni and Ni₃N are mainly situated in partially decomposed films, i.e, to determine if the growth proceeds from the surface and downwards to the substrate or vice versa. After partial decomposition of the film in UHV at 300°C, the films were measured by Gi-XRD. By varying the incidence angle and plotting the ratio of the integrated peak intensities for the Ni (002) and Ni₃N (110) phases as a function of incidence angle, the phase localization can be observed, Fig. 14. The data indicate that the main part of the Ni₃N phase is mainly localized closer to the surface, i.e, the decomposition would not only start at the surface of the film but also closest to the substrate. The same trend can be observed by XPS depth profiling. How-
ever, these data are unreliable because of the severe preferential sputtering of nitrogen in the material. In the partly decomposed polycrystalline films the Ni$_4$N phase should more easily be detected. All examined films contained a phase mixture of Ni$_3$N and Ni as the only phases present, why the decomposition appears to be direct from Ni$_3$N to Ni without any intermediate phases such as Ni$_4$N.

![Graph](image)

Fig. 14. Integrated peak intensity ratios as a function of the incidence angle in GIXRD.

By making the same analysis on films partially decomposed in 1 Torr H$_2$ at 180°C it can be observed (see Fig. 14) that the nickel phase is mainly concentrated to the surface. Thus the film decomposition in this case starts from the surface.

3.3.6 Ordering of the Ni films

The data from the two decomposition conditions showed as expected differences in decomposition mechanism. Also differences in the ordering of the obtained nickel films are expected. At the higher temperature, the Ni$_3$N decomposition starts from the substrate and continues towards the surface. A higher ordering of the nickel layer is expected on matched single crystalline substrates. By starting the decomposition at the film/substrate interface the film can get its initial ordering from the substrate. In the low temperature and H$_2$ case, the diffusion of the metal to form an ordered structure is lower. Also the film decomposition starts from the surface why the initial ordering of the Ni film is not affected directly by the substrate but by the underlying not yet decomposed Ni$_3$N film whose ordering is significantly lower than the substrate ordering. The differences in ordering can be observed by the out of
plane rocking curve broadening value where the films decomposed at 300°C show a Ni (002) rocking curve FWHM in the 6.5° range. The FWHM of the Ni (111) orientation is significantly larger (about 11°). The films decomposed at 180°C also show a Ni (111) rocking curve broadening of 11° but the Ni (002) broadening is about 9°, which shows that the out of plane ordering is lower.

Regardless of the annealing atmosphere, the decomposed films show a in-plane ordering as observed by the pole figures (see Fig. 15). Both films show a residue of a weak Ni$_3$N like (111) orientation which have a 120° cell angle as well as the (001) oriented cubic nickel.

![Diagram](image)

Fig. 15. A displays the Ni (111) pole after decomposition at 300°C and 760 Torr He and B after decomposition in 1 Torr H$_2$ atmosphere at 180°C. A2 shows the (111) orientation and A1/A2 shows overlapping reflections from both a Ni$_3$N like (111) and a Ni (001) orientation.

### 3.3.7 Film morphology

The morphology of the decomposed films is affected by the decomposition conditions. The film decomposed at 300°C resembles the morphology of the as-deposited films with rod or flake like grains and very few pin holes. However, the surface roughness is slightly increased and the grain size appears to be slightly larger, compared to the as-deposited film. The resistivity of the layer is a measure of how dense the films are. The resistivity for the films decomposed at 300°C shows a value of about 40 $\mu\Omega\cdot$cm, which is almost half the resistivity of the as-deposited film (71 $\mu\Omega\cdot$cm). The obtained resistivity value is about 6 times higher than that of bulk nickel. The measured resistivity value indicates that the formed nickel film is not very dense and the formation of a somewhat open microstructure could describe the second emission peak in the N$_2$ emission signal. The films decomposed in hydrogen show a smoother film surface. However, some cracks are observed
in the film surfaces. Despite the cracks, the film resistivity is 35 μΩ·cm for the in H₂ gas derived nickel film.

3.4 Deposition of nickel oxide.

3.4.1 Polycrystalline films

Ni(thd)₂ and H₂O, pulsed sequentially in an ALD process, gives a polycrystalline NiO product between 205-275°C on SiO₂ substrates. Typical Gi and θ-2θ diffractograms are displayed in Fig. 16. The θ-2θ diffractograms show a (001) texture at 230°C and a random orientation at 275°C.

![Graph showing 2θ vs. Intensity (Arb. U.) for NiO films deposited at 230°C and 275°C.](image)

Fig. 16. θ-2θ diffractograms (left) of 100 nm thick films deposited at 230°C and 275°C, respectively. The film deposited at 230°C shows a (001) texture. Gi-diffractograms (right) of the same films. All peaks can be attributed to NiO.

