<https://helda.helsinki.fi>

Atomic Layer Deposition of Nickel Nitride Thin Films using pöy NiCl₂(TMPDA) and Tert Butylhydrazine as Precu

Väyrynen, Katja

2019-06

Väyrynen , K , Hatanpää , T , Mattinen , M , Heikkilä , M J , Mizohata , K , Räisänen , J , Link
, J , Stern , R , Ritala , M & Leskelä , M 2019 , ' Atomic Layer Deposition of Nickel Nitride
pöy Thin Films using NiCl₂ (TMPDA) and Tert Butylhydrazine as Precursor
Solidi. A: Applications and Materials Science , vol. 216 , no. 11 , 1900058 , pp. 1900058 . <https://doi.org/10.1002/pssa.201900058>

<http://hdl.handle.net/10138/322267>

<https://doi.org/10.1002/pssa.201900058>

acceptedVersion

Downloaded from Helda, University of Helsinki institutional repository.

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Please cite the original version.

Atomic Layer Deposition of Nickel Nitride Thin Films using NiCl₂(TMPDA) and Tert-Butylhydrazine as Precursors

Katja Väyrynen,[†] Timo Hatanpää,[†] Miika Mattinen,[†] Mikko J. Heikkilä,[†] Kenichiro Mizohata,[‡] Jyrki Räisänen,[‡] Joosep Link,[§] Raivo Stern,[§] Mikko Ritala^{†} and Markku Leskelä[†]*

K. Väyrynen, T. Hatanpää, M. Mattinen, M. J. Heikkilä, Prof. M. Ritala, Prof. M. Leskelä
Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014 Helsinki, Finland
E-mail: mikko.ritala@helsinki.fi

Dr. K. Mizohata, Prof. J. Räisänen

Department of Physics, University of Helsinki, P.O. Box 64, FI-00014 Helsinki, Finland

J. Link, Prof. R. Stern

National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia

Keywords: atomic layer deposition, nickel, nickel nitride, tert-butylhydrazine, thin films

This article describes the atomic layer deposition (ALD) of nickel nitride and nickel thin films using a diamine adduct of Ni(II) chloride, NiCl₂(TMPDA) (TMPDA = *N,N,N',N'*-tetramethyl-1,3-propanediamine), as the metal precursor. Owing to the high reducing power of tert-butylhydrazine (TBH), the films are grown at low temperatures of 190–250 °C. This is one of the few low-temperature ALD processes that can be used to grow Ni₃N and Ni metal on both insulating and conductive substrates. The films are characterized in terms of crystallinity, morphology, composition, resistivity, and coercivity. X-ray diffraction shows reflections compatible with either hexagonal Ni or Ni₃N. Composition analyses suggest that the films are close to stoichiometric Ni₃N. Despite the nitride component, the films exhibit low resistivity values and at the lowest, a resistivity of 37 μΩ·cm is achieved. The result is lower than what is typically observed for Ni_xN films and not much higher than the best results concerning ALD Ni metal. The nitrogen content of the films is lowered down to 1.2 at.% by postdeposition reduction at 150 °C in 10% forming gas. After the reduction, the nonmagnetic nitride films are converted to ferromagnetic Ni metal.

1. Introduction

Nickel thin films find use in a myriad of applications ranging from microelectronics^[1–3] to protective coatings^[4] and catalysis.^[5,6] Alongside Co and Ru, Ni is one of the possible candidates to replace Cu as the dominant conductor material in future interconnects on integrated circuits.^[1] As opposed to Cu, Ni has a lower electron mean free path, which should increase the effective conductivity as the interconnect dimensions get smaller and smaller. Ni metal films can be converted to low-resistivity NiSi contacts when deposited on Si substrates and annealed at 500 °C.^[7–10] Fully-silicided (FUSI) Ni gates provide an alternative for TiSi₂ and CoSi₂ gates in complementary metal oxide semiconductors (CMOS).^[11] Owing to its ferromagnetic properties, Ni is a pivotal material in the development of magnetic memories.^[2,3] Spin-transfer torque random-access memories (STT-RAMs), for example, are faster and exhibit higher durability and energy efficiency than the memories we use today.^[12] STT-RAMs can even be considered as the universal memory which may someday revolutionize the entire microelectronics industry. STT-RAMs can also be made through nickel nitride films.^[13] In addition, Ni_xN is a suitable material for anodes in Li-ion batteries^[14] as well as electrocatalysis,^[15] and it also serves as a precursor to Ni metal formation.^[16,17]

Atomic layer deposition (ALD) is a thin film preparation technique that inherently provides conformal coverage of high aspect ratio structures and, at the same time, allows atomic level control over film thickness and composition.^[18–20] Thus, ALD is the method of choice to further the miniaturization of electronic devices and take the microelectronics industry forward. Despite the importance of Ni in many applications, the number of ALD processes for Ni has remained low. Because of its negative reduction potential ($E^\circ = -0.26$ V), the Ni(II) ion is much more difficult to reduce than, for example, its counterpart Cu(II) ($E^\circ = +0.34$ V).^[21] Ni precursors should therefore be highly reactive and combined with powerful reducing agents. The reactivity problems in Ni ALD have generally been circumvented by using plasma-

enhancement^[8–10,16,17,22–29] or postdeposition reduction of NiO.^[30–33] While plasma-enhancement often improves growth rates and affords high-purity films, the energetic plasma species may damage the underlying substrate and compromise the conformality of the process. Postdeposition reduction of NiO, on the other hand, requires high temperatures, making it challenging to deposit thin yet continuous films. Furthermore, the drastic density change from NiO to Ni induces structural collapse and pinhole formation to the reduced film.^[30]

