Atomic layer deposition in fabrication of micro- and nanodevices

Ville Rontu

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Atomic layer deposition (ALD) has become a widely used thin film deposition method in fabrication of many micro- and nanodevices. In this thesis, the reasons for this are investigated by studying what ALD has enabled for the applications based on available literature. In addition to reviewing existing applications, ALD was used in selected experimental case studies to enable better performing thin films and/or new improved device designs.

Based on the literature review the most important advantages that ALD offers are conformal deposition and precise thickness control combined with relatively low deposition temperatures. As the device dimensions and required film thicknesses have decreased, and the devices have turned from planar to three-dimensional, ALD has gained more momentum. However, due to the the biggest downside of ALD, slow deposition rate, ALD is selected as the deposition method only when other deposition methods fail to meet the requirements.

In the first experimental case, AlN deposition was studied from less used AlCl_3 precursor with aim of depositing pure and crystalline AlN thin films. The AlN deposition from AlCl_3 showed promise and enabled deposition of relatively pure AlN films. However, more work is still needed in order to determine whether it is a better precursor option for the deposition than the more commonly employed AlMe_3 . Additionally, the possibility to control residual stress of the AlN film was observed.

In the second experimental case, ALD was used to deposit heterogeneous catalyst into microreactors. ALD enabled deposition of even distribution of Pt nanoparticles in microreactor walls with controllable size, which showed high activity in hydrogenation of propene.

In the third experimental case, ALD Al_2O_3 and AlN was studied as thin free-standing membranes. The thin ALD Al_2O_3 membranes showed exceptional mechanical properties. Membranes of 400- μm diameter were fabricated as thin as 15 nm. The amorphous Al_2O_3 membranes were found more durable than polycrystalline AlN membranes.

In the final experimental case, ALD was used to enable new designs for fabrication of superomniphobic surfaces. Superomniphobic surfaces that could repel all room temperature liquids were realized with the help of ALD SiO_2 . Role of ALD in the fabrication of the superomniphobic surfaces could increase if the dimensions of the surface features are shrunk further. This could also enable decreasing the temperature budget of the process to $<120^\circ\text{C}$.

Keywords Atomic layer deposition, Thin film, Microfabrication, MEMS**ISBN (printed)** 978-952-64-0127-0**ISBN (pdf)** 978-952-64-0128-7**ISSN (printed)** 1799-4934**ISSN (pdf)** 1799-4942**Location of publisher** Helsinki**Location of printing** Helsinki**Year** 2020**Pages** 127**urn** <http://urn.fi/URN:ISBN:978-952-64-0128-7>

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Atomikerroskasvatuksesta (ALD) on tullut laajasti käytetty ohutkalvonkasvatusmenetelmä mikro- ja nanoteknologiassa. Tämän työn kirjallisuudessa on käyty läpi syitä, joiden johdosta ALDn suosio on kasvanut. Kokeellisessa osassa tarkastellaan ALD-kalvojen uusia sovelluskohteita, ja tutkitaan ALD-prosesseja erityisesti sovellusten vaatimuskäytännöistä käsin, tavoitteena laadukkaammat ohutkalvot ja/tai kokonaan uudenlaiset laiterakenteet.

ALDn merkittävimmät edut ovat konformaalinen pinnoitus ja tarkka paksuuskontrolli yhdistettyinä mataliin kasvatuslämpötiloihin. Mikro- ja nanoteknologian komponenttien koon pienentyminen ja komponenttien muuttumien kolmiulotteisiksi on lisännyt tarvetta ALDlle. ALDn suurin heikkous, hidas kasvunopeus, kuitenkin aiheuttaa sen, että menetelmä on usein kilpailukykyinen muihin pinnoitusmenetelmiin verrattuna vain, jos nämä muut menetelmät eivät kykene täyttämään asetettuja vaatimuksia.

Ensimmäisessä osatutkimuksessa selvitettiin puhtaan ja hyvän kidealaadun omaavan ALN:n kasvatusta harvemmin tutkitusta AlCl_3 -lähtöaineesta. ALN:n kasvatus AlCl_3 :sta oli lupaavaa ja sen avulla saatiin kasvatettua suhteellisen puhtaita ohutkalvoja. Lisäksi havaittiin mahdollisuus kontrolloida ALN-ohutkalvon jännityksiä.

Toisessa osatutkimuksessa ALD:tä käytettiin heterogeenisen katalyytin kasvattamiseen mikroreaktoreihin. ALD mahdollisti Pt-nanopartikkelien tasaisen jakautumisen mikroreaktoreiden pinnoille, ja nanopartikkelien koon kontrolloimisen. ALD-Pt-nanopartikkeleilla havaittiin olevan korkea aktiviteetti propeenin hydrauksessa propaaniksi.

Kolmannessa osatutkimuksessa tutkittiin ALD Al_2O_3 :n ja ALN:n soveltuvuutta itsekantaviksi kalvoiksi. ALD Al_2O_3 kalvoilla oli erinomaiset mekaaniset ominaisuudet, minkä johdosta pystyttiin valmistamaan jopa vain 15 nm paksuisia ja halkaisijaltaan 400 μm olevia itsekantavia kalvoja. Nämä amorfiset Al_2O_3 -kalvot osoittautuivat kestävyydeltään paremmiksi kuin monikiteiset ALN-kalvot.

Viimeisessä osatutkimuksessa ALD:tä käytettiin mahdollistamaan uudenlaisten superomnifobisten pintojen valmistaminen. Nämä superomnifobiset pinnat kykenivät hylkimään kaikkia tunnettuja nesteitä huoneenlämpötilassa. ALDn rooli näiden pintojen valmistamisessa saattaa kasvaa tulevaisuudessa, mikäli rakenteiden dimensioita pienennetään edelleen. Tämä mahdollistaisi pinnoille korkeamman painetoleranssin. ALDn käyttö mahdollistaisi myös koko prosessin maksimilämpötilan laskemisen jopa alle 120 °C:n.

Avainsanat Atomikerroskasvatus, Ohutkalvo, Mikrovalmistus, MEMS**ISBN (painettu)** 978-952-64-0127-0**ISBN (pdf)** 978-952-64-0128-7**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Helsinki**Painopaikka** Helsinki**Vuosi** 2020**Sivumäärä** 127**urn** <http://urn.fi/URN:ISBN:978-952-64-0128-7>

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List of Abbreviations and Symbols

ALD	Atomic Layer Deposition
BHF	Buffered Hydrogen Fluoride
CCP	Capacitively Coupled Plasma
CDU	Critical Dimension Uniformity
CMOS	Complementary Metal-Oxide Semiconductor
CTE	Coefficient of Thermal Expansion
CVD	Chemical Vapor Deposition
DRAM	Dynamic Random-Access Memory
DRIE	Deep Reactive Ion Etching
EVA	Ethylene-Vinyl Acetate
GPC	Growth Per Cycle
EUV	Extreme UltraViolet
EL	ElectroLuminescent
FIB	Focused Ion Beam
HAR	High Aspect Ratio
IC	Integrated Circuit
ICP	Inductively Coupled Plasma
IR	InfraRed
LDPE	Low-Density PolyEthylene
LHAR	Lateral High Aspect Ratio
MEMS	Micro-ElectroMechanical System
MFC	Mass Flow Controller
MFМ	Mass Flow Meter
MOCVD	Metal-Organic Chemical Vapor Deposition

NAND	Not AND, a type of non-volatile memory
NIL	NanoImprint Lithography
OLED	Organic Light-Emitting Diode
PCB	Printed Circuit Board
PEALD	Plasma-Enhanced Atomic Layer Deposition
PERC	Passivated Emitter Rear Contact
PET	PolyEthylene Terephthalate
PirSi	Piranha treated Silicon
PVD	Physical Vapor Deposition
RD NMR	Remote Detection Nuclear Magnetic Resonance
RF	Radio Frequency
RIE	Reactive Ion Etching
SADP	Self-Aligned Double Patterning
SAM	Self-Assembled Monolayer
SAQP	Self-Aligned Quadruple Patterning
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SOI	Silicon-On-Insulator
SWLI	Scanning White Light Interferometer
TEM	Transmission Electron Microscopy
ToF-ERDA	Time-of-Flight Elastic Recoil Detection Analysis
UV	UltraViolet
XRD	X-Ray Diffraction
XRR	X-Ray Reflectivity

List of Publications

This doctoral dissertation consists of a summary and of the following publications, which are referred to in the text by their Roman numerals

- I.**Rontu, Ville; Sippola, Perttu; Broas, Mikael; Ross, Glenn; Sajavaara, Timo; Lipsanen, Harri; Paulasto-Kröckel, Mervi; Franssila, Sami. 2018. Atomic layer deposition of AlN from AlCl₃ using NH₃ and Ar/NH₃ plasma. American Vacuum Society. J. Vac. Sci. Technol. A, volume 36, issue 2, article number 021508. ISSN: 0734-2101 DOI: 10.1116/1.5003381
- II.**Österlund, Elmeri; Kinnunen, Jere; Rontu, Ville; Torkkeli, Altti; Paulasto-Kröckel, Mervi. 2019. Mechanical properties and reliability of aluminium nitride thin films. Elsevier. J. Alloys Compds., volume 772, pages 306–313. ISSN: 0925-8388 DOI: 10.1016/j.jallcom.2018.09.062
- III.**Rontu, Ville; Nolvi, Anton; Hokkanen, Ari; Haeggström, Edward, Kassamakov, Ivan; Franssila, Sami. 2018. Elastic and fracture properties of free-standing amorphous ALD Al₂O₃ thin films measured with bulge test. IOP Publishing. Mater. Res. Express, volume 5, article number 046411. ISSN: 2053-1591 DOI: 10.1088/2053-1591/aabbd5
- IV.**Rontu, Ville; Selent, Anne; Zhivonitko, Vladimir; Scotti, Gianmario; Koptug, Igor; Telkki, Ville-Veikko; Franssila, Sami. 2017. Efficient catalytic microreactors with atomic layer deposited platinum nanoparticles on oxide support. Wiley. Chem. Eur. J., volume 23, issue 66, pages 16835–16842. ISSN: 1521-3765. DOI: 10.1002/chem.201703391.
- V.**Rontu, Ville; Jokinen, Ville; Franssila, Sami. 2020. Scalable superomniphobic surfaces. IEEE. J. Microelectromech. Systems, volume 29, issue 1, pages 54–61. ISSN: 1057-7157. DOI: 10.1109/JMEMS.2019.2950769

Author's Contribution

Publication I: Atomic layer deposition of AlN from AlCl₃ using NH₃ and Ar/NH₃ plasma

VR led the AlN process development, performed most of the depositions and carried out some film characterization. SP and MB assisted with the process development. MB carried out TEM analysis. PS, MB and GR performed XRD analysis. TS provided ToF-ERDA measurements and analysis. VR, SP and MB wrote the first draft of the manuscript and reviewed the manuscript. HL, MPK and SF reviewed the manuscript and supervised the work.

Publication II: Mechanical properties and reliability of aluminium nitride thin films

VR developed the ALD process used to deposit the ALD AlN thin film, deposited the film and measured its residual stress. VR assisted in the bulge test sample fabrication, bulge measurements and analysis, and reviewed the manuscript. JK and EÖ fabricated the bulge test samples and measured the properties. JK did the fatigue testing and reviewed the manuscript. EÖ did data analysis, XRD measurement, and wrote and reviewed the manuscript. AT provided sputtered AlN films and reviewed the manuscript. MPK reviewed the manuscript and supervised the work of JK and EÖ.

Publication III: Elastic and fracture properties of free-standing amorphous ALD Al₂O₃ thin films measured with bulge test

VR designed the experiments, fabricated the samples, characterized the samples, wrote and reviewed the manuscript. AN assisted with the bulge test measurement performed with white light interferometer and was supervised by EH and IK. AH carried out modelling. SF reviewed the manuscript and supervised the work of VR and AH.

Publication IV: Efficient catalytic microreactors with atomic layer deposited platinum nanoparticles on oxide support

VR developed the process for Pt nanoparticle deposition, characterized the nanoparticles and deposited them into the microreactors. VR also wrote the first draft of the article in collaboration with AS, VVT and VZ and reviewed the article with them. GS fabricated the silicon microreactors. AS, VVT and VZ carried out microreactor characterization with RD NMR. IK supervised the work of VZ. SF supervised the work of VR and GS and reviewed the article.

