Materials example guide

Oxford Instruments Plasma Technology Applications Group

Films deposited by ALD in Oxford Instruments ALD reactors

This report is a summary of development and research using both the FlexAL and OpAL reactors at:

- Oxford Instruments applications lab in the UK
- Development partners at Eindhoven University of Technology, Netherlands
- Other customers who have kindly shared their process results
- Published results available in the public domain

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List of materials in document

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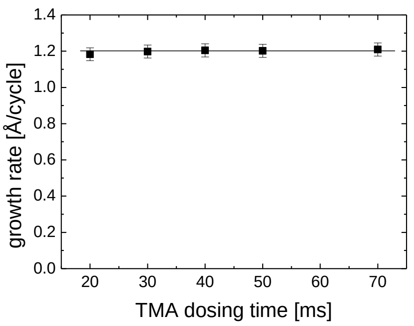
Al

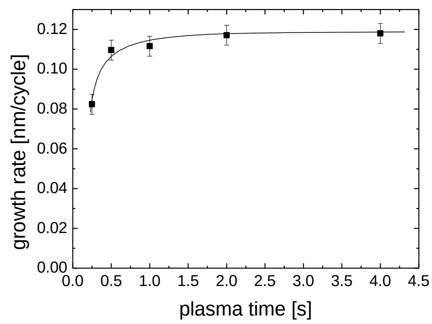
Al_2O_3

Precursor - properties	TMA - $Al(CH_3)_3$ - liquid vapour draw @ 30°C	
Non-metal precursors	H_2O thermal, O_3 thermal, O_2 plasma	
Temperature range	30°C - 400°C (50°C - 400°C for OpAL)	
Growth rate per cycle	1Å/cycle @ 300°C	
Deposition rate	1.5nm/min @ 300°C	
Refractive Index	O_2 plasma 1.59 (30°C) 1.62 (120°C) 1.64 (200°C) 1.64 (300°C)	H_2O thermal 1.60 (120°C) 1.62 (200°C) 1.64 (300°C)
Breakdown Voltage	>7.0 MV/cm @200 °C	>4.0 MV/cm @200 °C
Dielectric Constant	>7.0 @ 200 °C	>5.5 @ 200 °C
Uniformity	± 1% over 100mm, ± 1.5% over 150mm, ± 2.0% over 200mm	
Precursor consumption	100nm/g	

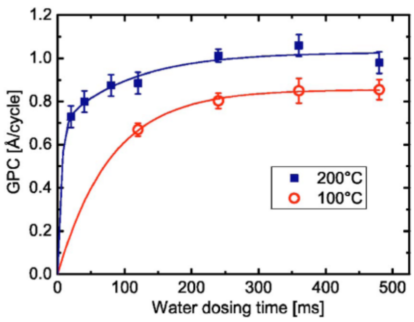
200mm data for FlexAL only



TMA saturation (O_2 process) @ 200°C



O_2 plasma exposure @ 200°C



Water saturation at 100°C and 200°C

Growth rate per cycle from the graphs is 1.2Å/cycle for plasma and 1.0Å/cycle for thermal at 200°C. Uniformity: < ±2.0% (200mm wafer).

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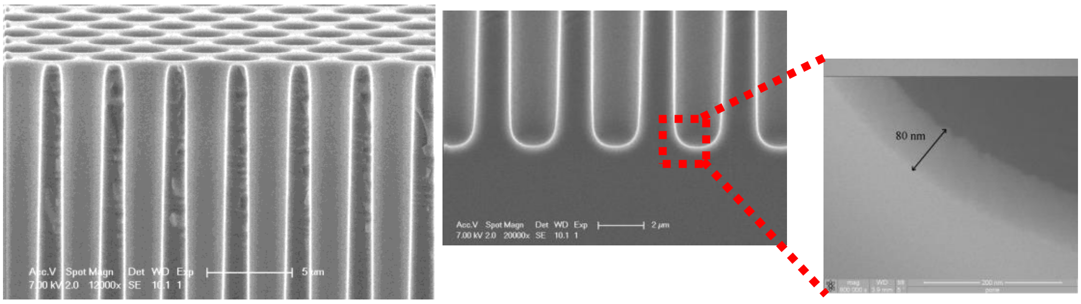
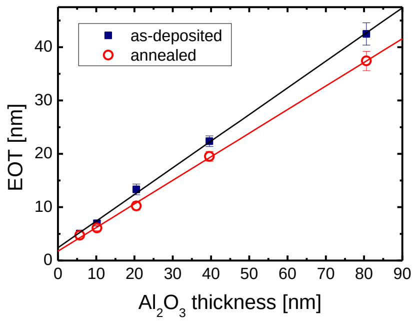
Deposition onto trenches:



