Author(s): Kinnunen, Sami; Malm, Jari; Arstila, Kai; Lahtinen, Manu; Sajavaara, Timo

Title: Characterization of ALD grown TixAlyN and TixAlyC thin films

Year: 2017

Version:

Please cite the original version:

Kinnunen, S., Malm, J., Arstila, K., Lahtinen, M., & Sajavaara, T. (2017). Characterization of ALD grown TixAlyN and TixAlyC thin films. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 406(Part A), 152-155. https://doi.org/10.1016/j.nimb.2016.12.032

Characterization of ALD Grown Ti_xAl_yN and Ti_xAl_yC Thin Films

S.A. Kinnunen[a], J. Malm[a], K. Arstila[a], M. Lahtinen[b], T. Sajavaara[a]

[a] *University of Jyvaskyla, Department of Physics, P. O. Box 35, FI-40014 University of Jyvaskyla, Finland*
[b] *University of Jyvaskyla, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyvaskyla, Finland*

Abstract

Atomic layer deposition (ALD) was used to grow Ti_xAl_yN and Ti_xAl_yC thin films using trimethylaluminum (TMA), titanium tetrachloride and ammonia as precursors. Deposition temperature was varied between 325 °C and 500 °C. Films were also annealed in vacuum and N_2-atmosphere at 600–1000 °C. Wide range of characterization methods was used including time-of-flight elastic recoil detection analysis (ToF-ERDA), X-ray diffractometry (XRD), X-ray reflectometry (XRR), Raman spectroscopy, ellipsometry, helium ion microscopy (HIM), atomic force microscopy (AFM) and 4-point probe measurement for resistivity. Deposited films were roughly 100 nm thick and contained mainly desired elements. Carbon, chlorine and hydrogen were found to be the main impurities.

Keywords: ALD, MAX-phases, ToF-ERDA

1. Introduction

Atomic layer deposition is a widely used technique to produce uniform and conformal thin films even on high-aspect-ratio structures [1]. ALD-process

contains sequential gas-phase precursor pulses divided by inert-gas purging. Volatile precursors react on substrate and form new film layer-by-layer which allows precise thickness control.

MAX-phases are a group of ternary carbides and nitrides that share properties common to both metals and ceramics. They were discovered already in the 1960's [2] although more systematic research began in the 1990's and currently some 60 different MAX-phases are known [3]. While many of them are heat and oxidation resistant like ceramics, they often posses metal-like thermal and electrical properties. MAX-phases have a common $M_{n+1}AX_n$ structure where n=1, 2 or 3. In the formula M designates early transition metal, A is an A- group element and X is carbon or nitrogen. MAX-phases have layered structure where MX-layers are separated by A-layers and thickness of MX-layer depends on n. This laminate-like structure makes most MAX-phases stiff and shock resistant.

In this work targeted MAX-phase thin films were Ti_2AlN, Ti_4AlN_3, Ti_2AlC and Ti_3AlC_2.

MAX-phase thin films have been deposited using several different methods like sputtering, cathodic arc deposition, chemical vapor deposition etc. [3]. Deposition of MAX-phase thin films has required deposition temperatures around 1000 °C. If deposition temperature is relatively low, post annealing can be used to produce MAX-phases [4]. However, ALD has not been utilized in making of MAX-phase thin films. Potentially, ALD could be used to deposit MAX-phases in lower temperatures due to its characteristic layer-by-layer deposition process.

2. Experimental details

All thin films were deposited using Beneq TFS-200 reactor at 1–2 mbar pressure on <100> silicon substrate. $TiCl_4$, TMA and NH_3 were used as precursors to deposit Ti_xAl_yN films by mixing TiN and AlN cycles. In addition, Ti_xAl_yC films were deposited using solely $TiCl_4$ and TMA. Nitrogen was used as a carrier and purge gas in both cases. TiN/AlN cycle consisted of 150 ms $TiCl_4$/TMA pulse, 750 ms purge, 300 ms NH_3 pulse and 2000 ms purge. Nitride films were deposited at 325, 400 and 450 °C. When depositing nitride films, ratio of TiN and AlN cycles were varied in order to achieve different atomic composition. Carbide cycle consisted of 300 ms TMA pulse, 2000 ms purge, 150 ms $TiCl_4$ pulse and 1000 ms purge, and deposition was done at 500 °C. In order to compensate relatively low deposition temperature for MAX-phases, as deposited films were also annealed in vacuum and nitrogen atmosphere at 600–1000 °C for 10 minutes.