There are only a handful of thermal ALD processes for Ni metal. Ni(acac)₂ (acac = acetylacetonate) has been combined with both H₂ and methanol at temperatures above 250 °C.^[30,34] No information on the growth characteristics was provided for the Ni(acac)₂ + H₂ system, though. The methanol process afforded films with low resistivity (27 μΩ·cm) but required relatively high deposition temperatures (250–300 °C). A combination of Ni(ⁱPrAMD)₂ (ⁱPrAMD = *N,N'*-diisopropylacetamidinate) and H₂ has also been studied for Ni ALD, but the films were deposited above the decomposition temperature of the Ni precursor.^[35] Ni(dmamb)₂ (dmamb = dimethylamino-2-methyl-2-butoxide) has been combined with both H₂ and NH₃ at temperatures ranging from 175 to 300 °C.^[7,26,36] However, a similar amino alkoxide precursor, Ni(dmap)₂ (dmap = dimethylamino-2-propoxide), decomposes to Ni metal already at 178–185 °C,^[37] questioning whether the Ni(dmamb)₂ processes are truly ALD. There are also a few area-selective ALD processes for Ni where films are grown only on catalytic metal substrates.^[38,39] While area-selectivity is important for certain applications, it is a problem in the preparation of STT-RAMs, for example. Ni_xN ALD has been realized with combinations of Ni(^tBu₂DAD)₂ (^tBu₂DAD = 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene) and 1,1-dimethylhydrazine^[40] as well as Ni(dmap)₂ and hydrazine with or without an intermediate formic acid pulse.^[37] Interestingly, pure Ni metal films with no nitride component were deposited when hydrazine was combined with Ni(acac)₂(TMEDA) (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) at 220–300 °C.^[41]

The halides of Co and Ni are poorly volatile polymeric compounds and thus unsuitable precursors for ALD. By adducting the halides with proper simple Lewis base molecules, monomeric compounds with high volatility and sufficient thermal stability can be prepared. For Co, TMEDA was found suitable, whereas for Ni, TMPDA (TMPDA = *N,N,N',N'*-tetramethyl-1,3-propanediamine) provided the desired properties.^[42] Unlike other Ni and Co precursors, the adducted metal(II) halides are inexpensive and easy to synthesize with a practically quantitative yield. So far, no suitable reducing agent has been found to reduce $\text{CoCl}_2(\text{TMEDA})$ or $\text{NiCl}_2(\text{TMPDA})$ to elemental Co or Ni in ALD. We have, however, shown that the diamine adducts of these metal(II) halides are suitable for the ALD of intermetallic Co_3Sn_2 and Ni_3Sn_2 as well as Co(II) oxide thin films.^[42,43]

We have previously demonstrated the low-temperature ALD of Cu metal using $\text{Cu}(\text{dmap})_2$ and tert-butylhydrazine (TBH) as precursors.^[44] TBH was first published for Ag ALD using $\text{Ag}(\text{hfac})\text{COD}$ as the metal precursor.^[45] 1,1-Dimethylhydrazine has been combined with $(\text{tBu-Allyl})\text{Co}(\text{CO})_3$ to deposit Co metal films,^[46] which led us to believe that hydrazine and its alkyl derivatives may well be suitable for the reduction of the diamine adducts of Co(II) and Ni(II) halides as well. Hydrazines have also been used for the ALD of various transition metal nitrides.^[37,47–49]

Herein, we introduce a new low-temperature process for the ALD of Ni_3N and Ni thin films. The films were deposited using the new Ni precursor, $\text{NiCl}_2(\text{TMPDA})$, and TBH as the reducing agent (**Figure 1**). With these results, we demonstrate that the diamine adducts of metal(II) halides can be used as low-cost precursors also for the low-temperature ALD of metal nitrides. Furthermore, we show a straightforward method for obtaining pure Ni metal through low-temperature reduction of the Ni_3N films.

2. Results

2.1. Precursor Properties

$\text{NiCl}_2(\text{TMPDA})$ is a strictly monomeric compound^[50,51] that can be sublimed quantitatively under reduced pressure (160–180 °C/0.5 mbar). The volatility is exemplified by the vacuum TGA shown in Figure 1b. The vapor pressure of the precursor was estimated from atmospheric pressure TGA data using the Langmuir equation in the way described in literature.^[52] Below 210 °C, that is, as a solid, the precursor vapor pressure is approximated to follow the Antoine equation (Equation 1).

$$\log P(\text{mbar}) = 10.85 - 5102.1/T(\text{K}) \quad \text{Equation 1}$$

A suitable source temperature in an F-120 ALD reactor is typically around the temperature where the precursor has 0.1 mbar vapor pressure. Based on Equation 1, this value is achieved at 157 °C. $\text{NiCl}_2(\text{TMPDA})$ melts at 216 °C and is thus a solid source.

The reason for selecting TBH over other hydrazines was that unsubstituted hydrazine is hazardous to use, and the methyl-substituted forms can lead to carbon contamination. TBH is safer to handle than hydrazine itself but can behave like it because of clean elimination of tert-butyl group by the beta-hydride elimination. The TBH source temperature of 15 °C was empirically found to yield an appropriate consumption in the Cu process^[44] and was used here, too. The decomposition of TBH at elevated temperatures was of no concern as it most likely produces hydrazine and other reducing species also useful for metal deposition. The upper limit of 250 °C for the Ni_3N process was dictated by the onset of $\text{NiCl}_2(\text{TMPDA})$ decomposition that leads to the formation of nonvolatile NiCl_2 . The decomposition was visually observed as color at the hot end of the Ni precursor source tube.

Figure 1. a) Schematic structures of $\text{NiCl}_2(\text{TMPDA})$ and TBH . b) Vacuum TG curve for $\text{NiCl}_2(\text{TMPDA})$.