The growth/cycle increases to a maximum of about 0.4 Å/cycle at 260°C. By further increasing the deposition temperature, the growth/cycle decreases, when reaching 275°C. The growth/cycle is depicted together with the thermal decomposition of the metal precursor on oxide surfaces in Fig. 17. If the deposition temperature is further increased to the region where the thermal decomposition is large also on oxide surfaces, the growth/cycle is decreasing and the deposit consists of metallic nickel mainly.
Fig. 17. Growth and decomposition of Ni(thd)$_2$ on oxide substrates as a function of temperature.

Fig. 18. AFM images of NiO surfaces deposited at different deposition temperatures. Scan area is 1000x1000 nm.

The microstructure changes with the applied deposition temperature as can be observed in Fig. 18. At 205°C the film surface is smooth with grain like structures and a surface roughness in the 1-2 nm range. At higher deposition temperatures more distinct grains are observed and when the temperature reaches 275°C an increase in the grain size can be observed and the surface roughness increases to 4-5 nm. Interestingly, the largest change in surface...
topography is observed when increasing the deposition temperature from 260 to 275°C. The change in surface topography is probably associated with a change in deposition mechanism when the deposition temperature exceeds 260°C. A decrease in growth/cycle when increasing the growth temperature from 260°C to 275°C is also observed. At 275°C the thermal decomposition of the metal precursor contributes to about 1% of the total growth, i.e., a different adsorption/reaction scheme occurs. By further increasing the temperature, the additional reaction scheme becomes dominant, explaining the large decrease in growth/cycle and change in phase content observed at 290°C.

Looking at the ALD process characteristics both precursors show saturation at 230°C as well as at 275°C, Fig. 19. The nickel precursor shows a fast saturation at both temperatures. The water pulse on the other hand saturates slowly and a water excess of about a 100 times the Ni(thd)₂ amount is needed for saturation. The large water excess can probably be attributed to a low reactivity of the adsorbed species towards water. Other possibilities are a reaction scheme which proceeds via Ni(OH)₂, which decomposes to the oxide. The nickel hydroxide is known to decompose to nickel oxide at temperatures close to what is employed here [52].

![Fig. 19. Growth/cycle as a function of the precursor supply and purge time at 230°C (left) and 275°C (right), respectively.](image)

![Fig. 20. Growth as a function of the number of ALD cycles deposited at 230°C.](image)
The growth as a function of the number of ALD cycles is linear. The linear fit does not go through origin which indicates an initially slower growth process (see Fig. 20).

By AFM examination of surfaces of films deposited with different number of cycles, a hint of the initial film growth process can be obtained. At 150 ALD cycles a low surface roughness of about 0.6 nm is observed. The observed structures are in the 30-70 nm range laterally and are observed as separated grains. By increasing the number of ALD cycles to 250 cycles, the surface RMS roughness is in the 0.4-0.5 nm range, while the lateral dimensions of the observed structures are still in the 30-70 nm range. However, these grains appear to be more densely packed. The film obtained at 250 ALD cycles appears to be nearly coalesced. By further increase of the number of ALD cycles, the surface roughness is increased to about 3 nm at 500 ALD cycles. The increased roughness is believed to be due to secondary nucleation. When proceeding to 1000 ALD cycles, the film surface roughness decreases again to the 1 nm range and the observed structures are now about 50-100 nm laterally (Fig. 21).

Fig. 21. AFM images of films deposited by different amount of ALD cycles. Scan area is 1000x1000 nm
When using ALD precursors with organic ligands there is always a risk of contamination of the film by carbon. The carbon impurities were found to be about 1-2% at most by using XPS and standard sensitivity factors. 1-2% is close to the detection limit of the XPS system.

3.4.2 Epitaxial films

(100) oriented films
Films deposited on MgO (100) substrates grow with a (100) out of plane orientation as observed in the θ-20 diffractogram, which only except for the substrate peaks reveals the NiO (200) and NiO (400) peaks. If a grain size is calculated from the peak broadening, a grain size close to the film thickness is obtained, which indicates that the individual grains go through the whole film.

Fig. 22. θ-20 diffractogram of the film and the substrate (200) peaks. The NiO film was 71 nm thick and deposited at 275°C. Notice the thickness fringes, indicating low film roughness.

High resolution θ-20 diffractograms of the films deposited on MgO (100) show thickness fringes on the diffraction peak. Thickness fringes are indications of a very smooth film surface and a uniform film thickness (Fig. 22). A smooth film surface was also observed by AFM (Fig. 23), which shows a surface RMS roughness of about 0.6 nm.
The nickel oxide and the MgO substrate have a very small crystal mismatch (less than 1% in a axis difference). The small mismatch gives good prerequisites for growth of high quality films. However, the similar unit cell dimensions also give small peak separation in XRD. The RSM reveals that the thinner films are almost complete strained to the substrate. The relaxed part of the films increases as the film thickness is increased (Fig. 24).
The rocking curves extracted from the relaxed part of the RSM show values of the order of 0.3° for the thicker films, which is in line with what is previously reported for NiO (100) films deposited on MgO (100) by other methods.