Publication V: Scalable superomniphobic surfaces

VR designed the actual fabrication process after original process concept of SF, fabricated the samples, and co-wrote and reviewed the manuscript with VJ. VJ carried out wetting characterization. SF reviewed the manuscript and supervised the work.

1. Introduction: atomic layer deposition in micro- and nanodevices

Microfabrication has been the enabler of modern society. Its touch can be encountered with everything we hold in our hands. In 1949 Popular Mechanics Magazine forecasted “*Where a calculator like the ENIAC today is equipped with 18,000 vacuum tubes and weighs 30 tons, computers in the future may have only 1000 vacuum tubes and perhaps weigh no more than 1.5 tonnes*” [1], and look at where we are now? We have a computer in almost every household item and we carry multiple computers in our daily personal items. Predicting the future can be difficult as we see from the quote. Vacuum tubes were replaced by transistors and instead of requiring less vacuum tubes to achieve same calculation power we have made smaller transistors and packed them more densely. Nowadays we have 3 billion transistors in processors of our modern smartphones (Qualcomm Snapdragon 835 in Samsung Galaxy S8) [2, 3].

Our modern processors could not have been made without atomic layer deposition (ALD) enabling deposition of nanometer thick films with thickness variation in level of a tenth of an ångström across a 300 mm substrate and its role is getting more and more significant [4]. In 2018, Technology Academy Finland awarded the Millenium Technology Prize [5], which is awarded to technological innovations “that enhance the quality of people’s lives”, are “applied in practice” and that “stimulate further cutting edge research and development” to Dr. Tuomo Suntola who is considered as the inventor of ALD [6].

In this thesis, the aim was to investigate applicability of ALD for selected applications in micro and nanotechnology. In Publication I, we investigated deposition of AlN thin films from previously little studied AlCl_3 precursors as a route to deposit thin films of high crystallinity and purity. In Publication II, we continued the investigation of the AlN thin films, and measured and compared the mechanical properties of the ALD AlN thin films with AlN thin films deposited by competing deposition methods. In Publication III, the mechanical properties of ALD Al_2O_3 membranes were investigated with the bulge test method. In Publication IV, applicability of ALD for catalyst deposition into silicon microreactors was investigated using ALD deposited Pt nanoparticles as an example catalyst. In Publication V, ALD SiO_2 was used as an enabler in fabrication of superomniphobic surfaces.

As a background, the thesis will first cover how ALD was discovered, followed by the breakthrough applications in microelectronics and microelectromechanical systems (MEMS). After this, the broadening of the ALD application field

outside micro- and nanodevices is briefly described. After introducing the ALD application field and the significance of ALD to modern technology to the reader, the thesis will introduce the deposition method itself in Chapter 2 starting from the basic principles. In Chapter 2, the reader is introduced also to different variants of ALD processes and process development using examples from the author's Publications I (AlN) and IV (Pt) in addition to some additional examples. In Chapter 3, introduction to measurement of thin film properties is given and measured properties of ALD thin films are described from Publications I, II and III. In chapter IV, two selected application areas, catalysts in microreactors and fabrication of superomniphobic surfaces based on Publications IV and V, are described.

1.1 Invention of atomic layer deposition

Atomic layer deposition was invented separately and unbeknown to each other in the former Soviet Union in 1960s under the name of Molecular Layering by Prof. Aleskovskii and Prof. Kolt'sov and in Finland in 1970s under the name of Atomic Layer Epitaxy by Dr. Tuomo Suntola [7]. Suntola developed the method in order to deposit sufficiently high-quality thin films that can prevent dielectric breakdown in electroluminescent (EL) displays, which operates at high electric fields ($2 \cdot 10^6 \text{ Vcm}^{-1}$) [8]. Suntola was successful with his method and EL displays became the first commercial application for atomic layer deposition [7, 9]. In the EL displays, ALD was used to deposit aluminium oxide or aluminium-titanium oxide nanolaminate dielectric and manganese doped zinc sulfide light emitting layers for the active EL element as well as aluminium oxide as a bottom layer to prevent sodium diffusion from soda lime glass substrate and as a protective top layer [7–9]. The EL displays made with ALD turned out to be superior in terms of brightness and contrast compared competitors EL displays [7].

1.2 Atomic layer deposition in microelectronics

In late 1990s semiconductor industry began showing interest in ALD, as new materials and deposition methods were required to keep up with the famous Moore's law formulated in 1965 by Intel's co-founder Gordon Moore [10]. Moore's law forecasted that the number of transistor in an integrated circuit (IC) chip would double every two years. The doubling was achieved by scaling down the transistor size and was driven by economics since scaling down enabled more transistors to be fabricated on a single wafer reducing costs associated with the fabrication.

The semiconductor industry's interest became the breakthrough for ALD and research on ALD has ever since kept growing (see Figure 1.1). Dielectrics in DRAM (Dynamic Random Access Memory) capacitors and CMOS (Complementary Metal-Oxide Semiconductor) transistors became so thin due to scaling down that conventional SiO_2 dielectrics were unable to meet the requirements in terms of leakage currents and were replaced with deposited high- κ materials [11–14]. In addition, DRAM capacitor area was scaled up while the cell footprint

Figure 1.1. Number of ALD publications per year according to search on Web of Science with key words “Atomic layer deposition” or “ALCVD” or “Atomic layer epitaxy” and further filtered with “nitride” and “oxide”.

on chip was scaled down. This led to development of new stacked and deep trench capacitor geometries, which had high aspect ratio (HAR) structures imposing stringent requirements for conformal dielectric deposition [13].

The research on high- κ dielectrics started in late 1990s and finally led to the implementation of ALD high- κ dielectrics by the semiconductor industry. Samsung was the first to implement ALD Al_2O_3 as the high- κ dielectric in their DRAM capacitor in the 0.13 μm node [15] although it did not enter production until 0.11 μm node [16–19]. The first commercially available CMOS utilizing hafnium-based high- κ dielectrics deposited with ALD was Intel’s 45 nm technology introduced to consumers in 2007 [14]. In addition to high- κ dielectrics, semiconductor industry implemented ALD to deposit TiN as the metal in metal-insulator-metal (MIM) capacitors introduced for DRAM capacitors in the 65 nm node [13]. ALD TiN was chosen as the electrode material because of the lower thermal budget compared to chemical vapor deposition (CVD) TiN [13]. The lower thermal budget was important as it helps to maintain the logic performance that was already fabricated before the capacitor structures in the stacked capacitor geometry (schematic shown in Figure 1.2), which became the more popular scheme over the deep trench capacitor [20].

ALD application areas in semiconductor industry has since expanded beyond high- κ and electrode materials and is constantly finding new roles. With demand for shrinking dimensions and delay in implementation of next generation extreme-UV (EUV) lithography, resolution enhancing scheme known as self-aligned double patterning (SADP), spacer defined double patterning (SDDP) or sidewall spacer double patterning (SSDP) was applied to stretch processability of 193 nm ArF immersion lithography for 3x nm memory nodes [21–23]. Logic manufacturers led by Intel followed in memory manufacturer’s example by im-

Figure 1.2. Schematic of capacitor under bitline stacked capacitor DRAM design. Not drawn to scale. ALD is used to make the capacitor structure with TiN top and bottom electrodes with ZrO₂/Al₂O₃/ZrO₂ dielectric stack between the electrodes. Conformality of the deposition is vital for the capacitor performance. Aspect ratio in the capacitor structure can be >50.

plementing SADP scheme at 14 nm node [24]. SADP is based on a single lithography step, which is followed by deposition and etching steps. In SADP, a mandrel is first formed either by lithography and etching steps followed by conformal deposition, or by lithography and direct deposition on photoresist (direct-SADP). Then the deposited layer is etched from the horizontal areas to form spacers around the mandrel. After removing the mandrel, the spacers form a new mask that can be transformed into the actual etch mask material. ALD enables the more cost-efficient direct-SADP option with low deposition temperatures (<100 °C plasma-enhanced ALD (PEALD) SiO₂) that do not deform the photoresist shape [25–27]. Later on, an extension to the scheme called self-aligned quadruple patterning (SAQP) was implemented. In SAQP, the first spacers act as the mandrels for the second deposition, enabling even smaller dimensions and pitch. It was used for the first time in 1x NAND Flash generation [28] and later by logic manufacturer's led again by Intel at 10 nm node [29]. Even with the emergence of the long delayed EUV lithography, the future nodes will require ALD enabled SADP for the smallest pitches – this time combined with EUV.

Future for ALD in semiconductor industry seems bright as demand for more conformal deposition and atomic level processing is still increasing. The required film thicknesses decrease complementing for the downside of ALD: slow deposition rate.

1.3 Atomic layer deposition in microelectromechanical systems

Another important field for application of ALD is MEMS. MEMS technology enables miniature sensors such as accelerometers, gyroscopes and microphones that are found in everyday devices like mobile phones and smart watches.

The MEMS industry has historically followed on semiconductor industry's footsteps in the processing technologies. The application of ALD to MEMS was initiated by Victor Bright's, Steven George's and Yang Chen Lee's groups in University of Colorado in early 2000s. They filed for a patent in 2002 [30] for application of ALD to deposit a conformal film on MEMS device that acts as protective, insulating or biocompatible film. The specific advantage, which they saw that ALD could bring to MEMS manufacturing, was the ability to coat released structures conformally at low temperatures.

ALD thin films have been used in fabrication of MEMS devices as an etch stop or hard mask layer as well as as functional material layer in MEMS devices providing electrical, optical, chemical or tribological properties for the device. Devices where ALD has been and is being used are thin film magnetic heads in hard disk drives [31–34], inkjet printheads [35–38], humidity sensors [39], bolometers [40–42], different RF resonators [43–48], Fabry-Perot interferometers [49–51] to mention some. ALD is also used in MEMS packaging to provide insulation [52], hermetic sealing [52, 53] and surface charge dissipation [54]. Table 1.1 gathers together different ALD films used in these applications and their purpose and key features that led to adoption of the said ALD film.

Table 1.1. Where and what ALD films are used, their purpose and key features in MEMS applications.

MEMS device	ALD film	ALD film purpose	Film thickness	Deposition temperature	Key features	References
Thin film magnetic head	Al_2O_3	Dielectric, assists in fabrication	<100 nm	80–200 °C	Low deposition temperature, conformality, thickness control	[31–34]
Inkjet printhead	$\text{RuO}_2/\text{TiO}_2$	Heater	100 nm	230 °C	Controlled mixture to neglect temperature coefficient of resistance	[35, 36]
Resistive humidity sensor	Ta_2O_5 , $\text{HfO}_2/\text{Ta}_2\text{O}_5$, $\text{ZrO}_2/\text{Ta}_2\text{O}_5$	Corrosion protection, dielectric	10–50 nm	<400 °C	Amorphous pin-hole free film	[37, 38]
	Pt	Sensing film: conductor	1–10 nm	270 °C	Uniformity, thickness control, discontinuous film	[39]
Bolometer	Pt	Sensing film: absorber, conductor	5–50 nm	200–300 °C	Conformality	[40–42]
	Al_2O_3	Seed layer, structural support, insulator	10 nm	<300 °C	Conformality	[40, 42]
	TiN	Seed layer, structural support, sensing film: absorber	5–60 nm	<300 °C	Conformality	[41]

Disc resonator gyroscope	Al_2O_3	Seed layer	1–2 nm	150–200 °C	Conformality, uniformity, thickness control	[45]
	Pt, Ru	Conductive layer	1–100 nm		Conformality, uniformity	[45]
Hemispherical resonator gyroscope	Al_2O_3	Resonator material, structural support	50 nm	130 °C	Conformality, uniformity, thickness control	[44]
	$\text{HfO}_2/\text{TiO}_2$	Resonator material, structural support	?	?	Conformality, uniformity, thickness control, controlled mixture for low thermal expansion coefficient	[46]
Acoustic resonator	TiO_2	Compensate temperature coefficient of resonant frequency of resonator	10 nm	?	Conformality, uniformity, thickness control	[48]
Bulk acoustic wave resonator	Al_2O_3	Passivation, moisture barrier, seed layer for SAM	10–25 nm	?	Conformality, uniformity, pin-hole free, thickness control	[47, 55]
	SiO_2	Seed layer for SAM	10 nm	?	Conformality, uniformity, pin-hole free, thickness control	[47]
Nanoplasmonic resonator	$\text{Au}/\text{SiO}_2/\text{Au}$	Resonator	25/5/25 nm	?	Conformality	[56]

Tuneable Fabry-Perot interferometer	$\text{Al}_2\text{O}_3/\text{TiO}_2$	Optical filter	300–500 nm	<150 °C	Thickness control, uniformity, low deposition temperature, low film residual stress, amorphous film	[49, 50]
General MEMS packaging	$\text{Al}_2\text{O}_3, \text{SiO}_2, \text{TiO}_2$	Hermetic seal, insulation, seed layer for SAM	10–20 nm, <100 nm	<200 °C	Conformality, pin-hole free, low deposition temperature,	[52, 53, 57–59]
	$\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3\text{:Pt}/\text{Al}_2\text{O}_3$	Passivation, protection against harsh environments	5 nm / 25 nm / 5 nm	100–300 °C	4 nm Pt nanoparticles encapsulated in Al_2O_3 matrix, conformality, pin-hole free, low deposition temperature	[60]
	Pt, TiN	Surface charge mitigation	5–10 nm		Low deposition temperature, conformality	[54]

1.4 Atomic layer deposition in other microdevices

In photovoltaics, ALD is mainly used to deposit a passivation layer for passivated emitter rear contact (PERC) solar cells, which are becoming an industry standard [61]. Photovoltaics has been one of the most demanding application for ALD in terms of throughput. To answer the throughput demand, high volume spatial [62, 63] and batch [64] ALD systems have been developed. Throughput of up to 10000 wafers/hour can be achieved with commercial ALD system made for solar cell passivation depositing Al_2O_3 passivation layer [65]. Al_2O_3 is the passivation layer material used by the industry for PERC solar cells, although other options such as TiO_2 and combinations of Al_2O_3 and TiO_2 are researched for PERC solar cells and emerging cell designs [66–69].