2.2. Film Deposition

The growth characteristics of the Ni_3N process are shown in **Figure 2**. The Ni_3N process was studied within a temperature range of 190–250 °C (Figure 2a). A low growth rate of only 0.04 Å/cycle was observed at 190 °C, but higher rates were obtained by increasing the deposition temperature. A constant growth rate of 0.075 Å/cycle was measured between 200 and 210 °C. The growth rate increased gradually from 0.075 to 0.12 Å/cycle when the temperature was raised from 210 to 250 °C. Higher temperatures were not studied to avoid the decomposition of $\text{NiCl}_2(\text{TMPDA})$. No deposition occurred without TBH at 200 °C; however, at 250 °C, very faint color was observed on the glass substrate, indicating the loss of the TMPDA ligand and formation of NiCl_2 on the substrate at this temperature. The growth rates were somewhat lower than what was observed previously for the Cu ALD process employing $\text{Cu}(\text{dmap})_2$ and TBH as precursors (0.15 Å/cycle at 120 °C).^[44] Because of the negative reduction potential of the Ni(II) ion, Ni precursors are more difficult to reduce than Cu precursors. Furthermore, the amino alkoxide precursors generally show higher reactivity than metal halides. Despite the lower temperatures, the growth rates observed here were higher than what has been reported for the $\text{Ni}(\text{iPrAMD})_2 + \text{H}_2$ (0.04 Å/cycle)^[35] and $\text{Ni}(\text{acac})_2 + \text{methanol}$ (0.07 Å/cycle)^[34] processes for

depositing Ni metal. A higher growth rate of 0.60 Å/cycle was measured for the area-selective $\text{Ni}(\text{tBuDAD})_2$ + tert-butylamine process on Pt,^[39] but because nucleation is substrate dependent, growth rates on insulators and metals are not comparable. When $\text{Ni}(\text{acac})_2(\text{TMEDA})$ was combined with hydrazine at 260 °C, a very high growth rate of 2.1 Å/cycle was measured on SiO_2 .^[41]

Saturation of the growth rate was observed at 200 °C with respect to both precursor pulse lengths (Figures 2b and 2c), but at 250 °C, the growth rate increased slowly with the increasing $\text{NiCl}_2(\text{TMPDA})$ pulse time. The saturative growth rate at 200 °C was 0.075 Å/cycle. At 250 °C, the growth rate increased from 0.11 to 0.15 Å/cycle, as the Ni precursor pulse time was lengthened from 0.5 to 2.0 s. With the 0.5 s pulse at 250 °C, the precursor dose was insufficient for full coverage of the substrate, and no film was grown at the exhaust edge of the substrate. The increase of the TBH pulse time had no effect on the growth rate at 250 °C, and saturation was observed with a pulse time of only 0.2 s. The purge times had no effect on the growth rate (Figure S1 in the Supporting Information).

Figure 2. Growth properties of the $\text{NiCl}_2(\text{TMPDA})$ + TBH process at 200 and 250 °C. Growth rate as a function of a) temperature, b) $\text{NiCl}_2(\text{TMPDA})$ and c) TBH pulse times. d)

Film thickness with respect to cycle count. e) Thickness profile of the Ni₃N films. The deposition conditions are depicted in the upper right corners of each graph (temperature, cycles, and pulsing sequence in seconds).

Figure 2d shows that the film thickness increased linearly between cycle counts of 1000 and 4000. Linear dependence was also seen at 250 °C despite the lack of complete saturation. Some nucleation delay was observed within the first 1000 cycles at 200 °C. The Ni₃N growth rate remained the same even after full coverage of the substrate, whereas with Cu, the growth rate decreased after the starting surface was covered.^[44] Despite the same reducing agent, the films grow differently as one is a nitride and the other is a pure metal. With Ni metal, the formation of a nitride is more favorable than with Cu. Furthermore, the nitrides of Ni are more stable at elevated temperatures than the nitrides of Cu.^[53]

Equation 2 shows the proposed mechanism for the adsorption and reaction of NiCl₂(TMPDA) during the Ni precursor pulse.

It is believed that upon adsorption, the neutral TMPDA ligand is dissociated from the Ni precursor and some of the chloride ligands react with the –NH surface groups if existing on the surface. The subsequent TBH pulse completes the reaction by eliminating the rest of the chlorides, forming the nitride, and regenerating any possible –NH surface species.

The Ni₃N films were evaluated for their uniformity across the substrate. As can be seen from Figure 2e, the films exhibited some nonuniformity across the 5 cm × 5 cm substrate. At 250 °C, this could be explained by the onset of the NiCl₂(TMPDA) decomposition but at 200 °C, the reason remains ambiguous. It is customary for a film deposited in a flow-type F-120 reactor to have profile within the first centimeter from the inlet edge, however, the rest of the film is

usually of uniform thickness. The $\text{Cu(dmap)}_2 + \text{TBH}$ process produced films with excellent uniformity,^[44] suggesting that the reducing agent is not the cause for the nonuniformity of the Ni_3N films. It is possible that HCl , which forms when the Ni precursor reacts with TBH and surface $-\text{NH}$ groups (Equation 2), readsorbs downstream and blocks adsorption sites from $\text{NiCl}_2(\text{TMPDA})$. Another option is that the TMPDA ligand occupies some of the surface sites, causing the lower growth rate at the exhaust edge of the substrate. This hypothesis is supported by the fact that Zhang et al. observed a lower growth rate with their $\text{Ni(acac)}_2\text{TMEDA} + \text{hydrazine}$ process when an intermediate pulse of the free TMEDA ligand was given before the Ni precursor pulse.^[41] It is also possible that some of the NiCl_2 surface species are lost as volatile $\text{NiCl}_2(\text{TMPDA})$ through a reaction with the free TMPDA ligands. This effect is stronger toward the exhaust edge due to an increased amount of byproducts at this area.^[54] Besides the thickness gradient across the substrate, all these side reactions could also explain the low growth rate of the process.