The films deposited on MgO (100) substrates show an increased growth/cycle with increasing deposition temperature and with the highest growth at 275°C. The film growth as a function of deposition temperature is depicted in Fig. 25. No peaks are observed in Gi-XRD at any of the deposition temperatures which indicate epitaxy also at the lowest deposition temperature, 205°C.

Cross-sectional transmission electron microscope images show a film with columnar grains (Fig. 26). A high resolution TEM image of the interface shows a low defect content within each grain. The growth as a function of applied ALD cycles is linear as expected for thicker films. However, for the growth initiation the growth /cycle is slightly enhanced. The enhancement is probably associated with either a higher concentration of –OH groups on the MgO (100) surface, compared to the concentration on the growing film, or a microstructure of the initially formed grains which increases the film surface area and hence increases the initial growth. Growth starting with individual and separated nuclei/grains would describe not only the growth / cycle increase for very thin films but also the columnar structure observed in the TEM images.
Fig. 26. TEM cross-section images of a 30 nm film deposited on MgO (100) substrate. To the left a columnar structure is observed. To the right the interface between the substrate and a grain is shown.

(111) oriented films

The α-Al₂O₃ (00l) surface resembles a hexagonal closest packing and a (111) oriented NiO film is expected. The θ-2θ diffratograms only reveal the NiO (111) and NiO (222) peaks as well as the α-Al₂O₃ (006) and α-Al₂O₃ (0012) substrate peaks. The out of plane peak broadening indicates a crystallite size of the order of the film thickness. By measurement of the in plane cell parameters, i.e., the (220) reflection, a significantly larger peak broadening is observed. The higher in plane peak broadening indicates a columnar growth of the crystallites, which can be observed by cross-sectional TEM.

Fig. 27. NiO (111) pole reflections marked T originate from one of the two rotation reflections. S originates from the substrate (104) reflection. In the TEM image to the right one of the twin boundaries has been highlighted by a line.

The NiO (111) pole figures show the expected intensity at both $\psi = 0^\circ$ and $\psi = 70.5^\circ$, which corresponds to the plane angle between the {111} planes in a cubic structure. However, six intensity maxima are observed together with
the three intensities from the substrate 104 reflection. The six intensities show the formation of a rotational twin, i.e., two orientations rotated 180° from each other on the substrate surface, Fig. 27. The twin can also be observed in the TEM image in Fig. 27.

In the temperature range 210 to 275°C, the so called ALD window, the growth/cycle is relatively constant. A temperature region with nearly constant growth/cycle is common in ALD [36]. The deposited films remain epitaxial throughout the whole temperature range.

Fig. 28. Film growth as a function of the deposition temperature for growth of NiO (111) films on α-Al₂O₃ (00l) substrates.

Fig. 29. Rocking curves of a 72 nm thick film (left) and a 5 nm thick film (right) deposited at 275°C.
The out of plane rocking curves show two contributions, one sharp peak of about 0.02° in FWHM at best and a broader contribution. Thin films (~5 nm) show only the sharp peak and as the film thickness is increased the broader peak arises. The two contributions to the rocking curves indicate films with a initial high in plane ordering. As the film thickness is increased the ordering is decreased, Fig. 29.

The pole figures show broad peaks and broadenings of about 2.5° are observed for the in plane rocking curves. High in plane broadening indicates that the grains are rotated with respect to each other. The interpretation of the data is connected to the initial growth process. By plotting the film thickness as a function of the number of deposition cycles, a low growth/cycle is observed for the thinnest films, which indicates nucleation problems on the substrate surface. Cross-section TEM of a 5 nm thick deposit reveals grains which start to coalesce. The image indicates a high alignment of the surface parallel planes, which was also observed by the rocking curve measurements. However, the initial grains are slightly rotated with respect to each other on the substrate surface. As the growth proceeds, the grains start to tilt with respect to each other, which gives rise to the broad contribution to the out of plane rocking curve. A TEM image (Fig. 30) of a 30 nm thick film reveals a columnar structure with tilting grain boundaries, which is expected from the rocking curve measurements.

The topography of the thinnest film (5 nm) was studied by AFM and an image of the surface can be seen in Fig. 31. The grain boundaries observed by TEM is not observable due to the limiting lateral resolution in the AFM, and the grains are observed by their differences in height over the substrate. The topography shows a surface roughness which is expected from the TEM cross-sections in Fig. 30.

Fig. 30. TEM cross sections of the initially formed grains (left) and from a thicker film (right).
3.5 The stability of CVD Ni$_3$N and ALD NiO films.