SEM image of a 80 nm remote plasma ALD Al_2O_3 film in 2.5 mm wide trenches with aspect ratio ~10 deposited in the FlexAL reactor, courtesy of Eindhoven University of Technology & NXP.

Film analysis:



Parameter	Before anneal	After anneal *(forming gas anneal 425°C, 30 minutes)*
Dielectric constant	7.8	8.9
Breakdown voltage	9.7 ± 0.5 MV/cm	8.4 ± 0.5 MV/cm

EOT vs physical thickness of Al_2O_3 films deposited at 200°C by remote plasma ALD. Results for both the as-deposited and the annealed (425°C, forming gas) material are shown.

RBS and ERD analysis for 200 °C film

Al_2O_x	at % C	at % H
x=3.05	< 2%	2.5%

Compositional data by Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection (ERD)

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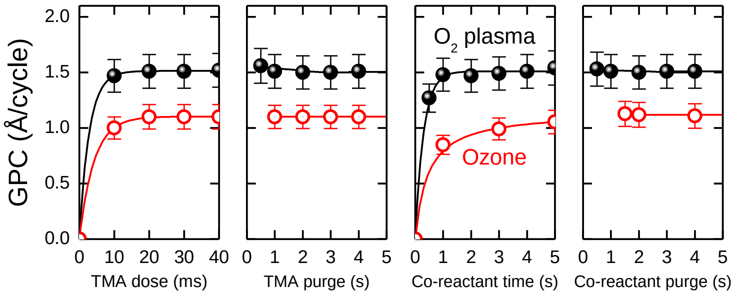
Reported in papers using Oxford Instruments tools

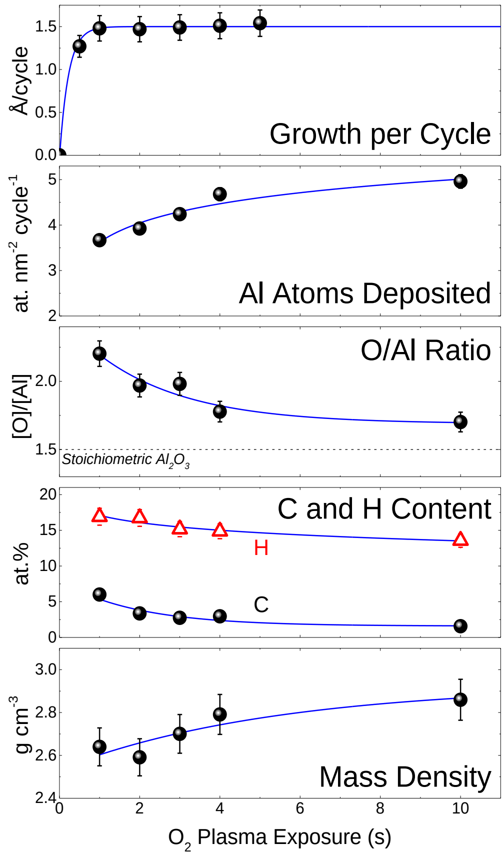
Room temperature ALD using TMA and O_2 plasma and ozone in FlexAL at Eindhoven University of Technology.

Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013)
http://dx.doi.org/10.1002/cvde.201207033

Technische Universiteit **Eindhoven** University of Technology



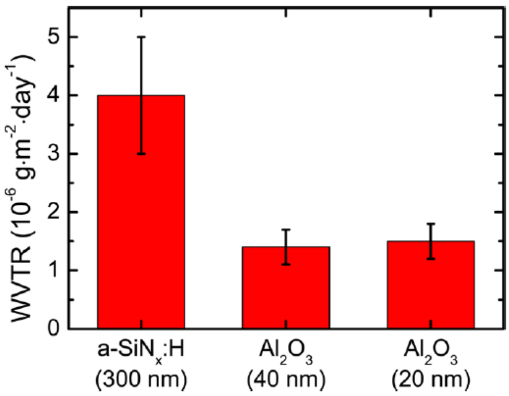
Fast saturation and short purging even at room temperature.