In the cross-flow F-120 reactor, the substrates are facing each other only a few millimeters apart, resulting in multiple collisions and reactions of the precursor molecules and byproducts with the growing film before being purged out. While this configuration ensures the shortest cycle times and the most efficient precursor utilization, the multiple collisions also increase byproduct readsorption probability significantly. For better uniformity, a perpendicular-flow rather than a cross-flow reactor should be tested.

2.3 Film Characterization

Figure 3 shows scanning electron microscope (SEM) images of films deposited with different cycle counts at 200 and 250 °C. As is typical with the ALD of metals, film agglomeration occurred at the early stages of deposition at both temperatures. Expectedly, the films suffered from more extensive agglomeration when deposited at 250 °C. The critical

thickness for a continuous film at 200 °C was approximately 10 nm, which is good given the deposition temperature; a similar value was observed also for the Cu process although the deposition temperature was as low as 120 °C.^[44] Interestingly at 250 °C, a 13 nm thick film was fully continuous, but an 18 nm thick film had cracks along the grain boundaries and was nonconductive. Apart from the film continuity, there were no significant changes in morphology as a function of increasing film thickness. The grain size increased to some extent as the films grew thicker.

Figure 3. SEM images of Ni_3N films deposited with different cycle counts at 200 °C (above) and 250 °C (below).

SEM images of Ni_3N films deposited on different substrates at 200 °C are shown in Figure S2 (Supporting Information). Both the morphology and the growth rate were dependent on the substrate. The extent of film agglomeration was suppressed on the conductive TiN, Ru, Cu, and Au substrates. The growth rate was almost doubled on Cu and Au (0.14 and 0.11 Å/cycle) compared to Al_2O_3 , native oxide terminated Si, TiN, and Ru (0.06–0.08 Å/cycle). The Scotch tape adhesion test was passed on TiN, Ru, and Au. The test was failed on Cu due to the poor adhesion of the Cu film to the underlying native oxide-terminated Si substrate. Given the versatility of the Ni applications, film growth on both insulating and conductive substrates is of immense value.

Figure 4 depicts top-view atomic force microscope (AFM) images of 19 and 30 nm Ni_3N films deposited on in situ Al_2O_3 at 200 and 250 °C. 3D images are included in the Supporting Information (Figure S3). All the films were quite rough, as is often the case with crystalline

metal and metal nitride thin films. The films deposited at 200 °C were rougher than the films deposited at the higher temperature. The carbon content was slightly higher in the films deposited at 250 °C (see below for ToF-ERDA results), possibly contributing to the smaller grain size and smoother morphology. It is also possible that the nucleation density is higher at 250 than at 200 °C, resulting in improved smoothness. Expectedly, the 30 nm films were rougher than the 19 nm films.

Figure 4. AFM images of 19 and 30 nm Ni_3N films deposited at 200 and 250 °C.

X-ray diffraction (XRD) was used to identify and evaluate the crystallinity of the deposited films (**Figure 5**). Figure 5a shows X-ray diffractograms of films deposited with different cycle counts, that is, films of different thicknesses, at 200 °C. Corresponding data for the films deposited at 250 °C is shown in Figure S4 in the Supporting Information. The reflections seen in the X-ray diffractograms can be assigned to both hexagonal Ni metal and Ni_3N . The crystal structure of Ni_3N is almost the same as that of Ni metal but slightly distorted due to the interstitial nitrogen atoms.^[55] When the films are grown thicker, a reflection corresponding exclusively to the nitride is observed at $30.5^\circ 2\theta$. The time-of-flight elastic recoil detection analysis (ToF-ERDA) results discussed below also suggest that the films are Ni_3N rather than Ni metal. Similar data was obtained for the films deposited at 250 °C. With $\text{Ni}(\text{acac})_2$ and methanol, the crystal structure of the Ni films was dependent on the deposition temperature; below 300 °C, the films exhibited a metastable hexagonal phase and above 300 °C, the films

crystallized in the fcc lattice.^[34] The $\text{Ni}(\text{tBuDAD})_2$ + tert-butylamine combination produced cubic Ni metal films also at low temperatures (180 °C),^[39] but the films were only moderately crystalline and deposited on cubic Pt substrates, which most likely affects the nucleation. Motamedi et al., on the other hand, obtained hexagonal Ni films at high temperatures (250–400 °C) by using sapphire substrates.^[29] In his Ph.D. Thesis, Knisley reported the ALD of Ni_xN but despite the nitride component, the films exhibited the crystal structure of cubic Ni.^[40]

The Ni_3N films were subjected to postdeposition high temperature XRD studies in 10% forming gas. The structure of a 30 nm thick film began to change from hexagonal Ni_3N to cubic Ni metal at a temperature of 150 °C (Figure 5b). The end product was cubic Ni exhibiting the (111) reflection at 44.5 °2 θ and (200) at 51.8 °2 θ . In vacuum, the decomposition of the nitride to the metal required a temperature of 325 °C. Similar reduction temperatures have also been reported by others.^[53,56,57] When reduced isothermally at 150 °C, the change from hexagonal Ni_3N to cubic Ni had no significant effect on the film morphology as can be seen from Figure S5 in the Supporting Information. The postdeposition treatment produced pure Ni metal as will be described in the next paragraph.

Figure 5. X-ray diffractograms of a) films deposited with different cycle counts at 200 °C and b) a 30 nm Ni₃N film deposited at 200 °C during postdeposition reduction in 10% forming gas. The reflection angles and crystal orientations for both hexagonal Ni and Ni₆N₂ are shown in the box below.