Elemental composition was determined using 1.7 MV Pelletron accelerator by ToF-ERDA with 13.615 MeV $^{63}Cu^{7+}$ incident ions [5]. Heavy ions were accelerated in order to produce recoiled atoms from the sample. In ToF-ERDA, time-of-flight (velocity) and energy of recoiled atoms are measured and different masses can be separated. When stopping forces, scattering cross-sections and measurement geometry are known, data can be used to produce elemental depth profiles. Even the lightest elements including hydrogen can be detected. [6]

Surface morphology and cross-sections of the films were investigated with Zeiss Orion Nanofab helium ion microscope. Surface roughness was measured with Digital Instruments, Dimension 3100 (NanoScope IV and V) Bruker

(Veeco) atomic force microscope.

Crystallinity of the films was investigated using XRD (PANalytical X'Pert Pro) with copper $K_{\alpha 1}$ X-rays. Film thicknesses and densities were measured with the same equipment using XRR-configuration.

Raman measurements were made with home build Raman setup using 532 nm excitation with back scattering geometry.

3. Results

Growth per cycle (GPC) of binary TiN and AlN at 450 °C were 0.36 Å/cycle and 1.9 Å/cycle, respectively. Mixing of TiN and AlN cycles did not have an effect on growth rates of individual cycles. TiN and AlN GPCs at 325 °C were 0.30 Å/cycle and 0.16 Å/cycle. Similar growth rates for AlN have been reported [7], although GPC reported in this work at 450 °C is relatively high. High growth rate can be due to decomposing TMA, which starts at 332 °C [8]. This may lead to more continuous CVD-growth instead of self-limiting ALD-growth. Growth rate of TiN was somewhat higher than reported elsewhere, for example Ahn *et al.* reported 0.17 Å/cycle [9] and Satta *et al.* 0.24–0.28 Å/cycle at 400 °C [10]. For Ti_xAl_yN films deposited at 325 °C the average TiN/AlN GPC was 0.45 Å/cycle and the average GPC was independent of TiN:AlN cycle ratio. The average growth per subcycle was higher than for either binary compound. This growth enhancing can be due to TMA, which can act as an extra reducing agent for TiN [11].

Densities of the binary films are lower than bulk densities of TiN and AlN (5.21 g/cm^3 and 3.255 g/cm^3 [12], respectively), as seen in Table 1. Increasing deposition temperature slightly increases film density, and densities

Table 1: Density, surface roughness and elemental composition of as deposited films. TiN:AlN cycle ratio is mentioned for Ti_xAl_yN films. Interface and surface region are excluded from composition analysis due to surface oxygen. Relative uncertainty for main components is 2 %, for impurities excluding hydrogen 5 % and for hydrogen 10 %.

Film	T [°C]	Density [g/cm^3]	RMS roughness [nm]	Ti	Al	N	O	C	Cl	H	Other
TiN	325	4.23	-	45	-	53	0.3	0.1	1.3	0.4	Na 0.2
AlN	325	2.15	1.2	-	36	39	2.9	1.5	0.5	20	-
$TiAl_xN_y$ 1:2	325	3.40	0.6	22	16	43	<0.1	3.1	5.9	10	-
$TiAl_xN_y$ 1:1	325	3.79	0.5	30	10	42	0.2	5.3	5.7	6.8	-
$TiAl_xN_y$ 4:3	325	3.74	0.3	32	9.0	41	<0.1	5.7	5.6	6.3	-
$TiAl_xN_y$ 1:1	400	-	-	22	23	47	0.1	3.0	1.4	3.5	-
TiN	450	4.70	0.8	45	-	53	0.6	0.1	0.1	<0.1	Na 0.2
AlN	450	-	2.1	-	43	43	0.2	4.2	-	9.7	-
$TiAl_xN_y$ 1:2	450	3.18	1.9	7.3	36	43	0.1	6.2	1.4	6.1	-
$TiAl_xN_y$ 1:1	450	4.07	-	24	20	45	0.1	7.9	0.8	2.7	-
$TiAl_xN_y$ 2:1	450	4.26	0.4	30	14	47	0.1	6.0	0.8	1.5	-
$TiAl_xN_y$ 4:1	450	4.57	0.4	36	8.0	46	0.1	7.7	0.8	1.8	-
$TiAl_xC_y$	500	3.18	1.1	26	6.2	-	0.1	62	2.3	3.7	-