RT-ALD films with 10 s plasma equivalent to films grown at 100 °C using standard process (2 s plasma).

Keuning et al., *J. Vac. Sci. Technol. A* **30**, 01A131 (2012)
http://dx.doi.org/10.1116/1.3664762

- Remote plasma ALD: Al_2O_3 barrier deposition at room temperature
- Excellent single layer barrier (20-40 nm Al_2O_3) → WVTR = ≤ $2\cdot10^{-6}$ $g\cdot m^{-2}\cdot day^{-1}$
- Development towards flexible electronics such as OLEDs



Excellent moisture barrier properties of room temperature Al_2O_3

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Other relevant papers:
Jinesh et al., *J. Electrochem. Soc.* **158**, G21 (2011)
http://dx.doi.org/10.1149/1.3517430

Dingemans et al., *Phys. Status Solidi RRL* **5**, 22 (2011)
http://dx.doi.org/10.1002/pssr.201004378

Hoex et al., *Phys. Status Solidi RRL* **6**, 4 (2012)
http://dx.doi.org/10.1002/pssr.201105445

Potts et al., *J. Electrochem. Soc.* **157**, P66 (2010)
http://dx.doi.org/10.1149/1.3428705

Potts et al., *J. Electrochem. Soc.* **158**, C132 (2011)
http://dx.doi.org/10.1149/1.3560197

Sagade et al., *Nanoscale* **7**, 3558 (2015)
http://dx.doi.org/10.1039/c4nr07457b

Cho et al., *Microelectronic Engineering* **147**, 277 (2015)
http://dx.doi.org/10.1016/j.mee.2015.04.067

Koushik et al., *Energy Environ. Sci.*, (2017), Advance Article
http://dx.doi.org/10.1039/c6ee02687g

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Al

AlN

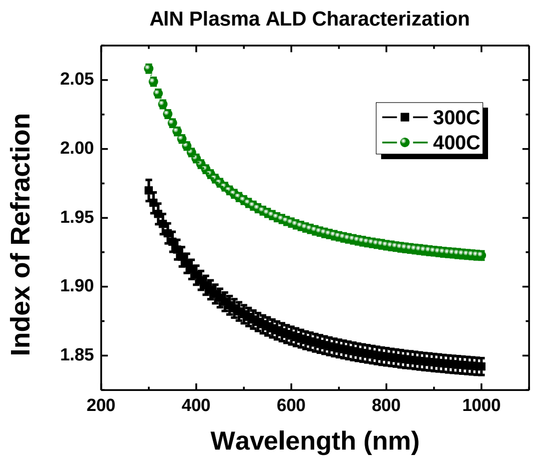
Precursor - properties	TMA - Al(CH_3)$_3$ - liquid vapour draw @ 30°C
Non-metal precursors	N_2 or N_2/H_2 plasma
Temperature range	300°C – 550 °C
Growth rate per cycle	0.6Å/cycle @ 300°C
Deposition rate	0.36nm/min @ 300°C
Refractive Index	1.90 – 1.95
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm (when using N_2 plasma)
Precursor consumption	75nm/g

200mm data for FlexAL only

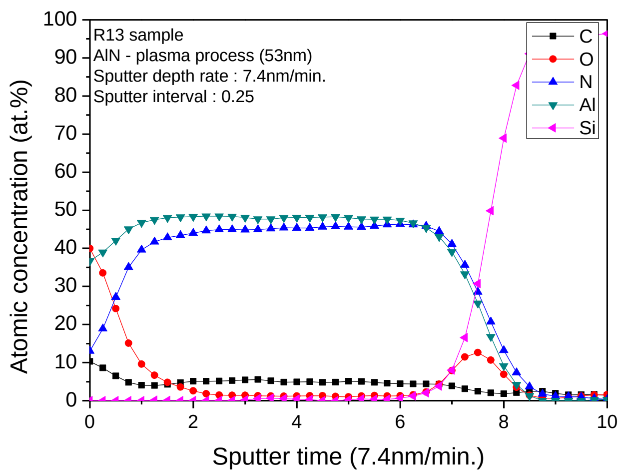
Saturation curves:

This process is well known in the literature to be a non-ideal ALD process in that it does not properly self limit. Better saturation and uniformity is obtained when using a pure N_2 plasma, however, the best stability of the films has been observed using N_2/H_2 plasmas.