According to ToF-ERDA, the films deposited at 200 and 250 °C were close to stoichiometric Ni₃N (**Table 1**). At 200 °C, the Ni and N contents in the film bulk were approximately 74 and 23 at.%, respectively. Otherwise, the films were pure, with low levels of C, O, H, and Cl impurities. Despite Cl being a constituent of the Ni precursor, the Cl level was negligible in all samples. The films deposited at 250 °C exhibited a slightly higher carbon content (1.4 at.% vs. 0.8 at.% at 200 °C). The postdeposition reduction at 150 °C in 10% forming gas decreased the amount of nitrogen from 23.3 to 1.2 at.% in the film deposited at 200 °C. The Ni content after reduction was as high as 93 at.%.

Table 1. ToF-ERDA results (at.%) from 30 nm Ni₃N films deposited on in situ Al₂O₃ at 200 and 250 °C. Red. stands for after reduction at 150 °C in 10% forming gas. The surface oxidation and Al₂O₃ are excluded from the analysis.

Element	200	250	200 red. [°C]
Ni	73.6	75.2	92.5
N	23.3	21.7	1.2
H	1.5	0.8	2.3
C	0.8	1.4	0.8
O	0.7	0.9	3.0
Cl	0.07	0.04	0.2

The film composition and the chemical states of the elements were further characterized by X-ray photoelectron spectroscopy (XPS). **Table 2** lists the XPS compositions of 30 nm thick films deposited at 200 and 250 °C before and after sputtering. Before sputtering, the Ni:N ratio on the surface was close to 3:1, but there was strong hydrocarbon contamination from ambient air. After sputtering, the films were over 86 at.% Ni, which is conflicting with the ToF-ERDA results. The amount of nitrogen after sputtering was only 11–12 at.%. It is likely that some

nitrogen is lost during the sputtering. Otherwise, the films were of high purity; no carbon or chlorine were detected whatsoever, and the oxygen level was below 2.0 at.%.

Table 2. XPS compositions in at.% after sputtering (sput.) and from the surface (surf.) of 30 nm Ni₃N films deposited at 200 and 250 °C.

Element	200 sput.	250 sput.	200 surf.	250 surf. [°C]
Ni 2p _{3/2}	86.2	87.3	28.6	28.2
N 1s	12.1	10.9	10.4	9.1
C 1s	-	-	27.6	22.3
O 1s	1.7	1.8	31.7	38.8
Cl 2p	-	-	1.7	1.5

Figure 6 shows the X-ray photoelectron spectra of a 30 nm thick Ni₃N film deposited at 200 °C. The spectra measured from the film deposited at 250 °C were almost identical and are shown in Figure S6 (Supporting Information). The XPS shows signals corresponding to Ni metal at binding energies of 852.8 and 858.7 eV (Ni 2p_{3/2}). XPS measurement from the film surface showed signals at 856.0 and 861.5 eV corresponding to oxidized Ni species. Because of oxidation, the peak at 852.8 eV was also shifted to slightly higher energies (853.2 eV). The N 1s signal deriving from the nitride component is visible at 398.2 eV. No distinct signals of a Ni–N bond were detected, suggesting that the film has the structure of an interstitial compound where the nitrogen atoms occupy specific interstitial sites in the Ni metal host. Similar spectra have been shown for CVD Ni_xN^[58] and for ALD Ni deposited with NH₃ plasma.^[16,23] The measured Ni 2p peak overlapped almost completely with a Ni metal reference.

Figure 6. The Ni 2p and N 1s peaks measured from 30 nm Ni_3N film deposited at 200 °C a), b) before and c), d) after sputtering.

The Ni_3N films were studied for their electrical and magnetic properties. Despite the nitride component, the films exhibited low resistivity once the substrate surface was fully covered. At the lowest, a resistivity of $37 \mu\Omega\cdot\text{cm}$ was obtained for a 30 nm thick film deposited at 200 °C. The result is lower than what has been reported for CVD or PVD Ni_xN films; there are no previous reports regarding the resistivity of ALD grown Ni_xN . Li et al. observed a resistivity of $100 \mu\Omega\cdot\text{cm}$ for 40 nm thick Ni_xN films deposited by CVD using a Ni amidinate precursor and ammonia.^[56] The resistivity was decreased to $50 \mu\Omega\cdot\text{cm}$ only when hydrogen was added to the process. Popović and co-workers measured a resistivity of $200 \mu\Omega\cdot\text{cm}$ for Ni_3N deposited by sputtering at room temperature and a resistivity of $58 \mu\Omega\cdot\text{cm}$ for films deposited at 100 °C.^[59] The low resistivity of the nitride films shown in our work can be ascribed to the high purity and good continuity of the films enabled by the reducing agent. TBH has been previously used to improve the continuity of ALD Ag and Cu films that often suffer from extensive island

growth.^[44,45] Despite the nitride component, the resistivity of the films described here is only a factor of two higher than what has been reported for ALD Ni metal. The lowest value obtained for ALD Ni ($\text{Ni}(\text{acac})_2(\text{TMEDA}) + \text{hydrazine}$) is $19 \mu\Omega\cdot\text{cm}$ ^[41]. The bulk resistivity of Ni metal is $6.9 \mu\Omega\cdot\text{cm}$.^[21] Low resistivities of around $22 \mu\Omega\cdot\text{cm}$ were also achieved with the $\text{Ni}(\text{tBu}_2\text{DAD})_2 + \text{tert-butylamine}$ process,^[39] but the measurements were done on metal substrates, possibly affecting the result. Resistivities below $30 \mu\Omega\cdot\text{cm}$ have been reached with only three other Ni ALD processes using $\text{Ni}(\text{dmamb})_2$ and ammonia,^[36] $\text{Ni}(\text{acac})_2$ and methanol,^[34] as well as $\text{Ni}(\text{Cp})_2$ and NH_2 radicals^[24].