of Ti_xAl_yN-films fall between binary compounds.

Surface root mean square roughness of the films was relatively low and varied from 0.3 to 2.1 nm (Table 1). Acquired AFM topographs did not show signs of crystallization.

Elemental compositions of as deposited films are presented in Table 1. Example of acquired time-of-flight and energy histogram is presented in Figure 1 a). As deposited films had uniform elemental composition with thin oxide layer at the surface. A representative example is presented in Figure 1 b).

Elemental depth profiles acquired by ToF-ERDA measurements show that films grow homogeneously and contain mainly desired elements. Ratio between titanium and aluminum can be controlled by selecting desired amount of TiN and AlN subcycles. Ti:Al ratio in the film is linearly dependent on

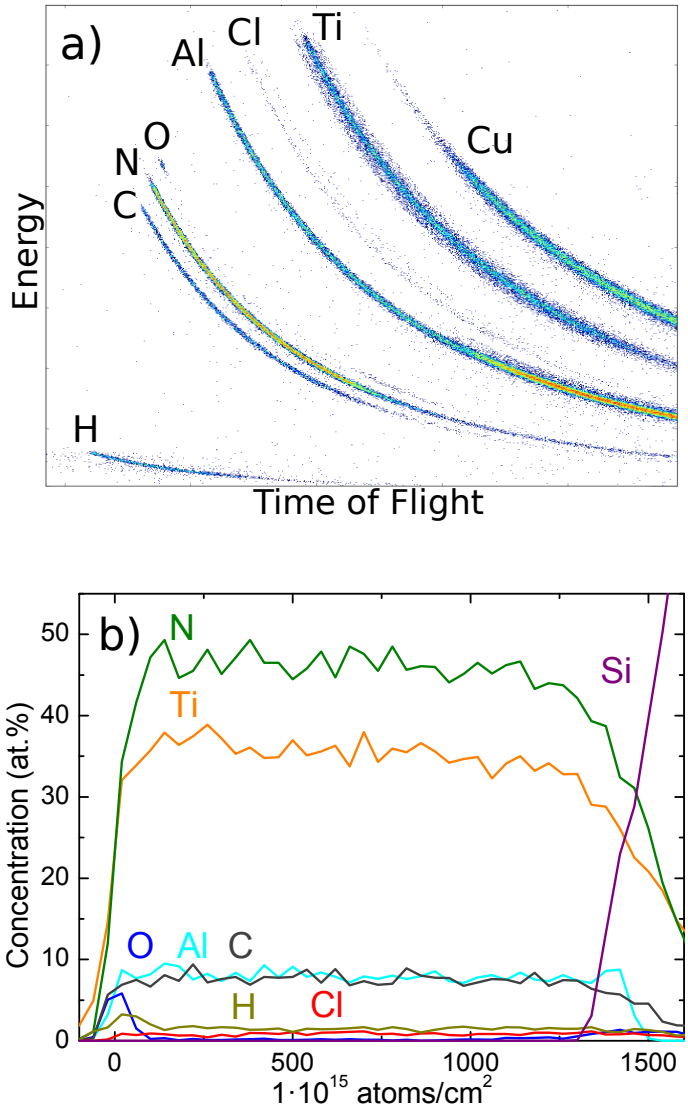

Figure 1: a) Coincidence time of flight and energy histogram. For Ti_xAl_yN film deposited at 450 °C with TiN:AlN cycle ratio of 4:1, different elements can be separated and identified. b) Corresponding elemental depth profile.