Analysis:



Refractive index of AlN using N_2/H_2 plasma; data courtesy of Cornell Nanofabrication Facility (CNF)



AES analysis of AlN using N_2/H_2 plasma showing near stoichiometric AlN.

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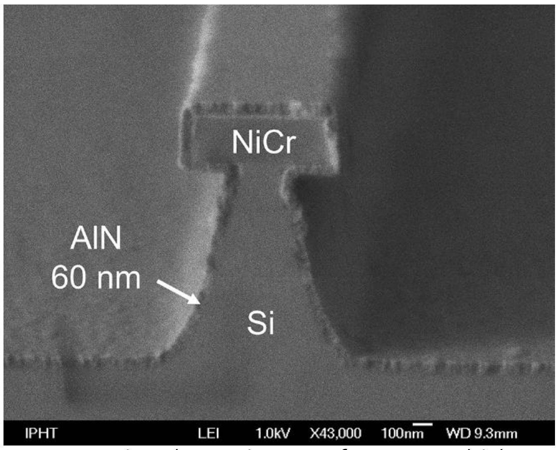
Reported in papers using Oxford Instruments tools

ALD of AlN for thin membranes using TMA and H_2/N_2 plasma in OpAL at Leibniz Institute of Photonic Technology (IPHT) in Jena.

Goerke et al., *Applied Surface Science* **338**, 35 (2015)
http://dx.doi.org/10.1016/j.apsusc.2015.02.119

LEIBNIZ-INSTITUT für PHOTONISCHE TECHNOLOGIEN ipht jena



Cross-sectional SEM-image of a 60 nm thick and conform ALD AlN film on a Si/NiCr structure with etched undercut.

Epitaxial growth of ALD AlN using TMA and H_2/N_2 plasma at 300 °C on OpAL at Hong Kong University of Science and Technology. Followed by ALD Al_2O_3 gate dielectric.

Liu et al., *IEEE Electron Device Lett.* **34**, 1106 (2013)
http://dx.doi.org/10.1109/LED.2013.2271973
Liu et al., *Phys. Status Solidi C* **11**, 953 (2014)
http://dx.doi.org/10.1002/pssc.201300442

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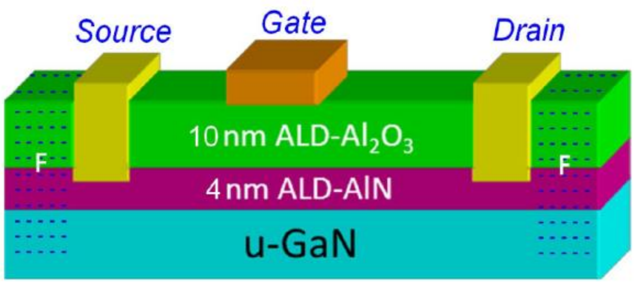
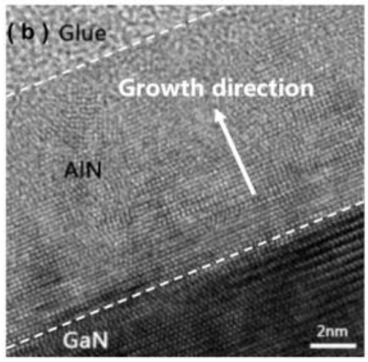
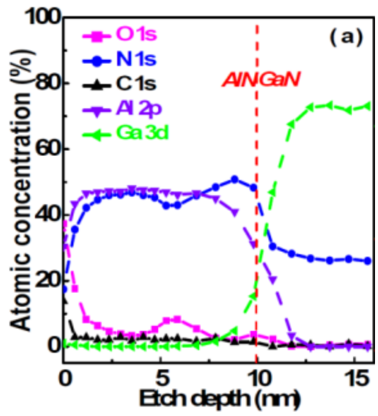


Thin-film transistor design

TFTs with good gate control with low subthreshold swing (~85 mV/decade) and low-field mobility (~27 cm²/(V·s)).