Most devices used commercially today are composed of multilayered structures based on combinations of materials of different properties. One of the challenges in growth of multilayers is to keep the two layers well phase separated. Phase separation is obtained if the individual layers are stable with respect to each other, or if the growth conditions are such that the kinetics for solid/solid reactions over the interface is low. CVD and ALD methods have certain disadvantages in the growth of multilayers of low stability, since they are usually using elevated temperatures. High temperatures lead to diffusion across the interfaces and the phase separation might be lost. Moreover, upon using CVD/ALD techniques residual gases might be trapped inside the films which might be released during heating processes. These gases might participate in reactions with subsequently grown layers, forming a third layer in between the two layers, an interlayer. In this thesis growth of dual layers of NiO and Ni$_3$N have been demonstrated, as well as the thermal decomposition of Ni$_3$N to Ni. The knowledge on how to grow and manipulate these layers have been used to grow multilayers of NiO/Ni$_3$N and NiO/Ni in different combinations.
3.5.1 Growth of polycrystalline Ni$_3$N on NiO and textured Ni$_3$N on epitaxial NiO (111) layers.

**Growth of polycrystalline Ni$_3$N on NiO**

Starting with a Si (100) substrate, a polycrystalline NiO film was grown by alternate pulsing of H$_2$O and Ni(thd)$_2$ in an ALD process at 250°C. After the last deposition cycle a 10 s extra purge time was introduced before a continuous flow of NH$_3$ and Ni(thd)$_2$ was admitted into the reactor at the same deposition temperature as in the ALD process. The result is a dual layer film of Ni$_3$N/NiO. In the SEM cross-section image two layers can be observed, Fig. 32. The NiO layer shows a columnar structure and the Ni$_3$N layer on top shows grains with a size of the order of the film thickness, Fig. 32.

![SEM image of the interface between the NiO and Ni$_3$N layer](image)

**Fig. 32.** SEM image of the interface between the NiO and Ni$_3$N layer. A, B, Gi-XRD diffractograms, recorded with 0.7° and 0.3° incidence angle, respectively. C. The integrated intensity as a function of Gi-XRD incidence angle.

The measurement of the films by Gi-XRD with a 0.7° incidence angle revealed a phase mixture of Ni$_3$N and NiO (Fig.32A). By decreasing the incidence angle to angles close to the total reflection of the Ni$_3$N layer, the intensities of the NiO peaks are decreased, while the intensities from peaks of the Ni$_3$N layer are increased (Fig.32B). The integrated intensity of the Ni$_3$N (112) and the NiO (022), respectively was plotted as a function of incidence angle. The result can be observed in Fig. 32C. The shape of the two curves is expected for two well phase separated layers, grown on top of each other.
Growth of textured Ni$_3$N on epitaxial NiO (111)

Changing the substrate from non-etched Si (100) to $\alpha$-Al$_2$O$_3$ (001) yielded epitaxial NiO (111) ALD films as described in [IV]. By growing a NiO (111) film by ALD on $\alpha$-Al$_2$O$_3$ (001) and subsequently depositing a Ni$_3$N layer a Ni$_3$N/NiO (111) dual film is obtained. A cross-section of a Ni$_3$N/NiO (111) film can be observed in Fig. 33. The NiO (111) layer shows a columnar structure and the Ni$_3$N layer appears to have large crystals with a size of the order of the film thickness.

![SEM image of a Ni$_3$N film deposited on top of an epitaxial NiO (111) film.](image)

Fig. 33. SEM image of a Ni$_3$N film deposited on top of an epitaxial NiO (111) film.

$\theta$-20 X-ray diffractograms indicate an out of plane texture of the Ni$_3$N layer to be mainly (002) but also a (111) orientation was observed. The NiO (111) rocking curve shows both a sharp and a broader peak with FWHM values as expected (see ref [IV]) which shows that the order of the NiO layer is not affected by the Ni$_3$N layer deposited on top. Out of plane rocking curve FWHM for the Ni$_3$N (002) is about 4.5°, indicating a low out of plane order. The Ni$_3$N (111) rocking curve shows a more complex shape with two maxima observed at 8° from the expected position with a local minimum at half the $2\theta$ value. Such a rocking curve indicates a tilt of the (111) orientation by 8°. The tilt of the Ni$_3$N (111) shows a six fold in plane rotation which is observed from the Ni$_3$N (111) pole figure. The tilt of the Ni$_3$N (111) orientation is also observed in the (002) pole figure, where the reflections, originating from the (111) orientation, is shifted to 8° higher values compared to what is expected (Fig. 34). Due to the low $2\theta$ resolution of the used diffractometer set-up also the NiO (002) reflections from the NiO (111) orientation as well as the substrate (113) planes are observed. The pole shows that the Ni$_3$N film grows with an in-plane ordering with respect to both the underlying NiO (111) film and the substrate (Fig. 34).
3.5.2 Decomposition of the Ni$_3$N layer on both polycrystalline and epitaxial NiO