1.5 Application field of atomic layer deposition to outside of micro- and nanodevices

In chemical engineering, ALD has been studied as a method for catalyst engineering for heterogeneous catalysis already in 1990s, initially by Neste Oy and Microchemistry Ltd. [70–72]. The research has focused mainly on deposition of catalyst material and/or catalyst support on porous substrates and powders. Catalyst engineering with ALD shows promise, but has not yet found an industrial breakthrough [73, 74]. Few companies such as ALD Nanosolutions [75] and Delft IMP [76] are attempting commercialization.

As a protective coating, ALD has found applications in many areas. Close to electronics industry, ALD has been used for example as a moisture barrier for organic light emitting diodes (OLEDs) [77, 78] and printed circuit boards (PCBs) [78]. For PCBs, ALD protective coating has also shown capability for mitigation of tin whisker formation [79]. Outside electronics industry, ALD has been used to prevent silver tarnishing since 2006 and more recently in corrosion protection of steel. As antitarnishing layer, Kalevala Jewelry and Lapponia use 10 nm Al_2O_3 coating on consumer jewelry [9, 80]. In corrosion protection of steel, ALD films have been used in conjunction with a thick physical vapor deposition (PVD) coating to form a duplex coating [81]. In these, ALD films function is to fill the pinholes present in the PVD coating that is thick enough to provide wear resistance.

1.6 Summary

ALD was for a long time a small niche deposition method, but in recent years, it has grown into a deposition method with applications in a variety of fields. Research on ALD is ever growing and new applications are finding ALD helpful. ALD's success is a result of shrunk device dimensions, change from planar to three-dimensional structures and increased requirement for precise control over the deposited material. These demands have rendered ALD as the only

suitable option for film deposition in some applications complementing the disadvantages of ALD. Therefore, it can be said that ALD excels at applications where no other film deposition method is possible.

2. Atomic layer deposition: processes and process development

As was shown in previous chapter, atomic layer deposition gained its momentum due to change in requirements posed by the applications for the deposition process into such that other deposition processes could no longer meet them. The unique characteristics of ALD thin films is result of fundamentals of the process. In the next subchapters, the basic principle of ALD and the film properties and characteristics of the deposition that follows are explained. The following subchapters will also address different reactor designs and details of process development for ALD. At the end of the chapter, time is taken to go over typical oxide, nitride and metal processes followed by discussion over what separates them from each other.

2.1 Basic principle of atomic layer deposition

Atomic layer deposition is based on sequential self-saturating gas-solid half-reactions of at least two precursors that are separated from each other either temporally or spatially and repeated in a cyclewise manner in order to deposit a thin film (see Figure 2.1). The term half-reaction arises from the fact that the full ALD cycle can be described as a chemical reaction that is broken down in two or more parts in the ALD process. For example, AlN deposition from AlCl_3 and NH_3 could be described with the following simple reaction equation

However, this is a simplification and the surface reactions that take place during the half-reaction on the surface are complex. This type of ALD process that consists of two precursors is described as an AB type process. A designates the first precursor and B the second. Typically A is the metal precursor, here AlCl_3 , and B the coreactant, here NH_3 .

The self-saturative reaction conditions are met only in certain operation conditions. These conditions are typically referred as the ALD window [8]. The ALD window (Figure 2.2) is commonly depicted as the temperature range where the self-saturating reactions can be found. The reasons for non-saturative conditions at too low temperatures can be condensation of the precursor on the surface leading to increased growth per cycle (GPC) or incomplete reactions resulting from insufficient driving force for the chemical reactions leading to decrease in GPC. On the other hand, too high temperatures might lead to decomposition of the precursor and deposition on the surface leading to increased GPC or desorption or loss of surface species leading to decreased GPC.

Figure 2.1. Basic principle of ALD: repeating a cycle of two pulse-purge sequences until desired film thickness is achieved.

Figure 2.2. ALD window is the temperature range where requirements for the ALD like growth are satisfied. Ideally, the GPC in this window would be constant, but small deviation is common. Outside of the ALD window the GPC is increased due to precursor condensation and decomposition and reduced due to incomplete reaction, desorption of precursor or surface species. Adapted from [86–87].

The ALD window is often depicted to show constant GPC. However, small deviation from ideal behavior is common. This can be due to activation and deactivation of certain reaction pathways, which can lead to a different saturation density. The ALD window of Al_2O_3 from trimethylaluminium (Me_3Al) and H_2O extends from room temperature to $300\text{ }^\circ\text{C}$, above which Me_3Al starts to decompose slowly. At low temperatures, removal of methyl groups from the surfaces during the H_2O pulse becomes more difficult and long pulse times are required [82]. The GPC of Al_2O_3 increases with temperature up to $250\text{ }^\circ\text{C}$ [82, 83]. In comparison, the ALD window of AlN from AlCl_3 and NH_3 starts only around $550\text{ }^\circ\text{C}$ due to low reactivity of NH_3 leading to difficulty of removing chlorine from the surface [84, 85].

The growth per cycle depends on deposited material and used precursors. In reality, the GPC is, however, less than a monolayer of the deposited material. For example, a monolayer of Al_2O_3 is approximately $3.8\text{ \AA}$ [86] whereas GPC of approximately $1\text{ \AA}$ is commonly observed for ALD of Al_2O_3 from Me_3Al and H_2O . Limitation of GPC to sub monolayer is a consequence of either steric hindrance posed by bulky molecules or due to availability of reactive sites on the substrate [87].

2.2 General properties of an atomic layer deposition process

The requirement of self-saturating reactions and separation of precursors separate ALD from other CVD processes and gives ALD processes their characteristic properties. In theory, self-saturation leads to perfectly conformal, uniform and homogenous film. It also defines a discrete layer thickness that is deposited after each precursor pulse enabling layer thickness control down to a single mo-

lecular layer. Moreover, the adhesion of the film is superior to other film deposition methods due to chemical reactions with the surface providing chemical bonds with the substrate. The downside with the requirement of saturation and separation of precursor is encountered in the deposition rate. A typical ALD cycle in a single wafer tool lasts for couple of seconds and deposits a 1 Å film. Using a 5 s cycle time this leads to deposition rate of 1.2 nm/min or 72 nm/hour, while deposition rate for LPCVD polysilicon is 10 nm/min and for some PECVD oxide processes 100 nm/min. Some ALD processes are able to reach 10 nm/min rate.

2.3 Thermal and plasma-enhanced atomic layer deposition

Thermal ALD uses thermal energy as the driving force for the chemical reactions. Thermal ALD is so common that often the prefix “thermal” is left unmentioned and simply ALD is used to refer thermal ALD processes when no special emphasis is seen necessary. However, alternative energy sources are also used and researched. The most common alternative is plasma energy that is used in plasma-enhanced atomic layer deposition (PEALD) to create highly reactive radicals. In PEALD, plasma is used for the second precursor pulse in a typical AB type ALD process. More recent innovation and rarely utilized alternative is photons [88] in photo-assisted ALD (Photo-ALD) where energetic photons, for example UV-light, provide needed energy to chemical reactions.

On planar substrates, both thermal ALD and PEALD result in similar ALD thin films in terms of uniformity and homogeneity. PEALD enables lower temperatures due to highly reactive plasma radicals, and can enable new processes and increased control over film properties [89]. However, on substrates with demanding high aspect ratio (HAR) features difference between thermal ALD and PEALD becomes obvious. Plasma species recombine on surfaces and cannot reach into deep features limiting conformality. Energetic ions in the plasma or UV-light generated by the plasma may also cause some damage to the substrate or the growing film.

2.4 Reactors for atomic layer deposition

Spatial vs. temporal

ALD reactors can be divided into few different categories and subdivisions depending on the configuration. Temporal and spatial reactors use different means to separate precursors from each other. In temporal reactors, the precursor pulses are separated in time and either pump down or inert gas purging is being used to prepare the reactor for the next precursors pulse. In spatial reactors, the precursor pulses are separated in space and the substrate is moved between different precursor zones. The zones are typically separated by inert gas curtains. Early ALD reactors were spatial reactors [8, 90], but temporal reactors have been the most common reactor type for a long time. Recently spatial reactors have been developed again for high throughput applications like solar cell passivation, with throughput of 1000's of wafers per hour for 10–30 nm Al_2O_3 [91].

Plasma vs. thermal

Division into thermal and plasma reactors is also a fundamental way of separation. It is based on what energy sources are used to drive the ALD reactions. Plasma reactors can typically be used to deposit films by thermal ALD, but not vice versa.

Plasma reactors can be divided into different categories by the type of plasma generation e.g. is it capacitively coupled, inductively coupled, hollow cathode or electron cyclotron resonance plasma and how it is connected to the reactor: is it direct plasma or remote plasma; is it downstream plasma or true remote radical enhanced plasma reactor [89].

In direct plasma, the substrate is engulfed in the plasma, which causes plasma damage to the surface. Remote plasma aims to remove the plasma damage by moving the plasma generation further away from the substrate. Downstream plasma is a type of remote plasma where the plasma is generated away from the substrate, but there is still a line-of-sight path to the substrate and some plasma damage is still present. In a true remote plasma reactor, the plasma generator is located around a corner, and only plasma radicals that diffuse can reach the substrate surface and plasma damage is minimized. The downside is that the further the plasma is away from the substrate the longer plasma pulse times are required to generate enough radicals to saturate the substrate surface due to recombination.

Continuous vs. stop flow

Typically, temporal ALD reactors are operated under continuous flow conditions where the reactor is continuously pumped and a constant flow across the substrate is maintained. With stop-flow functionality the pumping of the reactor is stopped after precursor pulse to allow the precursor sufficient time diffuse into cavities and react with the surface before pumping is continued. This way deposition into HAR structures, where reaction rate is limited by mass flow, is enhanced. Downside of this is significantly longer cycle times.

The reactors can also be divided into top-flow and cross-flow reactors based on how the precursor is introduced and spread over the substrate. Thermal reactors can be either top-flow or cross-flow reactors while plasma reactors are usually top-flow reactors. The cross-flow reactor is a simpler design. However, in cross-flow reactors, reaction by-products, that accumulate when progressing towards outlet, may impair the film growth towards outlet decreasing uniformity [92a].

Operating pressure

Another way to divide the reactors is the operation pressure. Often encountered operation regimes are molecular flow and viscous flow and occasionally atmospheric pressure. Atmospheric pressure ALD is mostly applied to spatial ALD configurations. Typical temporal ALD reactor operates around 1 hPa pressures where flow is viscous in the reactor, but in small features on the substrate becomes molecular.

Single wafer vs. batch

Throughput of ALD reactors is an issue for many applications. The slow deposition rate of ALD can be countered to some extent by using batch ALD tools. Most thermal ALD processes are suitable for both single wafer and batch processing whereas PEALD processes are typically single wafer processes. However, batch PEALD equipment exist *e.g.* Beneq's C2R [93]. Reactor design plays important role in the throughput as all unneeded volume increases pulse and purge times.