Epitaxial 4 nm AlN on GaN



close to AlN composition

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Al

AlF_3

Based on customer results

Precursor - properties	TMA - $Al(CH_3)_3$ - liquid vapour draw @ 30°C
Non-metal precursors	SF_6 plasma
Temperature range	50°C – 300 °C
Growth rate per cycle	0.85 Å/cycle @ 200°C
Deposition rate	0.25nm/min @ 200°C
Refractive Index	1.35
Uniformity	± 3.9% over 200mm (standard deviation, 1 sigma)

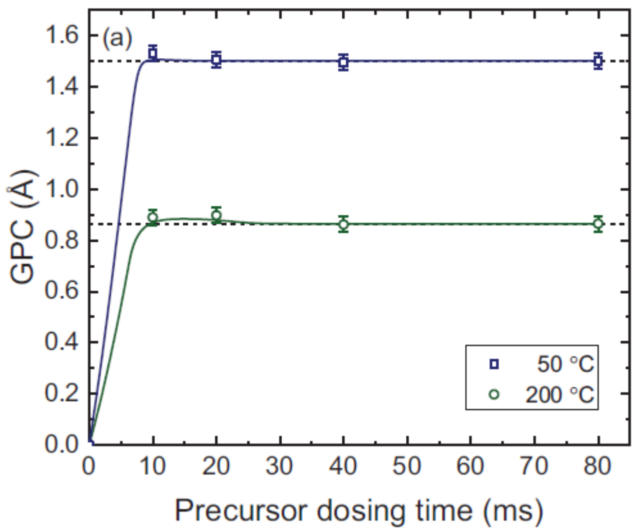
Note that SF_6 plasma can etch SiO_2 and Si surfaces. To avoid etching of the substrate, 20 Al_2O_3 ALD cycles using TMA and O_2 plasma can be performed prior to deposition of the AlF_3 which serve as a protective barrier.

Reported in papers using Oxford Instruments tools

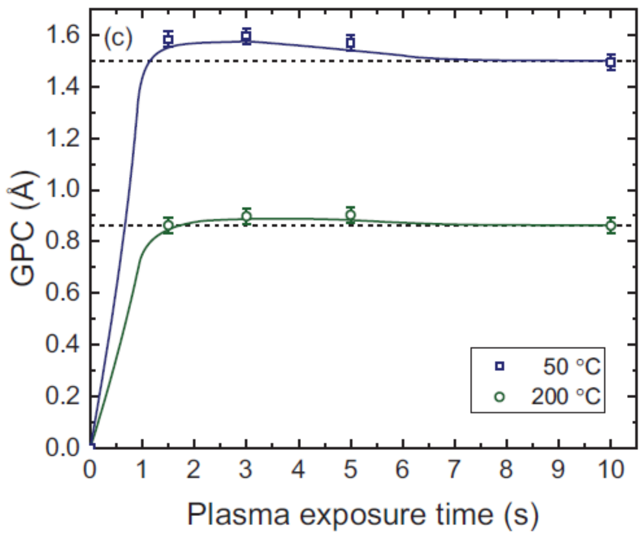
ALD using TMA and SF_6 plasma in FlexAL at Eindhoven University of Technology.

TU/e Technische Universiteit Eindhoven University of Technology

Vos *et al.*, *APL* 111, 113105 (2017)
http://dx.doi.org/10.1063/1.4998577



Growth per cycle (GPC) as a function of precursor dosing time showing fast saturation even at low temperature.



Growth per cycle (GPC) as a function of plasma exposure time showing saturation at both temperatures.