**Decomposition of polycrystalline Ni$_3$N layers on NiO**

Starting with a polycrystalline Ni$_3$N/NiO layered film, the top Ni$_3$N layer can be decomposed to form a Ni/NiO layer. For such a structure the decomposition parameters must be chosen carefully. High temperatures can lead to high diffusion rates across the interface and no defined layers are obtained. Not only the Ni$_3$N phase has a low stability but also the NiO, which though is somewhat higher and is reported to be of intermediate stability and decomposes in inert atmospheres to Ni and O$_2$ at elevated temperatures [50,54,55]. A Ni$_3$N/NiO film was analysed by Gi-XRD prior to decomposition of the Ni$_3$N layer at 300°C in UHV. By comparing the integrated peak intensities from Gi-XRD before and after the annealing it is obvious that not only the Ni$_3$N decomposes to Ni but also that the NiO is partly decomposed. The conclusion is that to succeed in producing a Ni/NiO layer a different strategy is needed.

The decomposition temperature of Ni$_3$N can be decreased by annealing in H$_2$. However, hydrogen annealing has the obvious risk of reduction of the Ni in the underlying oxide. After deposition of a Ni$_3$N/NiO layer and Gi-XRD analysis, the film was exposed to 1 Torr hydrogen at 180°C for 3 h. The result of the following Gi-XRD analysis can be observed in Fig. 35, where the integrated intensity for the NiO (022) is plotted as a function of incidence angle both before and after the hydrogen annealing. The data show small changes in the before and after plot, indicating that the underlying NiO layer is stable at the annealing conditions. The Gi-XRD data also indicate that the Ni layer is situated on top of the NiO layer and that the two phases are phase separated. A two layered film is also observed in the SEM image (Fig. 35).
The decomposition kinetics is low at 180°C and in an attempt to increase the decomposition rate the annealing temperature was increased to 200°C. The higher temperature did however lead to reduction of the Ni in NiO. 200°C annealing at the applied hydrogen pressure did not lead to reduction of a NiO film without the Ni layer on top. Nickel is known to dissociate hydrogen already at low temperatures why the Ni layer on top is probably decreasing the reduction temperature of NiO by supplying highly reactive atomic hydrogen to the NiO layer.

**Decomposition of Ni$_3$N layers on epitaxial NiO (111)**

The annealing conditions for decomposition of the Ni$_3$N layer grown on top of epitaxial NiO (111) film was chosen with the knowledge from the polycrystalline films and annealing at 180°C for 5 h in 1 Torr H$_2$ was used. After annealing, both the NiO (111) and the Ni (111) peaks are observed in the out of plane diffraction analysis. Despite the long annealing time, a Ni$_3$N (002) peak is also observed as a shoulder on the α-Al$_2$O$_3$ (006) peak in Fig. 36. The presence of residual Ni$_3$N, despite that the annealing times should be more than sufficient for decomposition of polycrystalline films, indicate...
lower decomposition kinetics compared to the polycrystalline films. Lower decomposition kinetics of the ordered films can probably be attributed to a different microstructure of the ordered films, leading to longer diffusion pathways. The Ni (002) pole, displayed in Fig. 36, shows six reflections at $\psi = 54.7^\circ$, which is the plane angle between the 001 and 111 planes in cubic structure. The six reflections show that the film grows with a 180° in plane rotation on the surface. This was observed also for NiO (111) grown on the same type of substrates [IV]. The reflections in the pole figure are broad and showing that the in-plane ordering is low.

![Fig.36. Left, Ni (002) pole. Right, out of plane XRD of a Ni/NiO (111) film. S1 originates from the substrate (024) planes and S2 from CuKα diffraction from the substrate (116) planes.](image)

Out of plane rocking curve confirms the low Ni ordering with a FWHM of about 11°. SEM image of the cross-section shows a NiO film with a weakly observable columnar structure and a very smooth surface. The Ni film shows large crystallites and a rough topography, Fig. 37.

![Fig. 37. SEM image displaying the Ni/NiO (111) interface.](image)
3.5.4 Growth of NiO on top of polycrystalline Ni$_3$N

Changing the stacking sequence of the layers, i.e., and starting with deposit of a CVD Ni$_3$N layer, followed by ALD of NiO, a two-layer structure is obtained, Fig. 38. XRR measurements reveal two total reflections, followed by a pattern which also indicates a two layered film. However, the Gi-XRD analysis shows a third phase in the film. A Ni layer is formed in the interface between the NiO and Ni$_3$N layer. Apart from the Ni layer the two phases are well separated.

An intermediate Ni layer can be formed from several different reactions which are listed below.