ALD reactors used in this thesis

In this thesis three different temporal ALD reactors were used; two from Beneq and one from Picosun.

The Beneq tools are both based on TFS-500 platform, but one is equipped with a thermal cross-flow reactor whereas the other one is equipped with a remote capacitively coupled plasma (CCP) reactor. The CCP generator is operating with 13.56 MHz radio frequency (RF) and operates up to 300 W plasma power. The reactor combines cross-flow and top-flow. Flow for the plasma gases are introduced to the reactor above the substrate through a showerhead whereas the non-plasma precursors are introduced in a cross-flow manner.

The tool by Picosun is R200 Advanced, which is a top-flow reactor capable of both thermal and PEALD. It also has a stop-flow functionality enabling deposition into HAR structures. The plasma generator is Advanced Energy's Litmas RPS 3001 inductively coupled plasma (ICP) generator located remotely upstream from the substrate. The plasma generator operates from 100–3000 W plasma power and automatically adjusts RF frequency in 1.9–3.2 MHz range to maintain efficient operation. All of the reactors are capable of depositing on up to 8" wafers. Figure 2.3 shows schematic illustration of each of the reactors.

Picosun R200 Advanced reactor was used in Publications I, II and IV. Beneq's thermal TFS-500 reactor was used in Publication III and plasma TFS-500 in Publication V.

Plasma operation of Picosun R200 Advanced

The plasma generator in Picosun R200 Advanced has self-diagnostics, which detects if the plasma has ignited properly. When operating outside correct operation conditions it is possible for capacitively coupled plasma to form inside the plasma source. This changes the plasma composition [94], which affects deposition and according to the manufacturer in long run damages the plasma source.

The correct operating conditions depend on used gases. In the tool, a constant Ar flow is maintained through the plasma generator controlled by a mass flow controller (MFC). Other gases are inserted into the Ar flow by opening and closing of a pulsing valve. A needle valve is used to control the flow of these gases and a mass flow meter (MFM) measures flow in the line prior to needle valve, which gives indication of the actual flow. Figure 2.4 shows acceptable operation conditions for different gases and flow rates at constant 40 sccm Ar flow.

The operating pressure and distance of the plasma generator from the substrate determines ion energy distribution at the substrate level when no external

Figure 2.3. Schematic illustrations of the Picosun R200 Advanced reactors in thermal mode with top flow through showerhead and plasma enabled mode with remote downstream inductively coupled plasma and Beneq TFS 500 reactor with thermal cross-flow reaction chamber and remote, downstream, capacitively coupled plasma. Picosun R200 Advanced reactor was used for ALD depositions in Publication I, II and IV. Beneq TFS500 was used in Publication III and V.

bias is applied [95]. At higher operating pressure, the ions undergo more collisions where they lose energy before reaching substrate level. The pressure of the Picosun R200 Advanced reactor is at approximately 5 hPa. The pressure is high enough that it would justify the assumption that ions do not contribute to the film growth [94], however, later on in this thesis with AlN (Publication I) we can see that this is not the case.

Figure 2.4. Acceptable gas flow regimes in plasma ALD for different gases for Picosun R-200 Advanced with Advanced Energy's Litmas RPS 3001 plasma generator. Constant Ar flow at 40 sccm was maintained through the plasma generator. The pressure of the reactor was approximately 5 hPa. H₂/N₂ mixture was fed at equal flow rates according to the MFM reading and the graph is showing the flow of individual component. The maximum range of the MFM was reached at high powers with O₂, N₂ and NH₃, which is why the flow plateaus in the graphs.

2.5 Process development for atomic layer deposition

2.5.1 Thermal processes

Process development for ALD is typically started by verifying the saturation of the precursor pulses. This is done by increasing the precursor dose and/or reaction time in the reactor gradually while monitoring the GPC. The dosing of the other precursor should be high enough so that it is not the limiting factor in the cycle. The saturation of the GPC would then correspond to the saturation of the surface coverage during the pulse of the precursor whose dose was varied. In Figure 2.5 is shown how surface coverage increases with time while reaction rate

coefficient and precursor partial pressure p are constant. Surface coverage of irreversible chemisorption can be calculated from

$$Q = 1 - e^{-k_a p t}, [87] \quad (2.1)$$

where Q is chemisorption coverage, k_a reaction rate coefficient, p precursor partial pressure and t time. The precursor dose is dependent on the vapor pressure of the chemical in its reservoir and pulse time. To reach saturation, sufficient dose and reaction time is required. The required reaction time to reach saturation density is affected by the reaction rate coefficient, which is a function of temperature and precursor partial pressure [87]. Typically, both reaction time and precursor dose is increased at the same time by increasing the pulse time.

Figure 2.5. Surface coverage of irreversible chemisorption at four different precursor vapor pressures calculated using Equation 2.1. Increasing precursor vapour pressure decreases reaction time needed to reach saturation when reaction rate coefficient remains the same. In the graph, the precursor partial pressure is always doubled from bottom series to top.

Initial process development should be performed with long purges to ensure that they are sufficient. When the purge time is too short, precursor pulse A and B are no longer separated from each other and gas phase reactions may occur leading to CVD type deposition. This CVD type growth increases apparent GPC, but the film quality is not as good and the uniformity suffers, which can be detrimental for the application. It can also make it more difficult to optimize the process. Once the saturating pulsing parameters have been established, it is easy to decrease the purge times. The moment when the purge time becomes too short, manifests itself as an increase in GPC and a deteriorated uniformity.

Thermal processes are relatively simple as after establishing the self-saturative conditions for the precursor pulses only thing that can be adjusted is the deposition temperature within the ALD window. The deposition temperature can affect the film properties such as crystallinity [96]. With processes having a large ALD window, optimal precursor pulse and purge time may depend on the temperature. For instance, Al_2O_3 process from Me_3Al and H_2O requires longer purge times for H_2O at low temperatures, as it gets more difficult to purge H_2O when temperature is at 100°C or below [97]. In addition, reactivity of the precursors decrease when temperature decrease and longer pulse times are needed to overcome this [82, 97].

In Publication I, process development was done in order to establish an AlN process utilizing AlCl_3 and NH_3 on Picosun R200 ALD tool. AlCl_3 was heated in a stainless steel bottle to ensure sufficient vapor pressure. AlCl_3 delivery into the reactor was boosted with a carrier gas by using the following procedure: first the pulsing valve was opened at a low line flow, then the line flow was increased and the pulsing valve was closed during this high flow period. This way the pressure in the precursor bottle is increased for the following pulse and the delivery of the precursor out of the bottle is enhanced. For AlCl_3 we kept pulsing parameters fixed at 1.5 s total pulse time consisting of keeping the pulsing valve open for 0.5 s at the low flow and then closing it during the 1 s high flow period. The purge time for AlCl_3 was kept constant at 3 s and for NH_3 at 6 s. AlCl_3 source bottle temperature was increased until saturation was observed with 4 s NH_3 pulse (Figure 2.6a). Saturation of NH_3 pulse was then verified by depositing AlN film with a fixed AlCl_3 dose and varying the NH_3 pulse time (Figure 2.6b). Long NH_3 pulse times were required to reach saturation at 475 °C reactor temperature. The GPC at the saturation was 0.7–0.8 Å.

Figure 2.6. Growth saturation graphs for AlCl_3 and NH_3 from publication I. AlCl_3 showed saturation above bottle temperature of 160 °C while NH_3 was reaching saturation after 8 s pulses. From Publication I.

By comparing the NH_3 pulse durations required to reach saturation with those of a thermal TiN process from TiCl_4 and NH_3 used on the same ALD equipment, it was concluded that the reaction kinetics were slow for NH_3 reaction with AlCl_3 . In TiN deposition, 0.1 s NH_3 pulse is enough to saturate the surface and hence the dosing is sufficient already at much smaller doses than what is required to reach saturation in deposition of AlN.

Despite the apparent saturation ToF-ERDA results showed 3.8 at. % of chlorine inside the film. It was concluded that the deposition temperature was too low to remove all the chlorine from the surface during the NH_3 step. Later on Chen et al. [85] investigated thermal AlN process at 500 °C and 550 °C. They observed GPC of 0.67 Å at 500 °C and 0.74 Å at 550 °C, which corresponds well with our results. The chlorine inside the film dropped from 2.7 at. % at 500 °C to 0.7 at. % when the temperature was increased to 550 °C. This implies that temperatures ≥ 550 °C are required to deposit AlN from AlCl_3 and NH_3 with low impurity content.

2.5.2 Plasma processes

Development of plasma processes differ from the thermal processes in that the parameter space that needs to be optimized is larger and film properties that can be affected is wider. By adjusting plasma power and plasma pulse time, the film properties can be adjusted.

In Publication I, a process for PEALD AlN using AlCl_3 and Ar/NH_3 plasma was developed. The same parameters for AlCl_3 pulsing were used as in the thermal process. The set temperature of the reactor was also kept at the same value, but due to the reactor configuration the actual wafer temperature during plasma operation was approximately 425 °C; 50 °C lower than during the thermal process. Plasma power was set to 2000 W, which enabled flow rates of 1:1 ratio for Ar and NH_3 at 40 sccm each. Ar flow rate was controlled with a mass flow controller whereas NH_3 flow rate was controlled by a needle valve. Higher NH_3 flow rates were outside the optimal operation conditions for the plasma generator and caused detection of capacitively-coupled plasma inside the plasma generator. The purge time for Ar/NH_3 -plasma was set to 6 s.

The GPC (Figure 2.7a) for normal AB type plasma process consisting of AlCl_3 pulse followed by Ar/NH_3 plasma pulse was low compared to the thermal process. Normally the pulse time would be extended in order to saturate the surface, however, increasing the plasma pulse time led to new problems. Residual stress (Figure 2.7b) was observed to become more compressive with longer plasma pulse time and above 6 s the films started to occasionally form blisters due to the mechanical stress [98]. In addition, the films with 3 s plasma time was found to be close to stress free. The change in stress was attributed to ion bombardment during the plasma pulse, which was supported by ToF-ERDA measurement from film deposited with 6 s plasma time showing 0.06 at. % of Ar inside the film.

Figure 2.7. a) Saturation studies for PEALD AlN process. Plasma AB is a typical PEALD process with AlCl_3 and Ar/NH_3 plasma. Plasma ABC means a process where AlCl_3 pulse is followed by an NH_3 pulse, which is then followed by the Ar/NH_3 plasma pulse. b) PEALD AlN process shows strong dependence of residual stress on plasma time. Results for thermal process and 2000 W processes are from Publication I.

Figure 2.8. ABC pulsing scheme used for AlN in Publication I and II.

In order to deposit films with low stress value an ABC type pulsing scheme was utilized (Figure 2.8). In the ABC pulsing scheme an intermediate NH₃ pulse was used before Ar/NH₃ plasma pulse, which filled the reactor with NH₃ and some of it, reacted thermally with the surface Cl species. However, since no purging was done after this step there was still NH₃ present from the intermediate NH₃ pulse in the reactor during the Ar/NH₃ plasma step and plasma activated some of the NH₃ that otherwise would have been poorly reactive towards the surface. As a result, the GPC increased while residual stress was still close to zero. However, it is likely that the growth was not completely saturated. According to ToF-ERDA the chlorine content in the film was 1.9 at. %. This is, however, much lower than what was measured for the thermal process.

Later the growth with higher plasma power was also tested as it was determined that higher plasma power enabled higher NH₃ gas flows as was shown in Figure 2.4 The 3000 W plasma power enabled higher GPC shown in Figure 2.7a compared to the plasma AB or ABC 2000 W process with same plasma time. However, the residual stress of the film was changed more strongly towards compressive stress.

Residual stress of the grown film is rarely measured even though it can be a significant factor in applying the film into device fabrication [50]. Especially in the case of plasma processes, the residual stress can be altered with the plasma pulse parameters [99].

2.5.3 ALD into high-aspect-ratio structures

High aspect ratios pose a new kind of challenge for film growth. Even though an ALD process produces self-limiting and conformal film growth over typical topographies, this may not be the case in high-aspect-ratio structures. In high-aspect-ratio structures, mass transport becomes the limiting factor and typical pulse times are not enough to allow precursor to diffuse into the structures.