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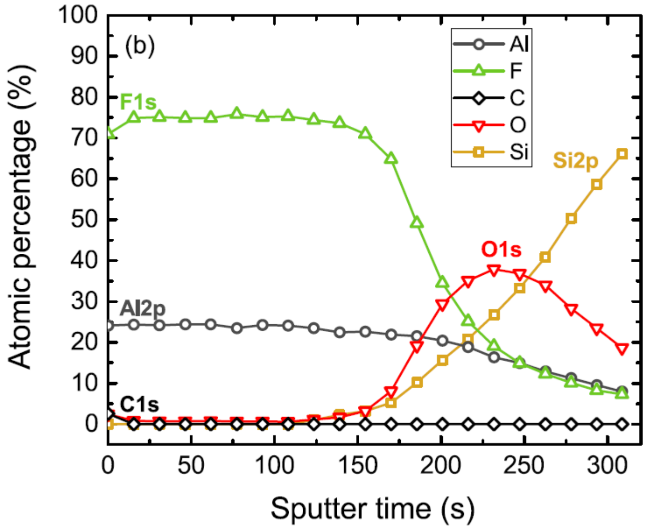
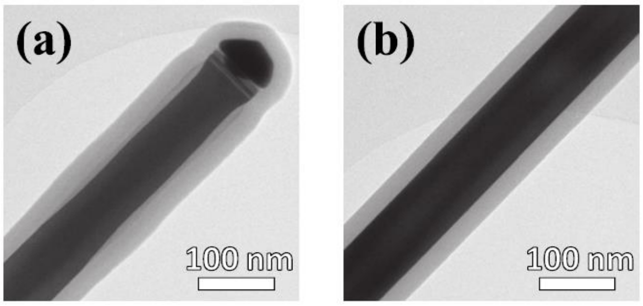
TABLE I. Properties of AlF_3 films for deposition temperatures between 50 °C and 300 °C. The growth per cycle (GPC) in terms of Al atoms $nm^{-2} cycle^{-1}$ and the chemical composition were determined from RBS and ERD, the refractive index from VUV-SE, and the mass density by combining the RBS and SE results. Typical errors are indicated in the top row, unless the error varies with temperature.

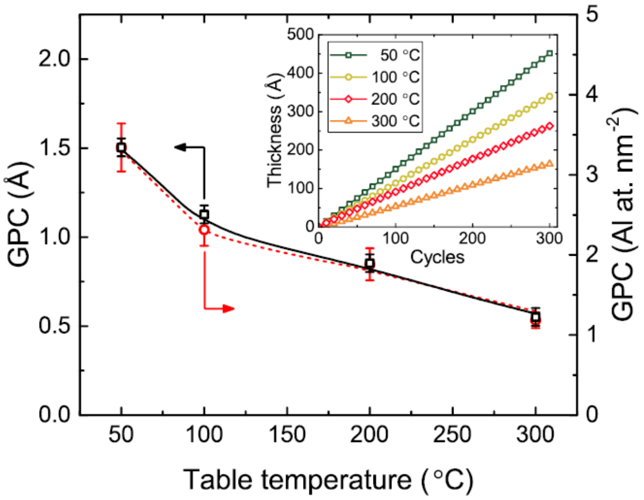
Deposition temperature (°C)	GPC (Å)	GPC (Al at. nm^{-2})	F/Al	[S] (at. %)	[H] (at. %)	Mass density ($g \cdot cm^{-3}$)	Refractive index
50	1.50 ± 0.05	3.3 ± 0.3	3.1 ± 0.5	0.5 ± 0.1	3.2 ± 0.8	2.8 ± 0.3	1.35 ± 0.01
100	1.13	2.3 ± 0.2	3.1	0.3	2.3 ± 0.5	2.7	1.34
200	0.85	1.9 ± 0.2	2.9	0.2	1.7 ± 0.3	2.9	1.35
300	0.55	1.2 ± 0.1	2.9	0.0	1.3 ± 0.2	2.7	1.35



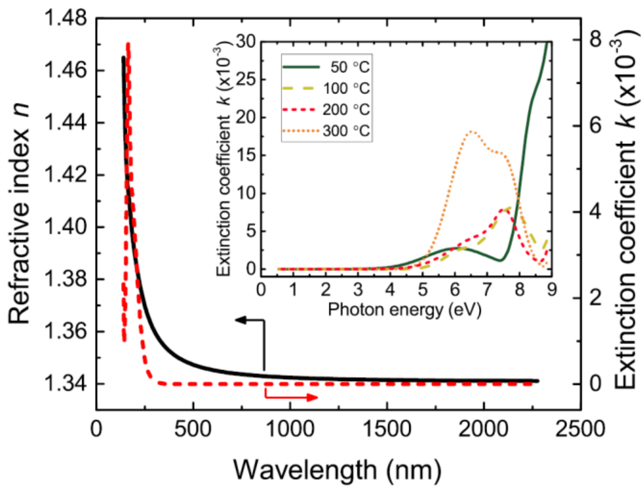
XPS depth profile of AlF_3 on Si wafer with Al_2O_3 interlayer. Low impurity levels and F/Al ratio very close to 3.