The Ni_3N and Ni films were also examined for possible ferromagnetic behavior with the VSM (vibrating sample magnetometer) option of a Quantum Design PPMS at room temperature. The measurements were done from 19 and 30 nm thick films deposited at 200 and 250 °C. Surprisingly, none of the Ni_3N films showed saturative magnetic behavior but only linear, diamagnetic response was detected (Figure S7a in the Supporting Information). Gajbhiye et al. observed a coercivity of 220 Oe for Ni_3N nanoparticles.^[13] According to Vempaire and co-workers, however, Ni_3N is nonmagnetic,^[60] and coercivity is measured only if the material has a Ni rich stoichiometry. The films presented were close to stoichiometric Ni_3N , which is why no magnetic saturation was observed. After the postdeposition reduction treatment, however, a coercivity of 30 Oe was measured from the 30 nm thick Ni film. Figure S7b in the Supporting Information shows the hysteresis loop for the film.

3. Conclusion

In this article, we established a new ALD process for Ni_3N thin films using a new metal precursor, $\text{NiCl}_2(\text{TMPDA})$, and a fairly unknown reducing agent, tert-butylhydrazine (TBH). The Ni_3N films were grown at low temperatures of 190–250 °C and on various substrates including both insulators and metals. The process exhibited self-limiting growth behavior at

200 °C, albeit with a low rate. For higher growth rates, higher temperatures should be used. Based on XRD, XPS, and ToF-ERDA, the films were close to stoichiometric Ni₃N. The films were of high purity, and even the chlorine content was low (0.04 at.% at 250 °C). The resistivities of the Ni₃N films grown by ALD were superior to those deposited by CVD or sputtering and only a factor of two higher than the lowest value obtained for ALD Ni metal. The amount of nitrogen could be lowered down from 23.3 to 1.2 at.% by postdeposition reduction at 150 °C in 10% forming gas. Based on their electrical and magnetic properties, the films shown here may find use in various microelectronic applications. This process also shows that the diamine adducts of metal(II) halides provide a low-cost alternative for depositing metal nitrides by ALD. In the future, other reducing agents should be explored to see if even lower deposition temperatures and higher growth rates could be reached, and if metallic Ni could be deposited directly. The process should also be studied in a hydrogen atmosphere for direct reduction of the growing nitride film. The results presented here suggest that the direct ALD of metals using similar metal precursors may be possible, provided that a co-reactant with sufficient reducing power is employed.

4. Experimental Section

Film Deposition: All deposition studies were performed in a hot-wall cross-flow F-120 ALD reactor (ASM Microchemistry). Nitrogen (AGA, 99.999 %; H₂O, ≤3 ppm; O₂, ≤3 ppm) was utilized as the carrier and purge gas. The films were deposited under a reactor pressure of ~10 mbar. The Ni₃N process was studied on 5 cm × 5 cm native oxide-terminated Si(100) and soda lime glass substrates coated with 10 nm in situ Al₂O₃ at 190–250 °C. The Al₂O₃ layers were deposited using AlCl₃ and water. Other substrates, such as Si with native oxide, TiN, Cu, Au, and Ru, were also tested. NiCl₂(TMPDA) was synthesized in-house according to the procedure described previously.^[43] TBH was purchased from EpiValence and AlCl₃ from Acros Organics.

$\text{NiCl}_2(\text{TMPDA})$ and AlCl_3 were sublimed from open glass boats held inside the reactor at source temperatures of 157 and 80 °C. TBH was supplied into the reactor from an external ampoule (15 °C) by vacuum draw. The pulse and purge times, varied from 0.2 to 2.0 s, were controlled by inert gas valving. After each precursor pulse, the reaction chamber was purged for 1.0 s, except when the effect of the purge time itself was examined.

Film Characterization: Film thicknesses were measured on 10 nm Al_2O_3 deposited in situ on Si(100) substrates by energy-dispersive X-ray spectrometry (EDS) using an Oxford INCA 350 microanalysis system connected to a Hitachi S-4800 SEM. The electron energy was 20 keV. The thicknesses were resolved from Ni $K\alpha$ X-ray lines using the GMRFILM program and assuming Ni bulk density (8.8 g/cm³). Each result was treated with an estimated uncertainty of 5%.

Film morphology was evaluated by SEM and AFM. The images were recorded in tapping mode using a Veeco Multimode V instrument. The analysis was carried out in air using Si probes with a nominal tip radius of 10 nm and a nominal spring constant of 40 N/m (NTESP from Bruker). Artifacts caused by sample tilt and scanner bow were removed by image flattening. Roughness was calculated as a root-mean-square value (R_q) from $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$ images.

XRD (PANalytical X'Pert Pro MPD X-ray diffractometer) was used to identify and analyze the crystallinity of the deposited Ni_3N and Ni films. The measurements were performed using parallel beam optics and grazing incidence geometry. The incident angle of the Cu $K\alpha$ ($\lambda = 1.54\text{ }\text{\AA}$) radiation was 1°. The same instrument but equipped with an Anton-Paar HTK1200N oven was used for postdeposition reduction studies. The high-temperature XRD measurements were carried out on $1.5\text{ cm} \times 1.5\text{ cm}$ samples in 10% forming gas (1 atm).

Film composition was determined by ToF-ERDA. The samples were bombarded with a 40 MeV $^{127}\text{I}^{8+}$ ion beam. XPS (PHI Quantum 2000, ESCA Microprobe) was used to identify impurities and chemical states of the elements. The system was operated at a 23.5 eV pass

energy. The films were exposed to 1486.6 eV X-rays emitted from an Al source (K_{α} line). The analysis was performed before and after sputtering.

The magnetic properties of the Ni_3N and Ni films were measured using the vibrating sample magnetometer (VSM) option of a Quantum Design PPMS. The measurements were done at room temperature and performed in the in-plane orientation of the films. The magnetic field was changed step by step and in non-overshoot mode. The magnetic moment was averaged for 10 seconds ($10\text{ s} \times 40\text{ Hz} = 400\text{ counts}$) at each magnetic field. The mass of the substrate was included in the analysis.