- The metal precursor is not stable on the Ni$_3$N surface and decomposes to Ni.
- The Ni$_3$N film is not stable towards the precursors (Ni(thd)$_2$ and H$_2$O) used for the growth of NiO and the film is partly decomposed to Ni.
- The Ni$_3$N film is not stable towards the reaction products formed when Ni(thd)$_2$ reacts with H$_2$O, and the Ni$_3$N film decomposes to Ni.
Residual gases such as hydrogen are stored in the film from decomposition of ammonia during the Ni$_3$N growth leading to reduction of the NiO film upon release.

It is well known that the –OH coverage is lower on metallic surfaces compared to oxide surfaces. The NiO growth is highly dependent on surface –OH groups as observed in [III]. It is reported that copper ALD is selective on metallic surfaces using the Cu(thd)$_2$ and H$_2$ precursor combination [48]. The possibilities for selective growth indicate a different surface chemistry on metallic surfaces for the used class of metal precursors. The coverage of –OH groups is lower but still not zero on metallic surfaces and two different reactions proceeds simultaneously initially. The result is a phase mixture of Ni and NiO.

The stability of the Ni$_3$N film and precursor stability were tested by growing a Ni$_3$N film and exposure it for 1 h for Ni(thd)$_2$. Gi-XRD analysis showed only the Ni$_3$N phase. The same experiment was conducted but the film was subjected to H$_2$O instead of Ni(thd)$_2$ with the same result. The result suggests that the Ni layer is not formed by decomposition of the Ni$_3$N film nor from decomposition of Ni(thd)$_2$ on the film surface.

The effect of residual gases within the film was tested by inserting a 600 s delay time between the Ni$_3$N and NiO growth to give time for the accumulated gases to be released. The delay time decreased the intensities from the subsequently formed Ni layer but did not disappear completely. By inserting a 20 s H$_2$O pulse just subsequent to the delay time, the intensities from the Ni layer was further reduced. The conclusion is that the formation mechanism of the Ni layer is complex and has probably its origin in both residual gases within the film as well as different reaction schemes between the Ni(thd)$_2$ precursor and metallic surfaces.

3.5.5 Decomposition of Ni$_3$N layers and subsequent deposition of NiO to produce NiO/Ni layers

A Ni$_3$N layer, grown directly on a Si (100) substrate, can be decomposed to nickel in a variety of ways as discussed earlier. For reasons of simplicity the Ni$_3$N was decomposed by using 1 Torr hydrogen at 250°C during 30 minutes just subsequent to the Ni$_3$N deposition. After a 15 s delay time a NiO layer was deposited on top using the same deposition temperature. The result is a NiO/Ni layer. The growth/ALD cycle is lower on the Ni surface compared to growth on oxide surfaces. The lower growth can be explained by the same reasons as for the growth on Ni$_3$N surfaces described above. By introducing both a delay time and a 15 s H$_2$O pulse before the NiO growth, the growth/cycle was increased. The Gi-XRD analysis indicates that the two layers are well separated, Fig. 39. However, in the SEM analysis of the
cross-section only one layer can be observed. The diffuse interface is an indication of the presence of two competing reaction schemes, resulting in a phase mixture at the interface. A systematic investigation of the reaction mechanisms on a monolayer level is needed to clarify the different growth kinetics on different surfaces.

Fig. 39. A, integrated peak intensities for the Ni (002) and NiO (022) reflections as a function of incidence angle for a NiO/Ni layer. B, C Gi-XRD data from the NiO/Ni dual layer at 0.7° and 0.3° incidence angle, respectively.

3.5.3 Growth of Ni (111) films by using a NiO (111) seed layer

The nucleation rate of Ni$_3$N is low on $\alpha$-Al$_2$O$_3$ (001) substrates. By growing a very thin nucleation layer of epitaxial NiO, the Ni$_3$N nucleation can be enhanced. Since both the NiO and Ni$_3$N layer decomposes to Ni at high temperature annealing, a pure epitaxial Ni film can possibly be grown.

Fig. 40. Ni (002) pole figure from a 40 nm thick Ni (111) film, reflections at $\psi = 54.7^\circ$ represent the two (111) orientations. T2 represents the (115) orientation. S originates from the substrate (024). The pole figure is measured using a Ni filter in the diffractometer to reduce the Cuk$\beta$ radiation, which is why the substrate (116) is not observed as in Fig. 36.
After deposition of a 7.5 nm thick epitaxial NiO layer by ALD on α-Al2O3 (00l) substrate a 40 nm thick Ni3N layer was deposited. The annealing was performed in UHV at 350°C for 1 h and 40 minutes or at 400°C for 50 minutes. The result is a Ni film, showing only its (111) peak in the out of plane diffraction. No residues can be observed from the NiO (111) peak. Pole figure measurements show two in-plane orientations, rotated 180° with respect to each other, marked T1 in Fig. 40. In the pole figure also a weak (115) orientation is observed (T2 in Fig. 40). The (115) orientation can be considered as a tilt from the (111) orientation and have been observed previously on Cu (111) films deposited on the same substrate [56].