TEM images of (a) the top and (b) the middle of a GaP nanowire, illustrating the conformality of the ALD process.



Wide temperature window. Growth per cycle (GPC) as a function of temperature in terms of thickness (left axis) and deposited Al atoms per nm^2 (right axis). Inset: No growth delay, thickness as a function of ALD cycles.



Refractive index and extinction coefficient for a film deposited at 200 °C. Inset: Extinction coefficient as a function of photon energy for deposition temperatures between 50 °C and 300 °C showing low absorption over a wide range.

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Alucone MLD

Al

Customer results show that alucone can be grown by ALD. Since a part of the resulting film is organic, this technique is often called molecular layer deposition (MLD). Other MLD processes are also expected to be able to run on Oxford Instruments tools.

Reported in papers using Oxford Instruments tools

Molecular layer deposition (MLD) using TMA and ethylene glycol on OpAL at 150 °C.

Ghazaryan, Kley, Tünnermann, and Szeghalmi,
J. Vac. Sci. Technol. A 31, 01A149 (2013)
http://dx.doi.org/10.1116/1.4773296

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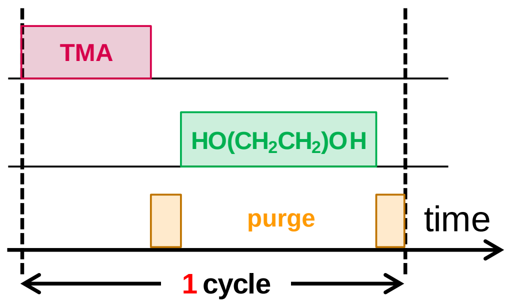
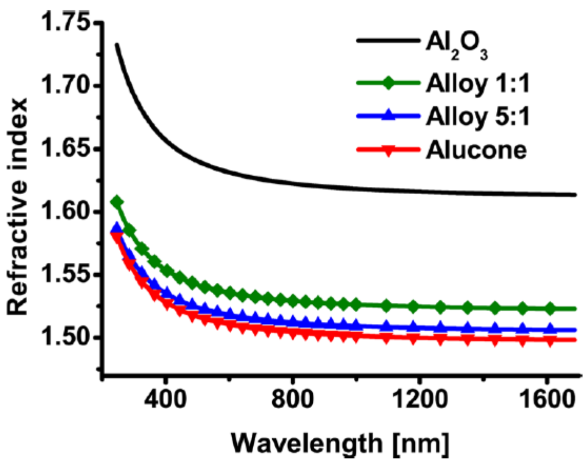
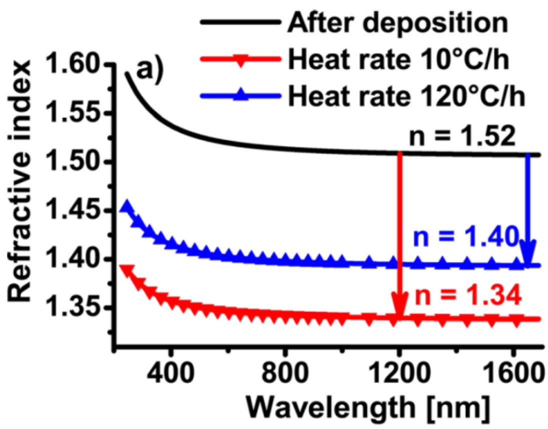


Alucone MLD cycle



Mixed with ALD Al_2O_3 to make alloys.



Slow heating up to 400 °C of 5:1 alucone/Al_2O_3 alloy provides novel, nanoporous, low index material.