This is demonstrated in Figure 2.9 where thermal TiCl₄ and H₂O process at 300 °C is used to deposit TiO₂ film into lateral-high-aspect-ratio (LHAR) test structure [100] with aspect ratio of 1000. The type of test structure used was

LHAR3 and they were provided by courtesy of Riikka Puurunen and Mikko Utriainen from VTT and PillarHall. The continuous-flow process is able to reach initial aspect ratio of 250 while the stop-flow process reaches initial aspect ratio of 550. The final aspect ratio is larger as the growing film decreases cavity height. The hold time in the stop-flow process was 13 s for both precursors and purge times were increased from 4 s for TiCl_4 and 10 s for H_2O to 45 s for both precursors. Both samples were deposited 500 cycles targeting at 25 nm. Film thickness on reference silicon samples determined with single wavelength ellipsometer was 20.4 nm for continuous-flow process and 29.7 nm for stop-flow process.

The continuous-flow process shows uniform film thickness 120 μm deep into the cavity before starting to decrease. In contrast, the stop-flow process shows uniform film thickness 190 μm deep into the cavity before showing an 80 μm wide peak showing increased film thickness before fading out. This peak is likely a result of CVD reaction in the cavity showing that one of the precursor would need even longer purges to be removed from the cavity. From this, it is evident that to successfully deposit conformal film into extreme HAR structures separate process development is required.

The diffusion of the precursor into the cavity depends on the precursor and profile in the cavity depends on the sticking coefficient [100–102]. Each precursor behaves differently in this sense and hence separate process development for each process is required.

Figure 2.9. Deposition of TiO_2 into high-aspect-ratio structure. At the top, continuous flow process and in the middle stop flow process. Contact profilometer scan shows height profile in the test structure. At the bottom is a schematic cross-section of the LHAR structures. Opening width of the LHAR test structure above is $80 \mu\text{m}$, cavity height 500 nm and lateral length $500 \mu\text{m}$. The LHAR-test structures were provided by courtesy of Riikka Puurunen and Mikko Utriainen from VTT and PillarHall.

The blistering issue is not limited to Al_2O_3 and blister formation has been observed when depositing iridium [103], ruthenium [108] and AlN [84, 98], however, in these cases the blisters can be observed already from the as deposited films and no annealing is required.

Figure 2.11. a) Blistering of 100-nm thick Al_2O_3 thin film observed after annealing at 600 $^{\circ}\text{C}$ in nitrogen atmosphere for 20 min. b) Stress evolution of Al_2O_3 when annealed in air showing irreversible change when held at 500 $^{\circ}\text{C}$ for 20 min. After annealing film blistering was observed. c) ToF-ERDA shows change in hydrogen content in the film after annealing.

2.7 Atomic layer deposition of nitrides

Nitrides are the second most common group of materials deposited by ALD. Much fewer materials have had nitride process demonstrated for them than for oxide (Figure 2.12). Notable materials that do not have a nitride processes are ScN that could be used to dope AlN and CrN that could be used for wear and corrosion protection.

NH_3 is used almost predominantly as the co-reactant in thermal ALD nitride process although reactivity of NH_3 requires high temperatures. Due to this, alternatives to NH_3 have been studied on few occasions. Notable alternative is hydrazine (N_2H_4) [105–107] and its alkyl derivatives [108, 109], which are more reactive than NH_3 enabling lower deposition temperatures and new processes. In conjunction with NH_3 , Zn has been used as an additional reducing agent [110–112]. This has enabled deposition of superconductive NbN , which has not

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
				56 La	57 Ce	58 Pr	59 Nd	60 Pm	61 Sm	62 Eu	63 Gd	64 Tb	65 Dy	66 Ho	67 Er	68 Tm	69 Yb	70 Lu
				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 2.12. Number of nitride processes demonstrated for ALD is much scarcer than for oxide processes. Table based on review by Miikkulainen et al. [96], updated by the author.

been possible with NH_3 without the intermediate Zn pulse [110, 112, 113]. In plasma processes, NH_3 plasma and N_2/H_2 plasma is used.

Deposition of nitrides is more demanding than that of oxides, as nitrides in elevated temperatures tend to oxidize in presence of oxygen. In order to deposit oxygen-free nitride films, sources of oxygen into reactor space needs to be minimized. Sources of oxygen can be reactor atmosphere, impure precursors and carrier gas or leaks in the reactor chamber.

Reactor atmosphere can contain oxygen from sample loading or previous oxide processes. In order to minimize the oxygen content in the reactor atmosphere, load lock should be used for sample loading and reactor conditioning should be performed after oxide processes or air break.

We have used TiAlCN passivation using ternary $\text{TiCl}_4/\text{NH}_3/\text{Me}_3\text{Al}$ process as first conditioning after an air break followed by TiN film deposition from TiCl_4 and NH_3 on oxidized Si wafer to monitor TiN film resistivity as it is sensitive to oxygen content in the film. When the TiN resistivity is no longer decreasing between the subsequent depositions, a baseline has been established that tells not only that all the excess oxygen has been driven out from the reactor, but also the current condition in respect to leaks in the reactor. After all, there is a balance between consumption and supply of oxygen into reactor. From Figure 2.13 we can see that after an air break and passivation of the tool with 4000 cycles of TiAlCN, 6000 cycles of TiN is enough to reach saturation of TiN sheet resistance. For our R200 reactor long conditioning is required, as it is equipped with ICP unit that is kept at room temperature. Therefore, we have a cold spot where water can adsorb. Later on, it is possible to compare saturated TiN sheet resistance levels to earlier to determine whether there is possible issues requiring further inspection. In 2018, we had a small leak in the reactor that manifested as increased baseline for sheet resistance and as increase in the sheet resistance level once the tool was idle for some hours between the second and fourth run that was performed overnight.

Figure 2.13. Conditioning and monitoring of tool performance for nitrides. After air break tool is conditioned for 4000 cycles with TiAlCN passivation followed by TiN monitor runs. Saturation of sheet resistance shows the current condition of the tool. In 2015 (11/15 series in legend) the ALD reactor had slightly lower background oxygen content than in 2016 (8/16 series in legend) as determined from the sheet resistance. 2018 (1/18 series in legend) we had clear leak in the reactor as sheet resistance was increased after longer wait times between runs (2nd and 4th runs).

Another important aspect with nitrides is exposure of the grown film to air. The surface of the nitride films oxidizes when exposed to air. Extent of this oxidation depends on the film properties and the temperature at which the film is exposed to air.

Often in reported literature, false accusations are claimed on sources of oxygen in the grown films of other authors, which suits better for the current authors. When in fact, the source of oxygen is mainly from the ambient, from leaks or from poor conditioning of the tool.

2.8 Atomic layer deposition of metals

Atomic layer deposition of metals is less mature subject than ALD of oxides or nitrides. For instance, successful deposition of Au by ALD was demonstrated only very recently [114, 115] due to difficulty of creating working precursor chemistry. Even though numerous metals have had a process demonstrated for them (Figure 2.14), only some of them are applicable and produce a stable elemental film with low impurity content. For instance, metal Ti process has been demonstrated using TiCl_4 and H_2 plasma, but the film was not stable in air [116]. The most well established processes exist for tungsten and platinum group metals. Tungsten was the first single element material deposited with ALD [117]. Aaltonen *et al.* demonstrated first processes for Ru, Rh, Ir and Pt in a series of articles in 2003–2005 [118–121] using organometallic precursors.

In contrast to nitride and oxide films, which tend to exhibit short nucleation delays, metal deposition often demonstrate long nucleation delay. Nucleation

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
				56 La	57 Ce	58 Pr	59 Nd	60 Pm	61 Sm	62 Eu	63 Gd	64 Tb	65 Dy	66 Ho	67 Er	68 Tm	69 Yb	70 Lu
				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 2.14. Elemental ALD films that have an ALD processes demonstrated are highlighted. Table based on review by Miikkulainen et al. [96], updated by the author.

delay means the number of cycles before a steady layer-by-layer growth demonstrating a constant GPC is achieved. This nucleation delay is partly due to difference in the surface of the grown film and the substrate. Especially noble metals on oxides surfaces show prolonged nucleation delay. The growth initiates as islands and film thickness can be several nm before the film coalesces and a steady GPC is achieved. This growth behaviour is problematic when trying to deposit thin continuous metal layers. However, it can be exploited in order to create nanoparticles as was done in Publication IV.

In publication IV, Pt deposition from MeCpPtMe₃ and oxygen plasma was investigated on TiO₂ support at 300 °C in order to deposit Pt nanoparticles into microreactors. The Pt nanoparticles were deposited on 50-nm thick Si₃N₄ TEM windows with 20 nm of ALD TiO₂ deposited at 300 °C prior to the Pt deposition. Figure 2.15 shows the evolution of Pt particle size as the number of deposition cycles is increased. Figure 2.16 shows the evolution of the particle size diagram, which widens as the number of cycles is increased. The number and size of the particles increase until they start to coalesce into a continuous film. The increase of the number of particles indicates that we are constantly creating new particles on the surface. The proportionally large increase in the size of some of the particles on the other hand indicate that some particle coalescence due to migration is taking place as well. Later on Grillo et al. [122] presented kinetic models for the Pt nanoparticle size evolution and identified that the growth mechanism for

Figure 2.15. Evolution of Pt nanoparticle size as number of deposition cycles is increased from 10 to 40 to 80. From Publication IV.

Figure 2.16. Evolution of Pt nanoparticle size as number of deposition cycles is increased from 10 to 40 to 80. From Publication IV.

the Pt nanoparticles in our study is a result of deposition on support and existing Pt nanoparticles, and dynamic coalescence of the Pt nanoparticles with weak size dependency on the nanoparticle mobility.

The growth behaviour of noble metals is strongly dependent on the starting surface. Different nucleation behaviour can be seen on fresh hot piranha treated silicon surface and on piranha treated silicon using old cold solution (H_2O_2 likely decomposed) in Figure 2.17. The fresh piranha silicon surface with 50 cycles is starting to coalesce whereas the piranha treated silicon using old cold solution is far away from starting to coalesce. The difference between the starting surfaces is that fresh piranha is able to oxidize the surface and terminate the surface with $-\text{OH}$ groups whereas the old solution has unlikely oxidized the surface and left the surface with a mixture of $-\text{H}$ and $-\text{OH}$ groups as untreated

Figure 2.17. Pt nanoparticles deposited on silicon surface treated with old cold piranha solution with 40 ALD cycles on left and on right with hot fresh piranha treated silicon surface with 50 ALD cycles. From publication IV.

silicon surface would be. Similar difference in Pt growth has been observed before with piranha treated silicon surface and untreated silicon surface by Lee and Bent [123]. According to their XPS measurements the surfaces does not differ significantly, but water contact angle decreases from 30–40° for the untreated to <5° for the piranha treated, which is due to termination of the surface with –OH groups.

3. Thin film properties

Thin film properties can be divided into physical properties that describe the state of the physical system and chemical properties that describe how the material behaves in chemical reactions. In this chapter, general considerations regarding the measurement of the thin film properties is covered by discussing the dependence of different properties to each other, how deposition method affects these properties, and by how the measurement can affect the material. After this measurement methods used in this thesis is introduced followed by material examples.

3.1 General considerations regarding measurement of thin film properties

Thin film properties are affected by the material itself, the deposition method, deposition parameters and post-deposition processing. Heat-treatment can change the elemental composition of a thin film, its crystallinity and mechanical properties. Etching of an overlaying material can change surface quality of the underlying thin film even though high selectivity exists between the materials leading to possible defect formation on the surface hindering mechanical durability. These are things to take into account when characterizing thin films with an application in mind. For instance, measurement of the mechanical properties from specimens that have gone through identical processing as the actual device is required for reliable determination of mechanical properties.

The characterization methods can be divided into different categories depending on how the film properties are derived from the measurement data, how the data is acquired or what kind of sample fabrication is required.

Film properties can be derived from the measurement data either directly or indirectly. Indirect methods rely on measurement of a secondary effect and determine the primary property from simulation of the material behaviour. An example of a common indirect measurement method is ellipsometry used to measure film thickness and optical constants. A direct measurement could be thickness measurement from a cross-section image.

Measurement from the thin film can be done either in contact or in non-contact. In contact characterization methods, the thin film is probed mechanically in order to measure the desired film property. This can cause damage or contamination to the thin film from the measurement probe. For this reason, non-

contact measurement methods are favoured for process control. Optical measurements e.g. optical microscopy, ellipsometry are common non-contact measurement methods whereas four-point probe can be used as an example of contact measurement method, which leaves a mark on the thin film.