TiN:AlN subcyle ratio but varies with deposition temperature as seen in Figure 2. The nitrogen content was not affected by cycle ratios or deposition temperature, and was between 41–47 at.%. Main impurities in the films

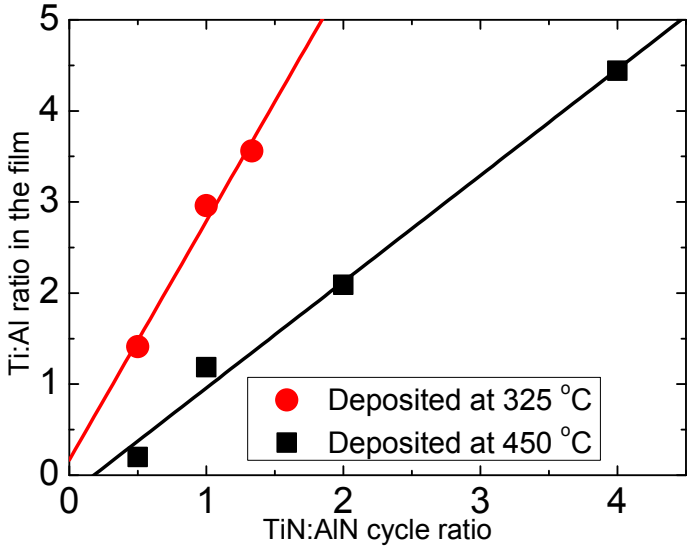

Figure 2: Ti:Al ratio in the Ti_xAl_yN films as a function of TiN:AlN cycle ratio at two different deposition temperature.

were carbon, hydrogen and chlorine which originate from precursors. Small amount of oxygen was detected at the film surface and interface. Increase in deposition temperature decreases amount of hydrogen and chlorine due to more complete surface reactions (Figure 3). However, carbon concentration increases at 450 °C. TMA starts to decompose at 332 °C [8], which is the probable reason for the increase of carbon at higher temperatures. Annealing of films in vacuum had little effect on film composition or crystallinity. Some chlorine and hydrogen was removed but main components of the film remained unchanged.

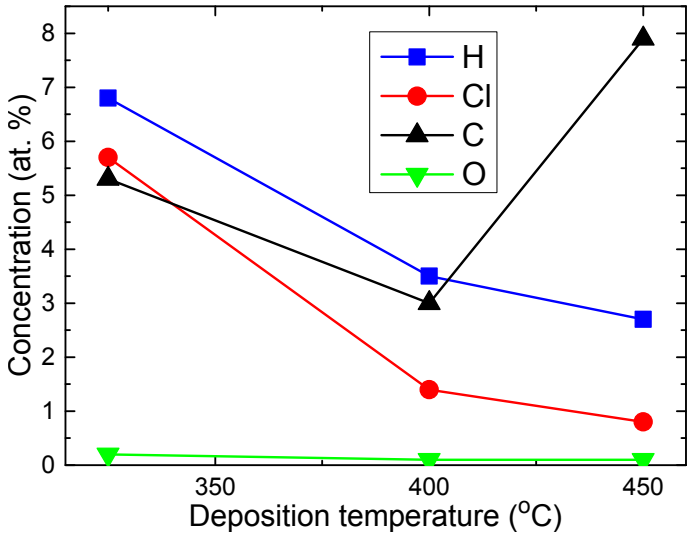

Figure 3: Impurity concentrations of Ti_xAl_yN films deposited at different temperatures.

Films annealed at N_2-atmosphere were oxidized due to unknown oxygen source. Relative amounts of main components remained unchanged after annealing, while impurity concentrations excluding oxygen decreased slightly.

ToF-ERD analysis showed that films deposited at 450 °C were more oxidation resistant than films deposited at 325 °C. During annealing aluminum accumulates at film surface where it forms aluminum oxide which can be seen in Figure 4 a). Protective aluminum oxide layer is formed independent of deposition temperature. However, oxygen incorporates films deposited at 325 °C thoroughly as seen in Figure 4 b), while oxidation stopped after few tens of nanometers in films deposited at 450 °C.