Out of plane rocking curve measurements of the Ni (111) films show FWHM in the 3.5° range. Analysis of the surface topography by AFM reveals continuous films with surface RMS roughness in the 3-4 nm range.

Use of an oxide as a sacrificial layer for growth of a metallic film might lead to oxygen impurities within the film. XPS depth profiling shows oxygen levels in the 1-2 % range in the film. When coming close to the substrate, the oxygen content is increased to 15 % before the Al 2p signal is observed. By analysis of the shape of both the Ni 2p peak and the O 1s peak it is evident that Ni-O bonds are present close to the substrate. This layer, containing residual oxygen, is probably responsible for the low film ordering obtained.
4. Summary and concluding remarks

It has been demonstrated in this thesis that metastable Ni$_3$N films can be grown by methods working as close to equilibrium as CVD by using right starting materials and conditions. The growth is highly surface sensitive. The nucleation is slow at low temperatures and on $\alpha$-Al$_2$O$_3$ (00l). When using low temperatures, the nucleation is also highly dependent on the precursor partial pressures. At the higher temperatures the growth rate is independent of the metal precursor supply despite that the material mainly consists of Ni. A growth rate, being limited by the ammonia partial pressure, indicates slow surface reactions between Ni(thd)$_2$ and NH$_3$. Similar reactions are expected between water and Ni(thd)$_2$ and the saturation curves for the ALD growth of NiO also show indications of slow surface reaction kinetics since large excess of water is needed for saturation.

The possibilities for manipulation of layers of low stability have been examined and exploited to produce materials combinations which are not possible to grow via direct deposition routes with chemical vapor growth techniques. The decomposition of Ni$_3$N was found to proceed via a one step process in contradiction to what is reported by others; and no phases except for Ni$_3$N and Ni during the film decomposition have been observed. The ordering of the films decomposed in H$_2$ atmospheres is lower compared to the films decomposed in inert atmospheres. The different orderings can be traced back to the start of the decomposition. In H$_2$ the decomposition is starting from the film surface while in inert atmosphere the film decomposition starts at the film/substrate interface. A start from the film/substrate interface gives a higher degree of ordering since the initial film ordering is directly influenced by the substrate ordering.

It has also been shown that polycrystalline and epitaxial NiO (111) and (00l) oriented films of good qualities can be grown at both low temperatures and low oxygen partial pressures. This gives the prerequisites for growth of multilayer combinations of Ni$_3$N and NiO which can be manipulated to form Ni and NiO. At the used annealing conditions, Ni films with an in plane ordering can be obtained on top of epitaxial NiO films, despite the relatively low annealing temperatures. The method presented in this work displays the possibilities of producing multilayered structures of low stability materials and materials combinations. By exploiting the stabilities of the individual layers, materials can be manipulated by low temperature annealing to form the target structure. The developed method to form multilayer structures, combin-
ing metals and metal oxides, displays a reaction route which is probably also applicable for other materials system, including metals such as iron and cobalt and possibly also manganese.

For future work it would be interesting to grow also cobalt and iron nitrides by chemical vapor phase methods. Growth of mixed Ni,Co,Fe nitrides and decomposition of ex (Ni,Fe)$_3$N would be interesting not only from a mechanistic point of view but also with respect to the properties of such a material. It might also be possible to put some Ni,Co,Fe into the cubic copper nitride without destroying the copper nitride structure. The properties of such a material are not very easy to predict and it would be very interesting to see if it is possible to produce.
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Sist och framför allt

Eva, du är bäst!
6. Sammanfattning på svenska

Den allmänna benämningen på en förening mellan en metall och kväve är metallnitrid. Med metallnitridern förknippas oftast de stabila föreningar som bildas mellan t.ex. kväve och titan, skandium, vanadin, hafnium etc. Dessa material används i hårdmetallskär och borrar men även i elektronik och optiska komponenter. Allmänt så minskar stabiliteten hos metallnitriderna åt höger i periodiska systemet, och till höger om mangan finns de metastabila föreningarna mellan järn, cobolt, nickel och kväve. Sammansättningen M₃N där M = Fe,Co,Ni är gemensam för dessa metallnitriderna. De har också samma struktur som kan beskrivas som en hexagonal tätpackning av metallatomer med kväve i oktaedriska hålrum. Dessa material är metastabila och sönderfaller till respektive metall och kvävgas vid förhöjd temperatur i icke reaktiv atmosfär. Det är möjligt att sänka sönderfalls temperaturen genom att nytta en annan reaktions väg; värms materialet i vätgas så avgår kvävet som ammoniak viket kräver mindre tillförd energi jämfört med bildning av kvävgas. Nickel nitrid (Ni₃N) är ett det studerade materialen i denna avhandling. Ni₃N är en icke magnetisk metallisk elektrisk ledare. Materialet sönderfaller till kväve och nickel metall vid 300°C i inert atmosfär eller vid 180°C i 1 Torr vätgas atmosfär. Tunna filmer av material är viktiga i många tillämpningar och tunna metallfilm används som elektriska ledare i elektriska komponenter, eller som magnetiska lager i tex läshuvuden till hårddiskar etc. För att ge fungerande komponenter är metallagren ofta kombinerade med material med andra egenskaper så som metalloxider, många av dessa metalloxider reduceras lätt av vätgas vilket gör att deponeringar med låga vätgas aktiviteter är intressanta.