The measurement methods can also be classified as destructive or non-destructive. In destructive measurements, the sample is unusable after the measurement. For this reason, destructive measurements cannot be used for process monitoring unless it is accepted that the sample is lost in the process. This may be acceptable when fabricating multiple chips on a wafer and a single chip is used for the process monitoring. Example of destructive measurement is secondary ion mass spectrometry (SIMS) and ToF-ERDA where the sample film is sputtered away. Contact measurements can also be considered destructive measurements in some cases.

Sample fabrication that is required by the characterization method in order to measure the film can also be used to divide the methods. For instance, ellipsometry requires no special sample fabrication whereas TEM typically requires tedious sample fabrication in order to fabricate thin filaments. Characterization methods that require little to no sample fabrication should be used for process controls.

3.2 Measurement of physical properties

3.2.1 Ellipsometry

In ellipsometry, polarized light shone on a sample is reflected from the surface to detector, which detects change in the polarization. This is then compared to a model to determine the desired physical parameters. Ellipsometry is commonly used in determination of film thickness, refractive index and absorption coefficient, although more parameters can be derived from the measurement.

In all of the publications, single wavelength ellipsometer (632.8 nm HeNe-laser) operating at 70° incident angle was used either to determine film thickness and refractive index or as means for process monitoring.

3.2.2 X-ray techniques

X-ray diffraction

X-ray diffraction (XRD) is based on scattering of x-rays from lattice planes of crystalline material causing constructive interference. Constructive interference occurs when wavelength of the radiation, λ , spacing, d , between the lattice planes and scattering angle, θ , satisfy Bragg's law:

$$n\lambda = 2d \sin \theta. \quad (3.1)$$

From XRD it is possible to determine crystal structure of the material and the orientation of the crystals.

In publication I and II, XRD was used to determine information about crystallinity of AlN.

X-ray reflectivity

X-ray reflectivity (XRR) is based on measurement of intensity of reflection of x-rays from sample surface in specular direction. By fitting a simulation into the measured data, it is possible to determine film density, thickness and surface roughness.

In publication I, AlN film thickness and density was determined with XRR.

3.2.3 Time-of-flight elastic recoil detection analysis

In ToF-ERDA, the sample is bombarded with a beam of heavy ions. The energy and velocity of the scattered atoms is measured, which allows identification of the elements. Determination of the depth profile is possible based on known scattering kinematics, scattering cross-sections and parameterized energy losses for incident ions and sample atoms.

ToF-ERDA is highly specialized characterization equipment requiring an ion accelerator. It, however, allows determination of concentration of light elements such as hydrogen in thin films.

In publication I, elemental composition of the 50–80 nm thick AlN thin films was determined with ToF-ERDA. The ToF-ERDA measurements and analysis was performed in University of Jyväskylä by Prof. Timo Sajavaara's group.

3.2.4 Four-point probe

Four-point probe allows measurement of thin films sheet resistance, which can be converted into resistivity or conductivity with the knowledge of film thickness. It is a destructive measurement technique, because the measurement probes are pushed into the film.

3.2.5 Electron microscopy*Scanning electron microscopy*

Scanning electron microscopy (SEM) is standard characterization tool in university environment. It enables visual representation of sample surface from response to scanning electron beam.

In Publication IV SEM was used to characterize Pt nanoparticle size. In Publication V SEM was used to image surface topography. In both cases, secondary electron imaging was used.

Transmission electron microscopy

Transmission electron microscopy is typically a tedious analysis method due to the extensive sample fabrication commonly required. As with SEM, TEM is also based on electron beam scanning across sample surface, but in contrast to SEM, the transmitted electrons are detected. In order to transmit electrons, the sample needs to be thin and commonly focused ion beam (FIB) milling is used to create sample filaments.

In Publication I, TEM was used to determine crystallinity of AlN film. In Publication IV TEM was used to characterize Pt nanoparticle size. In order to avoid

tedious sample fabrication the Pt nanoparticles were directly deposited on top of TEM windows in Publication IV.

3.3 Measurement of mechanical properties

3.3.1 Bulge test

In bulge test, a free-standing membrane is deflected by applying a pressure on one side of the membrane as shown in Figure 3.1. The pressure is typically applied by increasing pressure of a fluid such as air. Bulge test allows determination of elastic modulus, residual stress and fracture strength.

Figure 3.1. In bulge test, a free-standing membrane is deflected by applying pressure on one side of the membrane.

Elastic modulus and residual stress can be determined by measuring displacement of the membrane due to pressure as in Figure 3.2. The pressure, P , required to displace the amount of d a membrane with thickness h and diameter a is related to the mechanical properties of the membrane by the relation

$$P(d) = C_1 \frac{h\sigma_0}{a^2} d + C_2 f(v) \frac{E}{1-\nu} \frac{h}{a^4} d^3, \quad (3.2)$$

where σ_0 is the residual stress, E is the elastic modulus and ν is the Poisson's ratio of the film [124]. C_1 , C_2 and $f(v)$ are coefficients that depend on the geometry of the membrane.

Fracture strength can be determined by testing a set of membranes and applying pressure until each membrane ruptures. The stress at the point of rupture is the maximum stress and by performing Weibull analysis on this maximum stress data, fracture strength of the membrane material can be determined. The stress of a circular free-standing membrane in the presence of residual stress and pressure P can be determined by finding the real root to the equation derived in Publication III:

$$\sigma^3 - \sigma_0 \sigma^2 - \frac{1}{24} \frac{P^2 a^2}{h^2} = 0. \quad (3.3)$$

Figure 3.2. Pressure-displacement curve measured with bulge test. The 50-nm thick 450-μm diameter Al_2O_3 membrane was loaded three times and identical pressure displacement behaviour is observed. The behaviour is well matched with the fitting using Equation 3.2 and finite element model. From Publication III.

Bugle test was used to determine the mechanical properties in Publications II and III. Scanning white light interferometer (SWLI) was used to determine film displacement.

3.3.2 Wafer curvature measurement

Wafer curvature measurement allows determination of film stress state without knowing elastic properties of the film. In wafer curvature measurement, change in wafer curvature due to thin film deposition is measured. The change in curvature is due to film stress and related to the mechanical properties of the substrate and film thickness according to Stoney's equation

$$\sigma_f = -\frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_f} \left(\frac{1}{R_1} - \frac{1}{R_0} \right), \quad (3.4)$$

where σ_f is film stress, E_s the elastic modulus of the substrate, ν_s Poisson's ratio of the substrate, t_s and t_f substrate and film thickness respectively and R_0 initial radius of curvature and R_1 radius of curvature after film deposition [125].

In publication I, residual stress of AlN film was determined with wafer curvature measurement.

3.4 Properties of Al₂O₃ by atomic layer deposition

3.4.1 Physical properties

Crystallinity

Al₂O₃ is used as a model case for ALD, however, it is unique in the sense that in normal ALD conditions it is always amorphous [96]. In order to crystallize Al₂O₃, annealing or deposition temperatures above 700 °C is required.

3.4.2 Mechanical properties

ALD Al₂O₃ has elastic modulus in range of 140–180 GPa depending on the deposition temperature [83, 126, 127]. At low deposition temperature (close to 100 °C), the elastic modulus tends to be closer to the 140 GPa range while above 200 °C the elastic modulus is closer to 180 GPa. The decrease in elastic modulus as the deposition temperature is decreased correlates with decrease in density of the film and increase in hydrogen concentration in the film [83]. The correlation between density, hydrogen concentration and elastic modulus has been noted before with other deposition methods [128]. The elastic modulus values for ALD amorphous Al₂O₃ thin films are comparable to those deposited by other methods [128, 129, 130]. However, compared to the crystalline Al₂O₃, it is only half. In publication III, elastic modulus of Al₂O₃ was determined with bulge test for two different film thicknesses deposited at 300 °C. The elastic modulus of the 15-nm thick film was 177 GPa, which is comparable to the generally observed trend. However, the elastic modulus of the 50-nm thick film was only 115 GPa. Ylivaara et al. [83] did not observe thickness dependence on the elastic modulus for films ranging from 10–560 nm. However, elastic modulus of amorphous Al₂O₃ has positive dependency on film density linked to higher ordering of molecules and/or lower impurity concentration [83, 128, 131]. The density of the 15 and 50 nm thick films was 3.28 and 3.11 g/cm³, respectively, which could partly explain the measured difference in the elastic modulus.

Residual stress in the ALD Al₂O₃ is also deposition temperature dependent. The residual stress consists of intrinsic stress and extrinsic stress. The intrinsic stress arises from the film growth process whereas the extrinsic stress consists mainly of stress due to difference in coefficient of thermal expansion (CTE) between substrate and the film. On silicon, the stress of ALD Al₂O₃ varies from 200 MPa at 300 °C to 500 MPa at 100 °C [83] as measured with wafer curvature method. In Publication III, residual stress was determined to be 100–150 MPa at 300 °C with bulge test. The CTE of amorphous Al₂O₃ varies between 4.2–7.1 ppm/°C [132] while silicon has CTE of 2.6 ppm/°C. The difference between CTE creates tensile stress that increases with increasing deposition temperature. Since the ALD Al₂O₃ stress decreases with increasing deposition temperature, the intrinsic stress arising from the film growth is decreased significantly with increasing deposition temperature. At deposition temperature of 300 °C, the residual stress is mainly due to difference in CTE.

Fracture strength of thin ALD Al₂O₃ membranes is exceptional. In Publication III, fracture strength of 4.25 GPa for 15-nm thick 400-μm diameter membrane

Figure 3.3. Pressure-displacement curves measured with bulge test for 50- and 15-nm thick 450- μm diameter Al_2O_3 membranes.

was measured with pressure ramp rate of 100 mbar/s. The thicker 50-nm membrane also had high fracture strength of 1.74 GPa even though the film had low elastic modulus. Berdova et al. [133] measured fracture strength of 2.56 GPa for 75 nm thick, 500- μm diameter Al_2O_3 membranes, although she did not take into account tensile film stress, which would increase the value. The Weibull modulus, which represents variation in the fracture strength values, was high meaning small variation between measured samples. For the 15-nm membranes the Weibull modulus was 55 and for the 15-nm membrane it was 49. Berdova et al. observed Weibull modulus of 13.4 for her samples. Both fracture strength and Weibull modulus of amorphous ALD Al_2O_3 are high compared to other thin film materials [134].

The average pressure at which the membranes broke at the fracture strength tests with 100 mbar/s pressure ramp rate were 1740 ± 190 hPa for 50-nm thick films and 1810 ± 90 hPa for 15-nm thick film. These are considerably higher than the maximum pressures reached during measurement of pressure-displacement curves shown in Figure 3.3, where maximum pressures were below 600 hPa for all samples. These two measurements differ in pressure ramping. When measuring the pressure-displacement curves, pressure was held at each displacement measurement point for few minutes to enable SWLI measurement.

The 15-nm thick membrane exhibits higher response to pressure in terms of film displacement while enabling as high displacements as the thicker film. This could open up applications for thin membranes.

3.5 Properties of AlN by atomic layer deposition

3.5.1 Physical properties

Chemical composition

Chemical composition AlN films depends on the precursors used and deposition temperature. When using Me_3Al as the aluminium precursor high amounts

of hydrogen and carbon impurities have been observed in the grown film. Even epitaxial films have contained 5–10 % of carbon and oxygen [135]. The hydrogen concentration is usually not measured, as few techniques are able to detect it.

In Publication I, AlN was deposited using AlCl_3 and NH_3 and/or NH_3 plasma. The thermal AlN film deposited at 475 °C contained 11 % H and 4 % Cl (Figure 3.4a), indicating incomplete reactions due to low NH_3 reactivity. The thermal AlN film had also large peak in oxygen concentration in the surface layer indicating strong surface oxidation. The reactivity of NH_3 at 475 °C is not high enough to effectively remove chlorine during the second half cycle. Later on Chen et al. [85] investigated thermal deposition of AlN between 500–550 °C and observed decreasing Cl content from 2.7 % to 0.9 % with increasing temperature.