According to XRD-measurements, as deposited films as well as annealed films were mostly amorphous containing only small crystals. No detectable MAX-phases were found. Cubic TiN and wurtzite-like AlN crystals with

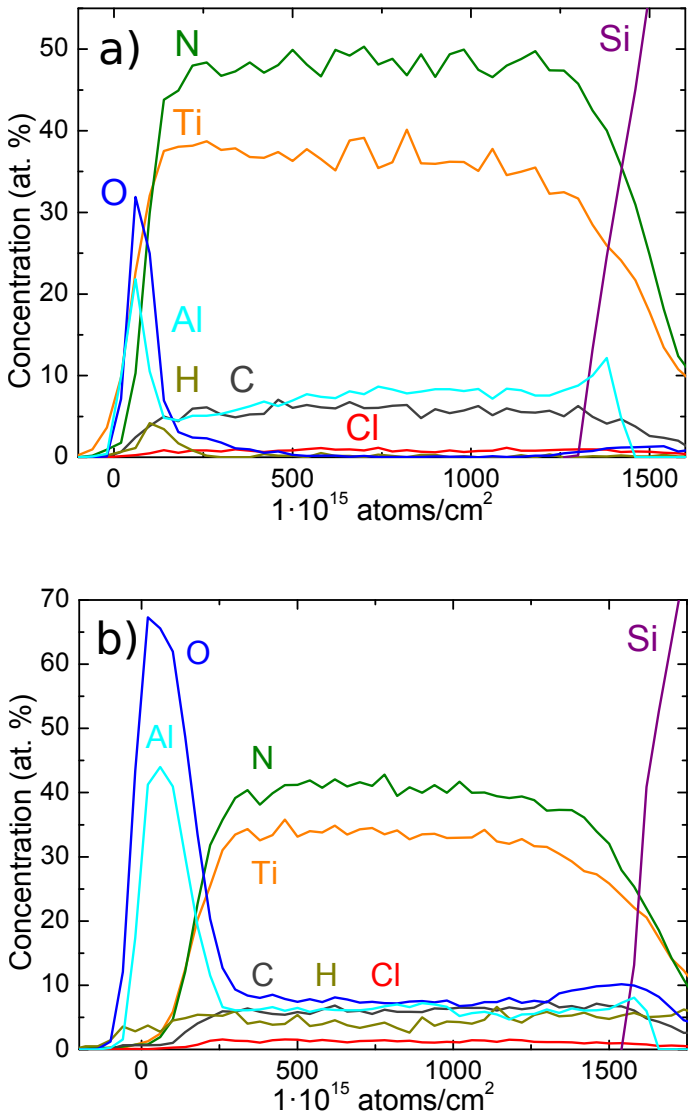

Figure 4: a) Depth profile of a Ti_xAl_yN film (4:1) deposited at 450 °C after 10 minute annealing in N_2-atmosphere at 1000 °C. b) Depth profile of Ti_xAl_yN film (4:3) deposited at 325 °C after 10 minute annealing in N_2-atmosphere at 1000 °C.

115 average size around 10 nm were detected. Annealing increased slightly crys-

tallinity of the films but did not cause formation of MAX-phases. Likewise, Raman spectroscopy could not find traces of MAX-phases. However, according to Raman measurements impurity carbon seems to form C–C double bonds during annealing. Home made 4-point probe was used to determine resistivity of the films. Films deposited at 325 °C had resistivity at $10^{-5}\,\Omega$m region while films deposited at 450 °C had resistivity roughly one order of magnitude lower. Resistivity decreased with increasing titanium concentration.