Direkt deponering av nickel med kemiska gasfas tekniker kräver ofta höga aktiviteter vätgas men eftersom nickelnitriden lätt sönderfaller till nickel kan den användas för att skapa metall filmer vid förhållanden där direkt deponering inte är möjliga, till exempel på metalloxid substrat som lätt reduceras till metall av vätgas.

Tidigare har nickelnitrid deponerats som tunna filmer men pga. materialets metastabila natur så har de flesta deponeringar gjorts med metoder som arbetar långt från jämvikt, så som sputtering, jonimplantation etc. Den här avhandlingen visar att det är möjligt att deponera metastabila material med metoder som arbetar nära jämvikt så som chemical vapor deposition (CVD). Fördelen med CVD framför många andra metoder för tunnfilms tillväxt är att substrat med mer komplicerad form kan beläggas. I CVD bildas...
materialet genom kemiska reaktioner på eller aldeles i närheten av den yta som skall beläggas. Som utgångs material används molekyler eller atomer i gasfas innehållande de element som det önskade materialet skall innehålla. Dessa utgångsmaterial förs samtidig och kontinuerligt in i reaktionszonen där tillväxten sker. I det här arbetet har bis(2,2,6,6-tetramethyl-3,5-heptanedionato)nickel(II) (Ni(thd)2) använts som nickel källa och som kväve källa har ammoniak använts. Nickelnitrid tillväxten följer ett Arrhenius’ uttryck med aktiverings energier som indikerar att tillväxthastigheten begränsas av kinetiken hos reaktioner på substrat ytan vid temperaturer över 230°C. Trots att materialet nästan bara innehåller nickel atomer så styrs tillväxthastigheten endast av mängden tillförd ammoniak vilket tyder på att reaktionen mellan Ni(thd)2 och ammoniak är långsam.


Om en yta exponeras för ammoniak (NH3) bildas adsorberade –NH grupper på dess yta vilka reagerar med Ni(thd)2 för att bilda Ni3N. Om NH3 byts ut mot vatten (H2O) bildas i stället –OH grupper på ytan och reaktionen mellan -OH och Ni(thd)2 bildar då nickeloxid (NiO). Om exponeringen av Ni(thd)2 och H2O separeras, dvs. varje reaktant förs in till reaktionszonen en i sänder och åtskilda av sköljpulser av inert gas så fås en annan deponerings metod, nämligen atomic layer deposition (ALD). En deponerings cykel i ALD innefattar för tillväxt av NiO; exponering av substratet med H2O/ sköljning med argon/ exponering av substratet med Ni(thd)2/sköljning med argon. Denna deponerings cykel upprepas sedan tills den önskade tjockleken på materialet är uppnådd. Vid varje puls genereras som mest ett adsorberat monolager av respektive utgångs material. Genom denna pulsade teknik byggs materialet upp med som mest ett atomlager per puls. ALD metoden är långsam men ger väldigt god kontroll över tjockleken på det deponerade skiktet. Det ger också möjlighet att växa filmer på substrat med extremt komplicerade former eller i djupa och trånga kanaler. Med denna teknik har både slumpvis ordnade (polykristallina) och filmer som växer med en ordning relativt substratet (epitaxiella) NiO filmer växts. Genom att växa NiO filmer med vatten som syre bärande utgångs material hålls aktiviteten av syre låg, så att NiO kan växas även på material som lätt oxideras tex Ni3N och Ni. Eftersom Ni3N kan växas med låga aktiviteter av vätgas så kan Ni3N deponeras på NiO. Det nybildade Ni3N lagret kan sedan sönderdelas till Ni metall utan att det underliggande NiO lagret påverkas och således kan multilager av Ni,NiO och Ni3N växas.

Tillväxt av multilager är viktiga för de flesta tillämningar där material med olika egenskaper läggs i olika lager för att nå de speciella egenskaper
som krävs för den aktuella komponenten. För dessa multilager komponenter är det viktigt att materialen inte blandas med varandra genom kemiska reaktioner i kontakt ytorna. Genom att nyttja de reaktioner som studerats i denna avhandling (tillväxt och sönderfall) kan väldefinierade flerlager skikt av en ferromagnetisk elektrisk ledare (Ni) en icke ferromagnetisk elektrisk ledare (Ni$_3$N) och en antiferromagnetisk halvledare (NiO) växas med metoder som har hög stegtäckning som CVD och ALD.
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