The plasma AlN deposited at 425 °C using ABC process with 3 s plasma time (Figure 3.4b) contained less hydrogen and chlorine impurities than the thermal AlN. However, the small amount of chlorine indicates that the surface reactions were not completely saturated with the 3 s plasma time. The film is, however, more resistant against surface oxidation compared to the thermal AlN film. The plasma AlN deposited at 425 °C using AB process with 6 s plasma time (Figure 3.4c) was almost free of chlorine impurities, but it still had 6.5 % hydrogen in the film. It also exhibited the lowest surface oxidation. The film had a small amount of Ar incorporated in the film indicating ion bombardment during the plasma step. During the film deposition, a constant Ar flow of 40 sccm was maintained through the plasma unit.

All of the films contained small amount of oxygen (<3 %) in the bulk of the film, which is likely due to background oxygen in the reactor even though the reactor was passivated with TiN before starting AlN depositions. The higher oxidation tendency of the thermal AlN film is likely due to lower density.

Crystallinity

ALD AlN is typically polycrystalline as deposited. The exceptions include some impure amorphous films deposited at low temperatures [136, 137] and epitaxial films [135, 138]. The epitaxial films were achieved with extensive ex-situ and in-situ surface preparation on lattice matching surfaces promoting the growth.

The AlN films studied in Publication I were all polycrystalline with weak preferred (002) orientation according to XRD (Figure 3.5) and TEM. The crystallinity could possibly be improved by using a starting surface that promotes growth of (002) oriented AlN. The significant shift in the peak of the plasma AB 6 s process corresponds with the high compressive stress state measured for the film.

Figure 3.4. ToF-ERDA elemental depth profile for a) thermal AlN, b) ABC 3 s plasma process and c) for AB 6 s plasma process. The thermal film shows strong surface oxidation compared to the plasma processes and high concentration of Cl in the film. The chlorine impurities are decreased with the longer plasma times. From Publication I.

Figure 3.5. XRD showing that the AlN films are crystalline. The plasma ABC process shows superior crystallinity. From Publication I.

Density and refractive index

Refractive index of the PEALD AlN films ranged from 1.80–2.02 and the density from 2.67–3.23 g/cm³. However, it should be noted that density was not measured from the film with lowest refractive index film as the refractive index and density are linked together. A clear trend that can be seen in the Figure 3.6 on the dependence and interlink between plasma time and plasma power, and the film density, refractive index and residual stress.

Film density and refractive index depends on the film composition and degree of crystallinity and are also affected by the film stress state. Bosund et al. [136] showed that PEALD AlN film density from Me₃Al and NH₃ plasma was inversely proportional to growth temperature, which correlated with decrease in hydrogen concentration in the film. Epitaxial ALD AlN has showed refractive index ranging from 1.8–2.05 [135] with higher values correlating with decrease in impurities. In our case, the AB type process with 6 s plasma time contained less chlorine, hydrogen and oxygen than the ABC process with 3 s plasma time and exhibited refractive index of 1.99 and density of 3.23 g/cm³ whereas ABC process had refractive index of 1.94 and density of 2.84 g/cm³. However, the residual stress of the AB 6 s was around -4 GPa whereas the ABC 3 s had 160 MPa, which is very small and attractive for potential MEMS applications.

3.5.2 Mechanical properties

In Publication II, mechanical properties of ALD AlN were characterized with a bulge test method and compared with PVD and metal-organic chemical vapour deposition (MOCVD) films. The ALD AlN film selected for the study was a low stress PEALD film characterized in Publication I. The ALD AlN film had 160 MPa residual stress measured with wafer curvature method. According to

Figure 3.6. Effect of plasma time on AlN film properties: a) refractive index, b) residual stress c) density. Thermal and 2000 W plasma results are from Publication I.

the bulge test, the residual stress was 272 ± 58 MPa. The difference between these two values can be because the wafer curvature method averages the stress across the wafer, whereas bulge test measures stress locally. PEALD AlN residual stress is also controllable with the plasma pulse parameters (Figure 3.6b) giving freedom into design. Long plasma times, however, can lead to high compressive stress state, which can lead to blistering as was observed with some of our films. When compared to the MOCVD AlN film stress (1500 MPa), the PEALD process enables significantly lower film stress level.

Elastic modulus of ALD AlN was 257 ± 102 GPa, which is less than the elastic modulus of the MOCVD (350 GPa) or sputtered AlN films (340 GPa) measured in the Publication II. Crystallinity of the ALD AlN film was lower than that of MOCVD and sputtered AlN films studied, which may explain the difference.

The fracture strength of ALD AlN was only 0.6 GPa, which was again lower than MOCVD and sputtered AlN. Compared to ALD Al_2O_3 , ALD AlN has higher elastic modulus, but lower fracture strength. Even the MOCVD and sputtered AlN had lower fracture strength than ALD Al_2O_3 . This can be due to amorphous crystal structure of Al_2O_3 resisting crack formation and propagation more strongly than polycrystalline structure of AlN. The Weibull modulus of ALD AlN was 5.66, which is very low compared to Weibull modulus of ALD Al_2O_3 .

4. Applications

4.1 Microreactors

Microreactors are miniature chemical reaction chambers that take advantage of the small dimensions. The small dimensions enhance heat and mass transport by increasing the surface to volume ratio. Hydrodynamics change in the micrometer scale channels, and controllable and predictable laminar flow is attained easily in contrast to chaotic turbulent flow in the large-scale reactors. This enables better control over the chemical reactions increasing quality of the production [139]. The microreactors also enable chemical reactions at very small reactant quantities, which might be desirable, when demand for products is small or when the reactants are very expensive. The small quantity of reactants also makes the operation with dangerous chemicals safer [139]. Safe operation of highly exothermic chemical reactions is possible in microreactors thanks to the small reactant quantities and enhanced heat transport. Continuous flow chemistry and stable catalysts would enable microreactors to be operated continuously. Development of new processes at laboratory and scaling it up would be easier with microreactors compared to conventional way of scaling up the batch size, because with microreactors the scaling could be done by adding up the number of microreactors without a need to re-optimize the process parameters for the larger batch size [139, 140].

Silicon microfabrication techniques enable easy fabrication of microchannels for microreactors. The methods are proven in mass production in IC and MEMS industry. Silicon as a material offers good material properties and a known starting surface for catalyst deposition by ALD. Other often-used materials for microreactors are stainless steel and glass. The former suffers from lack of homogeneity in the surface and the latter has poor heat transport characteristics.

The catalytic microreactors can be divided into different categories depending on how the catalyst is packed in the channel. In a wall-coated microreactor, the catalyst is only applied on the walls of the microreactor. In this case, the active catalytic surface area is the smallest, but with the efficient mass transport, high yields are attainable also with the wall-coated microreactors. Advantage in operation of wall-coated microreactors is small pressure drop after the microreactor as there is very little resistance to the flow. Another scheme for catalyst application is a packed microreactor where the whole channel is filled with a porous catalyst network such as a zeolite. In this case, the catalyst surface area is very high, but the down side is a high resistance to the flow leading to a large pressure drop. An intermediate option would be a semipacked channel, which

could be realized for instance by creating a pillar forest in the channel and applying the catalyst on the surfaces. This kind of a microchannel could be easily fabricated into silicon.

ALD is a suitable technique to deposit various catalysts, catalyst supports or overcoats into microreactors [141]. Most of the research has focused on applying ALD to deposit catalyst material on particles [142–146]. However, not all the methods developed to control catalyst deposition by ALD are applicable to deposition on particles. Deposition on very high surface area and aspect ratio substrates such as nanoparticles is not straightforward and is limited mainly to thermal ALD processes. Deposition on moderate surface area and aspect ratio substrates such as microchannels enable, much more control over the catalysts. ALD enables conformal deposition of catalyst into microchannels and control over the catalyst. Metal deposition by ALD on oxide supports initially leads to deposition of nanoparticles until the nanoparticles grow in size and coalesce into a film. By exploiting this, it is possible to deposit different sized nanoparticles that may have different catalytic activities.

In Publication II, we fabricated silicon microreactors where we deposited the Pt catalyst nanoparticles on oxide support. The microchannels were fabricated by standard microfabrication techniques: lithography, etching and deposition. After this, the microchannels were decorated with the catalyst support and the catalyst. The number of ALD cycles was varied to deposit different sized Pt catalyst nanoparticles to investigate the effect of nanoparticle size on catalysis performance.

The catalysts were deposited on two different oxide supports: ALD TiO_2 and piranha treated silicon (PirSi). The ALD TiO_2 was deposited thermally at 300 °C from TiCl_4 and H_2O for 850 cycles resulting in a 50 nm thick TiO_2 layer. Piranha treatment was carried out by dipping the the microreactors into room temperature solution of 4:1 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ creating a thin hydroxyl terminated SiO_2 layer on the Si wafer. ALD Pt nanoparticles were deposited at 300 °C from trimethyl-(methylcyclopentadienyl)-platinum(IV) (MeCpPtMe_3) and O_2 -plasma for 5, 10, 20, 40 or 50 cycles. The corresponding Pt nanoparticle size is shown in Table 4.1.

Table 4.1. The Pt nanoparticle size on TiO_2 support.

Number of Pt ALD cycles	Mean particle size (nm)
5	0.8 ± 0.2
10	0.9 ± 0.4
20	1.1 ± 0.5
40	2.8 ± 1.2

After the catalyst deposition, the microreactors were capped with a laminate foil consisting of 75 μm of polyethylene terephthalate (PET), 25 μm of ethylene-vinyl acetate (EVA) and 25 μm of low-density polyethylene layers (LDPE). The LDPE layer was turned towards the channels. This allowed easy sealing of the microreactors.

Figure 4.1. Time of flight images of pure propene flowing through the 20 mm long chip. Change in signal amplitude is due to relaxation of the encoded signal. On the right image of a similar silicon microreactor chip as used in this study showing the 36 individual microreactor channels and the inlet and outlet channels. Adapted from Publication IV.

The performance of the microreactors were evaluated in propene hydrogenation. Remote detection nuclear magnetic resonance (RD NMR) was used to monitor the reactions. Detailed information regarding the RD NMR method can be found in ref. [147]. RD NMR enabled monitoring both mass transport in the microreactors as well as the progress of the reaction. Time of flight RD NMR images in Figure 4.1 shows that the flow path of propene in the microreactors forms a chevron like front, as the path length via outer channels is longer.

Table 4.2 shows the results from the propene hydrogenation experiments. The highest catalyst activity was observed for Pt nanoparticles deposited with 20 ALD cycles corresponding to average Pt nanoparticle size of 1.1 ± 0.5 nm. Activity of the Pt nanoparticles was observed to be higher on TiO_2 than on SiO_2 and irrespective of the support, the activity of the Pt nanoparticles was higher than continuous Pt surface. Increasing the reaction temperature increased also the Pt surface activity.

The reaction yield decreased as a function of time likely due to poisoning of the catalyst surface by carbonaceous species. The yield in TiO_2 , 40 cycles, 20 mm microreactor decreased from 100 % to 50 % over the course of 4 hours and eventually the catalyst surface was deactivated completely. The catalyst surface could be previously reactivated by flowing pure H_2 gas through the microreactor at 50 °C temperature [147]. However, this did not reactivate the microreactors used in this study and the polymer capping used in these microreactors prevented the use of higher temperatures.

Table 4-2. Active Pt surface area for samples with different oxide support, number of Pt ALD cycles and channel length. Values for the reaction yield, reaction rate k and activity at the beginning of the flow for the non-heated and heated situation. * Overestimate as assumption of hemispherical particles is invalid due to particle coalescence. ** Reaction conditions different from others in this work. From Publication IV.