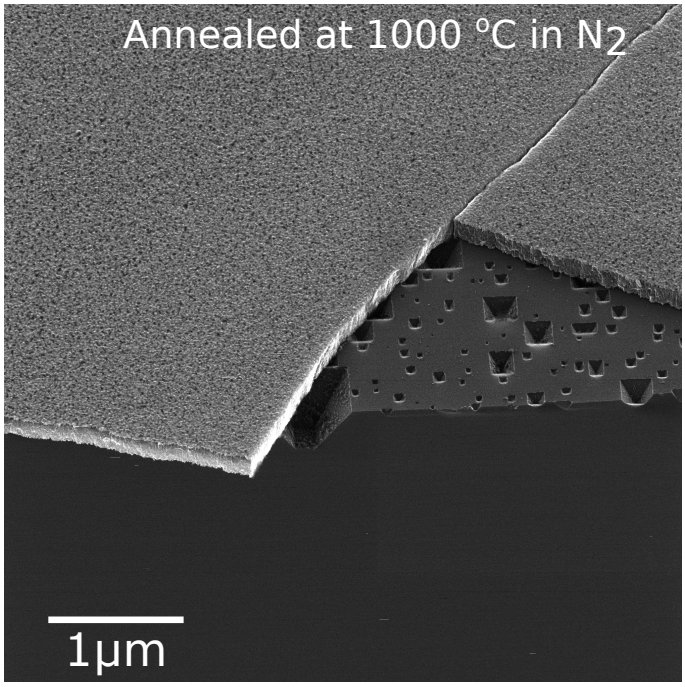

Figure 5: HIM micrograph of Ti_xAl_yN film deposited at 325 °C after annealing in N_2-atmosphere at 1000 °C. Sample is tilted at 45°.

HIM micrographs revealed unexpected anisotropic etching of silicon wafer underneath the film after annealing in N_2-atmosphere. Micrograph of Ti_xAl_yN

film after annealing is seen in Figure 5. Etching seems to take place only in the films deposited at 325 °C and not in the films deposited at 450 °C. Strong bases which typically contain hydroxyl group are used to anisotropically etch silicon [13]. It could be possible, that oxygen which penetrated films deposited at 325 °C during annealing (Figure 4 b)), forms OH^- -groups with impurity hydrogen. These hydroxyl groups could possibly cause anisotropic etching.

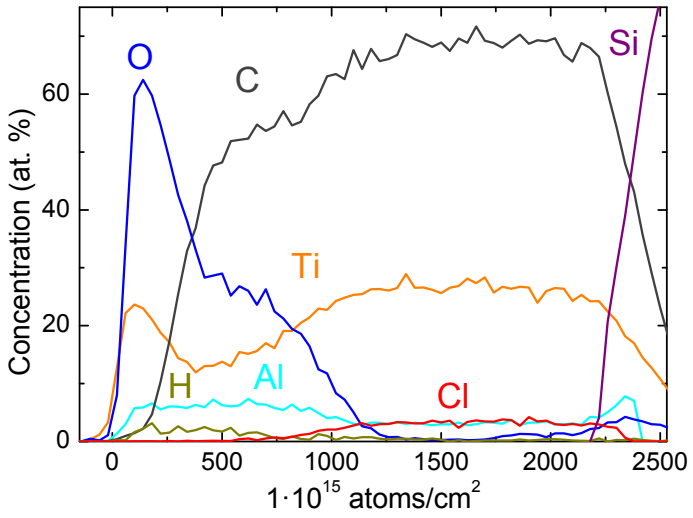

Figure 6: Elemental depth profile of Ti_xAl_yC film after annealing in N_2-atmosphere at 1000 °C.

Ti_xAl_yC films were successfully deposited and elemental composition was uniform. Films were carbon rich and contained only little aluminum (see Table 1). Growth rate of Ti_xAl_yC was 1.5 Å/cycle. Films contained TiC crystals with average size less than 10 nm and no MAX-phases could be identified. Annealing of the film in N_2-atmosphere also lead to oxidation of the film similar to nitride films. Interestingly, titanium accumulates in the

surface as an oxide, while aluminum seems to form a second layer on the surface with titanium oxide layer, as seen in Figure 6. Rutile (TiO_2) crystals were detected by XRD in annealed carbide films.