Film resistivity was measured with a four-point probe (CPS Probe Station, Cascade Microtech combined with a Keithley 2400 SourceMeter). First, the sheet resistance was measured and then multiplied by film thickness to obtain the resistivity. The measurements were done on soda lime glass substrates coated with 10 nm in situ Al_2O_3 .

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Funding from ASM Microchemistry Oy and Finnish Centre of Excellence in Atomic Layer Deposition is appreciatively acknowledged. J.L. and R.S. would like to thank the Estonian Research Agency grant PRG4 and the European Regional Development Fund project TK134 for financial support. Top Analytica Oy Ab is acknowledged for performing the XPS measurements.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] D. Gall, *J. Appl. Phys.* **2016**, *119*, 085101.
- [2] G. Wang, Z. Gao, S. Tang, C. Chen, F. Duan, S. Zhao, S. Lin, Y. Feng, L. Zhou, Y. Qin, *ACS Nano* **2012**, *6*, 11009.
- [3] P. Kumar, *Nanoscale Res. Lett.* **2010**, *5*, 1596.

- [4] Y. S. Huang, X. T. Zeng, X. F. Hu, F. M. Liu, *Electrochim. Acta* **2004**, *49*, 4313.
- [5] Z. Gao, M. Dong, G. Wang, P. Sheng, Z. Wu, H. Yang, B. Zhang, G. Wang, J. Wang, Y. Qin, *Angew. Chem. Int. Ed.* **2015**, *54*, 9006.
- [6] J. Zhang, C. Chen, W. Yan, F. Duan, B. Zhang, Z. Gao, Y. Qin, *Catal. Sci. Technol.* **2016**, *6*, 2112.
- [7] K.-W. Do, C.-M. Yang, I.-S. Kang, K.-M. Kim, K.-H. Back, H.-I. Cho, H.-B. Lee, S.-H. Kong, S.-H. Hahm, D.-H. Kwon, J.-H. Lee, J.-H. Lee, *Jpn. J. Appl. Phys.* **2006**, *45*, 2975.
- [8] C.-M. Yang, S.-W. Yun, J.-B. Ha, K.-I. Na, H.-I. Cho, H.-B. Lee, J.-H. Jeong, S.-H. Kong, S.-H. Hahm, J.-H. Lee, *Jpn. J. Appl. Phys.* **2007**, *46*, 1981.
- [9] J.-B. Ha, S.-W. Yun, J.-H. Lee, *Curr. Appl. Phys.* **2010**, *10*, 41.
- [10] J. Kim, W. Jang, J. Park, H. Jeon, H. Kim, J. Yuh, H. Jeon, *J. Korean Phys. Soc.* **2015**, *66*, 821.
- [11] J. A. Kittl, A. Lauwers, O. Chamirian, M. Van Dal, A. Akheyar, M. De Potter, R. Lindsay, K. Maex, *Microelectron. Eng.* **2003**, *70*, 158.
- [12] F. Tabrizi, The Future of Scalable STT-RAM as a Universal Embedded Memory, in *Embedded*, 2007, <https://www.embedded.com/design/real-time-and-performance/4026000/The-future-of-scalable-STT-RAM-as-a-universal-embedded-memory>, accessed: November, 2018.
- [13] N. S. Gajbhiye, R. S. Ningthoujam, J. Weissmüller, *Phys. Status Solidi A* **2002**, *189*, 691.
- [14] F. Gillot, J. Oró-Solé, M. R. Palacín, *J. Mater. Chem.* **2011**, *21*, 9997.
- [15] B. Liu, B. He, H.-Q. Peng, Y. Zhao, J. Cheng, J. Xia, J. Shen, T.-W. Ng, X. Meng, C.-S. Lee, W. Zhang, *Adv. Sci.* **2018**, *5*, 1800406.
- [16] Y.-P. Wang, Z.-J. Ding, Q.-X. Liu, W.-J. Liu, S.-J. Ding, D.-W. Zhang, *J. Mater. Chem. C* **2016**, *4*, 11059.
- [17] J.-M. Park, S. Kim, J. Hwang, W. S. Han, W. Koh, W.-J. Lee, *J. Vac. Sci. Technol. A* **2018**, *36*, 01A119.

- [18] M. Leskelä, M. Ritala, *Thin Solid Films* **2002**, 409, 138.
- [19] M. Ritala, J. Niinistö, Atomic Layer Deposition, in *Chemical Vapour Deposition: Precursors, Processes and Applications*, (Eds: A. C. Jones, M. L. Hitchman), Royal Society of Chemistry, Cambridge, U.K. **2009**, Ch. 4.
- [20] S. M. George, *Chem. Rev.* **2010**, 110, 111.
- [21] J. R. Rumble, ed., *CRC Handbook of Chemistry and Physics*, 99th Edition (Internet Version 2018), CRC Press/Taylor & Francis, Boca Raton, FL, USA.
- [22] H.-B.-R. Lee, G. H. Gu, J. Y. Son, C. G. Park, H. Kim, *Small* **2008**, 4, 2247.
- [23] H.-B.-R. Lee, S.-H. Bang, W.-H. Kim, G. H. Gu, Y. K. Lee, T.-M. Chung, C. G. Kim, C. G. Park, H. Kim, *Jpn. J. Appl. Phys.* **2010**, 49, 05FA11.
- [24] G. Yuan, H. Shimizu, T. Momose, Y. Shimogaki, *Microelectron. Eng.* **2014**, 120, 230.
- [25] G. Yuan, H. Shimizu, T. Momose, Y. Shimogaki, *J. Vac. Sci. Technol. A* **2014**, 32, 01A104.
- [26] S. W. Ryu, J. Yoon, H.-S. Moon, B. Shong, H. Kim, H.-B.-R. Lee, *Nanotechnology* **2017**, 28, 115301.
- [27] S.-B. Qian, Y.-P. Wang, Y. Shao, W.-J. Liu, S.-J. Ding, *Nanoscale Res. Lett.* **2017**, 12, 138.
- [28] Q.-H. Ren, Y. Zhang, H.-L. Lu, Y.-P. Wang, W.-J. Liu, X.-M. Ji, A. Devi, A.-Q. Jiang, D. W. Zhang, *ACS Appl. Mater. Interfaces* **2018**, 10, 468.
- [29] P. Motamedi, K. Bosnick, K. Cui, K. Cadien, J. D. Hogan, *ACS Appl. Mater. Interfaces* **2017**, 9, 24722.
- [30] M. Utriainen, M. Kröger-Laukkanen, L.-S. Johansson, L. Niinistö, *Appl. Surf. Sci.* **2000**, 157, 151.
- [31] J. Chae, H.-S. Park, S. Kang, *Electrochem. Solid-State Lett.* **2002**, 5, C64.
- [32] E. Lindahl, M. Ottosson, J.-O. Carlsson, *Surf. Coat. Technol.* **2010**, 205, 710.
- [33] M. Daub, M. Knez, U. Goesele, K. Nielsch, *J. Appl. Phys.* **2007**, 101, 09J111.