Sample (support, number of Pt ALD cycles, channel length)	Pt surface area, A_{Pt} (mm ²)	Contact time (ms)	Yield at 21 °C (%)	k at 21 °C (s ⁻¹)	Activity of Pt surface at 21 °C, A (mmol s ⁻¹ m ⁻²)	Yield at 50 °C (%)	k at 50 °C (s ⁻¹)	Activity of Pt surface at 50 °C, A (mmol s ⁻¹ m ⁻²)	Data from
TiO ₂ , 40 c, 20 mm	96	1100 ± 150	90 ± 3	0.28 ± 0.05	2.0 ± 0.4	100	-	-	This work
TiO ₂ , 20 c, 20 mm	12	1100 ± 150	62 ± 2	0.19 ± 0.04	10.7 ± 2.2	100	-	-	This work
TiO ₂ , 10 c, 20 mm	8	1100 ± 150	21 ± 2	0.06 ± 0.02	5.3 ± 1.3	40 ± 2	0.12 ± 0.02	9.1 ± 2.0	This work
TiO ₂ , 20 c, 10 mm	7	550 ± 80	46 ± 1	0.29 ± 0.05	16.5 ± 3.7	93 ± 3	0.59 ± 0.03	30.8 ± 3.4	This work
TiO ₂ , 10 c, 10 mm	4	550 ± 80	10 ± 2	0.06 ± 0.02	6.1 ± 2.3	31 ± 2	0.19 ± 0.02	17.9 ± 2.4	This work
TiO ₂ , 5 c, 10 mm	3	550 ± 80	0	0.00	0.0	-	-	-	This work
PirSi, 50 c, 20 mm	123*	650 ± 120	46** ± 2	0.24** ± 0.06	1.1** ± 0.3	100**	-	-	This work
Sputtered, 5 mm	48	170 ± 50	11	0.22 ± 0.09	0.4 ± 0.2	50	1.00 ± 0.02	1.6 ± 0.2	[147]
Sputtered, 10 mm	82	230 ± 60	-	-	-	22	0.32 ± 0.01	0.5 ± 0.1	[147]
Sputtered, 20 mm	149	380 ± 100	28	0.25 ± 0.09	0.4 ± 0.2	-	-	-	[147]

4.2 Superomniphobic surfaces

Superomniphobic surfaces are surfaces that prevent all liquids from wetting them. A droplet of any liquid on a superomniphobic surface remains in a Cassie state (contact angle $>150^\circ$) and rolls off at a low sliding angle. With simple vertical structures (Figure 4.2a), it is possible to achieve superhydrophobicity; that is, the surface is able to sustain a Cassie state for water. Re-entrant or overhang geometry (Figure 4.2b) extends the repellency of the surface to oils and superoleophobicity can be achieved. However, this is not enough to repel all oils; namely fluoro-oils. Superomniphobic surfaces that rely on strict topography requirements are able to repel all liquids. In 2014, Liu and Kim [148] demonstrated a doubly re-entrant topography (Figure 4.2c) that was able to repel even perfluorohexane, which has surface tension of 11.91 mN m^{-1} at 20°C ; [149] the lowest of known liquids at room temperature. However, their process is based on critical timed etching steps. This makes it difficult to scale down the pillar size, which would increase the stability of the Cassie state. Also due to very high etchable area ($>90\%$), the etching is not trivial and non-uniformity of the etching may prevent fabrication of large-area structures.

Figure 4.2. a) Simple vertical structures are able to repel liquids into Cassie state with inherent contact angle of $> 90^\circ$. b) Re-entrant geometry repels liquids with inherent contact angle $0^\circ < 90^\circ$. c) Doubly re-entrant geometry repels liquids with inherent contact angle of 0° . From Publication V.

In Publication V, a scalable process for superomniphobic surfaces was created based on the doubly re-entrant topography using microfabrication techniques. The surfaces were able to sustain liquids in Cassie state similarly as those of Liu and Kim [148]. By downscaling the pillar size to $5 \mu\text{m}$, we were able to sustain perfluorohexane in the Cassie state down to $200 \mu\text{m}$ droplet diameter, which is the smallest perfluorohexane droplet repelled to date.

The process shown in Figure 4.3 does not contain any critical timed etching steps and is scalable in two different ways. The size of the pillars can be easily downscaled to achieve higher breakthrough pressure and the area that can be covered with the structures can be upscaled due to removal of the critical timed etching step.

We fabricated the doubly re-entrant surfaces on 150-mm silicon-on-insulator (SOI) wafers. The process starts by etching holes through the device layer of the SOI wafer with deep reactive ion etching (DRIE) using lithographically patterned photoresist etch mask (Figure 4.3a–e). This hole is then filled with a material, in this case CVD SiO_2 that eventually becomes the stem and cap of the pillar (Figure 4.3f). Then a lithography is done to define etch mask (Figure 4.3g–

Figure 4.3. Fabrication process for doubly re-entrant pillars: a) SOI wafer, b–c) lithography, d) Si DRIE, e) resist removal, f) CVD oxide fill, g–h) lithography, i) oxide RIE, j) Si DRIE, k) resist removal, l) ALD oxide deposition, m) oxide RIE, n) Si isotropic etching. Adapted from Publication V.

h), which is used to etch pillar cap (Figure 4.3i) and recess for the vertical overhang (Figure 4.3j). This lithography step requires alignment with the previous lithography step. Oxide pillar cap was etched by reactive ion etching (RIE) and the recess into Si with DRIE using a process that resulted in smooth sidewalls. Then the surface was covered by conformal PEALD SiO_2 deposition followed by anisotropic oxide etching using RIE leaving vertical oxide overhangs (Figure 4.3l–m). Finally, the Si on the device layer was etched with isotropic etching process in a DRIE tool leaving all SiO_2 doubly re-entrant pillars on the surface (Figure 4.3n and Figure 4.4).

The beauty of this process is that it can tolerate non-uniformity in high-surface area release etch, it is downscalable and is transferrable to alternative materials.

In our process, the pillars and the substrate they are attached to are all made of SiO_2 , which has high selectivity to the Si in etching with SF_6 , the isotropic release etch process is completely non-critical. This is important when trying to fabricate wafer scale surfaces as the isotropic etching has etchable surface area of close to 90 %. This high etchable surface area can affect the non-uniformity of the etching across the wafer, which can be around 5–10 % to start with. The effect of the non-uniformity is doubled in the fabrication of the pillars as they are etched from two directions. The non-critical release etch not only allowed us to tolerate the non-uniformity of the release etch, but also enabled us to fabricate all of the 5-, 10- and 20- μm pillars on the same wafer.

Downscaling of the pillar cap size while keeping the solid fraction the same is beneficial as the smaller the spacing between the pillars, the higher the break-through pressure. Disadvantage of the downscaling is that the mechanical durability of the pillars weakens even though the aspect ratio of the pillars remains the same. However, as silicon pillars in general are, our pillars are already fragile as such and easily damaged by tweezers so the situation is not remarkably changing, if the size is downscaled.

Figure 4.4. a) 10- μm doubly re-entrant pillar, b) 5- μm doubly re-entrant pillar, c) Array of 5- μm pillars and d) showing edge of a 5- μm pillar array. D means pillar diameter, which was 5, 10 or 20 μm . p is the pitch, which was 3, 4 or 5 times D . w and h mean width and height of the overhang, which were 200 nm and 1 μm respectively. From Publication V.

We demonstrated pillars with 2- μm pillar stem, because this can be done still with conventional 365 nm lithography tools. Smaller pillar stems can be realized with steppers or by nanoimprint lithography (NIL). Because of the 2- μm wide holes requiring 1- μm thick deposition to fill them, the deposition was done with high temperature CVD oxide. When the hole fill dimensions are decreased to 200-nm range, ALD becomes a viable alternative for the hole fill.

Sidewall spacer thickness, which should be kept minimal in order to minimize projected solid surface area, can also be easily downscaled when an ALD process is used.

By using low temperature ALD processes for the hole fill and spacer deposition, the temperature budget of the whole fabrication process could be brought to $<120^\circ\text{C}$ enabling the fabrication of the surface on temperature sensitive substrates.

Alternative materials can be used to realize doubly re-entrant pillars using this process scheme. At minimum two different materials are required: a sacrificial material and pillar material. For the selection of these materials the requirements are that, the sacrificial materials need to be etchable both isotropically and anisotropically with selectivity to the pillar material and the pillar material needs to be anisotropically etchable. Etch stop layer can be made either of the same material as the pillar or from some other material that is not etched in the sacrificial material etches.

5. Conclusions

In this thesis, there were two main themes: literature survey on the use of ALD in fabrication of micro- and nanodevices, and selected experimental case studies on the use of ALD to enable better performing thin films and/or new improved device designs.

Based on the literature survey, in fabrication of micro and nanodevices, ALD is an important tool in the toolbox. It is not a tool fit for everything, but certainly has its uses. When ALD is chosen as the deposition method, it is enabling new designs or better performance of the device with the old design. Due to the slowness of the deposition and associated costs, its use must always be justified. Typically, the justification is that no other method can do what needs to be done. These requirements can be precise thickness control, conformality or low deposition temperature. If another method can fulfil the requirements the other method is usually faster and cheaper, however, this is not always the case. With film thicknesses in 10 nm range, the speed of deposition is no longer so significant.

The ALD AlN process from AlCl_3 developed in this work as the first experimental case study showed promise as the PEALD process enabled films with very low impurity concentration. However, the low stress films were not fully saturated due to restricted NH_3 flow rate with low plasma power. Using higher plasma power enabled better control of the process, as it enabled higher NH_3 flow and based on few additional experiments performed for the thesis it is concluded that this could provide better approach in order to deposit low stress AlN film. The higher powers, however, increase the effect of ion bombardment on residual stress and residual stress is changed more strongly with duration of plasma pulse. Further tuning of the process parameters is required to establish a well-working process. The films with higher plasma power should be investigated further as only two quick tests were done without further characterization apart from ellipsometry and residual stress measurement.

The obtained film crystallinity for AlN was not on adequate level to compete with sputtered or MOCVD AlN films. However, literature has shown that it is possible to deposit epitaxial AlN with ALD with extensive ex-situ and in-situ surface preparation. The crystallinity can be possibly improved by using a seed layer, even though epitaxial growth is not sought. Use of seed layers to promote preferred orientation is more commonly employed strategy in sputtering and

MOCVD than in ALD. In this work, all of the depositions were carried out on <100> oriented Si wafers with native oxide present meaning that starting surface was amorphous.

Overall more research is needed on controlling crystallinity of ALD thin films. Typically, the studies on ALD processes have focused on characterization of the films grown on silicon wafers often with the native oxide present, as was the case in this work as well. This is ok for initial process development or when depositing amorphous films. However, when depositing crystalline films the underlying layer affects the crystallinity.

The process developed in this work, which made possible the deposition of AlN film with no stress, is a significant advantage. The process enabled control of the stress from tensile to compressive residual stress state. Since the control of the residual stress was a result of ion bombardment of the growing film, the difference in properties between planar and vertical surface should be studied. However, measuring film properties on vertical surface is difficult. One option to simplify this could be utilizing LHAR-test structures.

In near future, it may be possible to deposit the ALD AlN with high crystal quality and preferred orientation enabling its use for piezoelectric applications. The possibility to deposit the film conformally with low stress might open up new designs for the devices.

In the next experimental case study, catalyst deposition into microreactors were investigated. Microreactors are under extensive research due to the potential benefits associated with them. ALD is seen as a viable candidate to deposit heterogeneous catalyst into the microreactor. ALD offers control to the catalyst design that is not possible by other means. With ALD, it is possible to deposit continuous catalyst film, metal nanoparticles with controlled size and overcoats for catalyst particles that can change the catalyst behaviour or increase stability. In this work, it was shown that Pt nanoparticles deposited with ALD enabled microreactors with increased activity compared to continuous Pt catalyst films. It was also shown that ALD enabled particle size control, and that particle size affected activity of the nanoparticle catalyst.

Conformality of the thermal ALD is sufficient to coat catalyst particles that can be packed into a microchannel, whereas PEALD can be used to deposit tailored metal nanoparticles onto wall-coated or semi-packed microreactors, where aspect ratios are modest. However, ALD is highly special method requiring special equipment and that are not easily available for a chemist working with microreactors.

Silicon as a material for microreactors face similar challenges. Fabricating silicon microreactors requires special infrastructure, which is available, but often not familiar to the users of the microreactors. Silicon microfabrication, however, would offer advantages when scaling up production as the methods have been scaled up by the MEMS and IC-industry. ALD has also made breakthrough in the MEMS and IC-industry and is readily available at the manufacturing facilities.

In the final experimental case study, superomniphobic surfaces that could repel all room temperature liquids were created. The fabrication scheme presented in this work enables easier approach to fabricate wafer scale surfaces for research, as the superomniphobic surfaces are at this stage mainly of academic interest. Miniaturization of the features could increase the breakthrough pressure of the superomniphobic surfaces. This could also increase the need for ALD in the fabrication process. The use of ALD could also bring down the thermal budget of the process down to $<120\text{ }^{\circ}\text{C}$ vs. $1000\text{ }^{\circ}\text{C}$ in the seminal work enabling easier integration into process flow of some potential device.

To conclude, ALD excels when film thicknesses are low, precise film thicknesses or precise coverage over topography are needed or when low deposition temperatures are desired. These are requirements that are becoming more and more common boding bright future for ALD.

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