4. Conclusions

Titanium and aluminum concentration in Ti_xAl_yN films can be controlled by varying TiN and AlN pulse ratios. Nitrogen content in the films remained approximately constant and it was too high considering MAX-phases. Impurity concentrations decreased with increasing deposition temperature excluding carbon. Films deposited at 450 °C were more resistant to oxidation compared to films deposited at lower temperature. During annealing aluminum seems to accumulate in the film surface yielding a protective aluminum oxide layer. Films were mostly amorphous containing only small TiN and AlN crystals while no MAX-phases were detected. Unexpected anisotropic etching of the <100> silicon wafer underneath Ti_xAl_yN film deposited at 325 °C was discovered, after films were annealed in N_2 at 1000 °C.

In addition carbon rich Ti_xAl_yC films were deposited and annealed. Aluminum content in carbide films was too low for MAX-phases. Films contained small TiC crystals but no trace of MAX-phases.

Acknowledgments

This work was supported by Academy of Finland Center of Excellence in Nuclear and Accelerator Based Physics (Ref. No. 251353).

References

[1] V. Miikkulainen, M. Leskelä, M. Ritala, and R. Puurunen. *Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends.* Journal of Applied Physics, 113, 021301 (2013)

[2] H. Nowotny. *Strukturchemie einiger Verbindungen der Übergangsmetalle mit den elementen C, Si, Ge, Sn.* Progress in Solid State Chemistry, 5, (1971)

[3] P. Eklund, M. Beckers, U. Jansson, H. Högberg, and L. Hultman. *The $M_{n+1}AX_n$ phases: Materials science and thin film processing.* Thin Solid Films, 518(8):1851–1878, (2010).

[4] R. Grieseler, T. Kups, M. Wilke, M. Hopfeld and P. Schaaf. *Formation of Ti_2AlN nanolaminate films by multilayer-deposition and subsequent rapid thermal annealing.* Materials Letters, 82, 74–77 (2012)

[5] M. Laitinen, M. Rossi, J. Julin and T. Sajavaara. *Time-of-flight – Energy spectrometer for elemental depth profiling – Jyväskylä design* Nucl. Instrum. Meth. B 337, 55–61 (2014)

[6] M. Putkonen, T. Sajavaara, L. Niinistö and J. Keinonen. *Analysis of ALD-processed thin films by ion-beam techniques.* Analytical and Bioanalytical Chemistry, 382 (2005)

[7] C. Ozgit, I. Donmez, M. Alevli, and N. Biyikli. *Self-limiting low-temperature growth of crystalline AlN thin films by plasma-enhanced atomic layer deposition.* Thin Solid Films, 520(7):2750–2755 (2012)

[8] S. Yamashita, K. Watanuki, H. Ishii, Y. Shiba, M. Kitano, Y. Shirai, S. Sugawa, and T. Ohmi. *Dependence of the Decomposition of Trimethylaluminium on Oxygen Concentration.* Journal of Electrochemical Society, 158(2):93–96, (2011)

[9] C. Ahn, S. Cho, H. Lee, K. Park, and S. Jeong. *Characteristics of TiN thin films grown by ALD using $TiCl_4$ and NH_3.* Metals and Materials International, 7(6):621–625 (2001)

[10] A. Satta, J. Schuhmacher, C. Whelan,W. Vandervorst, S. Brongersma, G. Beyer, K. Maex, A. Vantomme, M. Viitanen, H. Brongersma, and W. Besling. *Growth mechanism and continuity of atomic layer deposited TiN films on thermal SiO_2.* Journal of Applied Physics, 7641–7646 (2002)

[11] V. Juppo, P. Alén, M. Ritala, and M. Leskelä. *Trimethylaluminium as a Reducing Agent in the Atomic Layer Deposition of Ti(Al)N Thin Films.* Chem. Vap. Deposition, 7, 211 (2001)

[12] David R. Lide. *CRC Handbook of Chemistry and Physics, 85th edition.* CRC Press, Boca Raton, 2005

[13] H. Seidel, L. Csepregi, A. Heuberger and H. Baumgärtel. *Anisotropic Etching of Crystalline Silicon in Alkaline Solutions.* J. Electrochem. Soc. 137:3612 (1990)