- [34] M. Sarr, N. Bahlawane, D. Arl, M. Dossot, E. McRae, D. Lenoble, *J. Phys. Chem. C* **2014**, *118*, 23385.
- [35] B. S. Lim, A. Rahtu, R. G. Gordon, *Nat. Mater.* **2003**, *2*, 749.
- [36] W.-H. Kim, H.-B.-R. Lee, K. Heo, Y. K. Lee, T.-M. Chung, C. G. Kim, S. Hong, J. Heo, H. Kim, *J. Electrochem. Soc.* **2011**, *158* (1), D1.
- [37] T. C. Ariyasena, *Ph.D. Thesis*, Wayne State University, Detroit, MI, USA, **2015**.
- [38] L. C. Kalutarage, P. D. Martin, M. J. Heeg, C. H. Winter, *J. Am. Chem. Soc.* **2013**, *135*, 12588.
- [39] M. M. Kerrigan, J. P. Klesko, K. J. Blakeney, C. H. Winter, *ACS Appl. Mater. Interfaces* **2018**, *10*, 14200.
- [40] T. J. Knisley, *Ph.D. Thesis*, Wayne State University, Detroit, MI, USA, **2012**.
- [41] Y. Zhang, L. Du, X. Liu, Y. Ding, *Nanoscale* **2019**, Advance article. DOI: 10.1039/c8nr08040b.
- [42] K. Väyrynen, T. Hatanpää, M. Mattinen, M. Heikkilä, K. Mizohata, K. Meinander, J. Räisänen, M. Ritala, M. Leskelä, *Chem. Mater.* **2018**, *30*, 3499.
- [43] K. Väyrynen, T. Hatanpää, M. Mattinen, K. Mizohata, K. Meinander, J. Räisänen, J. Link, R. Stern, M. Ritala, M. Leskelä, *Adv. Mater. Interfaces* **2018**, *12*, 1801291.
- [44] K. Väyrynen, K. Mizohata, J. Räisänen, D. Peeters, A. Devi, M. Ritala, M. Leskelä, *Chem. Mater.* **2017**, *29*, 6502.
- [45] Z. Golrokhi, P. A. Marshall, S. Romani, S. Rushworth, P. R. Chalker, R. J. Potter, *Appl. Surf. Sci.* **2017**, *399*, 123.
- [46] J. Kwon, M. Saly, M. D. Halls, R. K. Kanjolia, Y. J. Chabal, *Chem. Mater.* **2012**, *24*, 1025.
- [47] M. Juppo, M. Ritala, M. Leskelä, *J. Electrochem. Soc.* **2000**, *147*, 3377.
- [48] B. B. Burton, A. R. Lavoie, S. M. George, *J. Electrochem. Soc.* **2008**, *155*, D508.
- [49] Z. Fang, H. C. Aspinall, R. Odedra, R. J. Potter, *J. Cryst. Growth* **2011**, *331*, 33.

- [50] D. A. Handley, P. B. Hitchcock, T. H. Lee, G. J. Leigh, *Inorg. Chim. Acta* **2001**, 314, 14.
- [51] D. A. Clemente, *Inorg. Chim. Acta* **2005**, 358, 1725.
- [52] G. V. Kunte, S. A. Shivashankar, A. M. Umarji, *Meas. Sci. Technol.* **2008**, 19, 025704.
- [53] A. Baiker, M. Maciejewski, *J. Chem. Soc. Faraday Trans. 1* **1984**, 80, 2331.
- [54] K.-E. Elers, T. Blomberg, M. Peussa, B. Aitchison, S. Haukka, S. Marcus, *Chem. Vap. Deposition* **2006**, 12, 13.
- [55] A. Leineweber, H. Jacobs, S. Hull, *Inorg. Chem.* **2001**, 40, 5818.
- [56] Z. Li, R. G. Gordon, V. Pallem, H. Li, D. V. Shenai, *Chem. Mater.* **2010**, 22, 3060.
- [57] I. M. Neklyudov, A. N. Morozov, *Phys. B Condens. Matter* **2004**, 350, 325.
- [58] A. N. Cloud, L. M. Davis, G. S. Girolami, J. R. Abelson, *J. Vac. Sci. Technol. A* **2014**, 32, 020606.
- [59] N. Popović, Ž. Bogdanov, B. Gončić, S. Štrbac, Z. Rakočević, *Appl. Surf. Sci.* **2009**, 255, 4027.
- [60] D. Vempaire, S. Miraglia, A. Sulpice, L. Ortega, E. K. Hlil, D. Fruchart, J. Pelletier, *J. Magn. Magn. Mater.* **2004**, 272–276, e843.