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Ba BaO and $BaTiO_3$

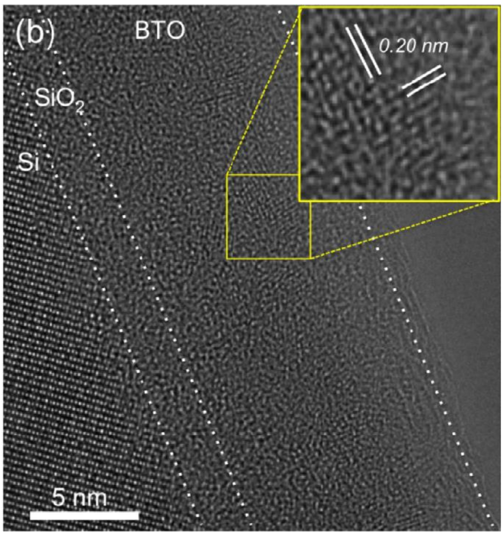
Customer results show that both BaO and $BaTiO_3$ can be grown by plasma ALD.

Reported in papers using Oxford Instruments tools

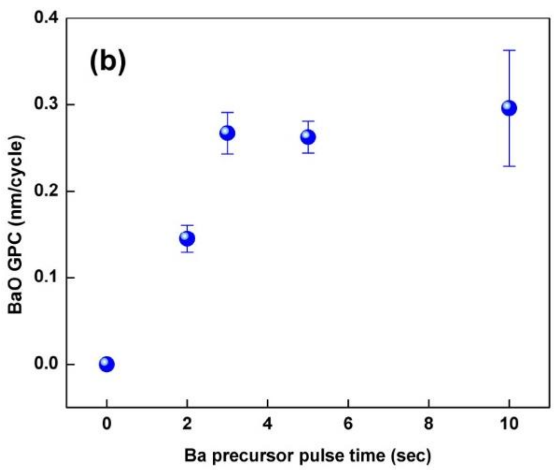
Perovskite $BaTiO_3$ interesting due to high k value. $BaTiO_3$ and BaO deposited using FlexAL. $Ba(^iPr_3Cp)_2$ heated to 180 °C as precursor and O_2 plasma as reactant.

Schindler et al., *Scripta Materialia* **111**, 106 (2016)
http://dx.doi.org/10.1016/j.scriptamat.2015.08.026

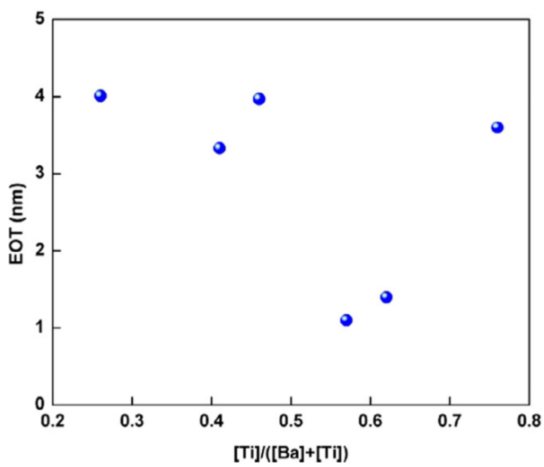
Stanford University



Zoomed in TEM view showing crystalline lattice fringes.



Saturation of Ba precursor pulse.



Low EOT values for 12 nm-thick films deposited at 250 °C.

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Co

Co_3O_4

Based on customer results

Precursor - properties	Cobaltocene - $CoCp_2$ – solid carrier gas assisted @ 80°C
Non-metal precursors	O_2 plasma
Temperature range	100°C – 400 °C
Growth rate per cycle	~0.5Å/cycle @ 300°C
Uniformity	± 2.0% over 100, ± 3.0% over 150mm, ± 3.5% over 200mm

200mm data for FlexAL only

This material is untested on substrates greater than 2”. We will support the improvement in uniformity remotely and expect that levels similar as those indicated can be obtained.

Reported in papers using Oxford Instruments tools

Plasma ALD using $CoCp_2$ and O_2 plasma in FlexAL at Lawrence Berkeley National Laboratory (LBNL)

Yang et al., *Nature Materials* (2016) Advance online
http://dx.doi.org/10.1038/nmat4794

Yang et al., *J. Am. Chem. Soc.* **136**, 6191 (2014)
http://dx.doi.org/10.1021/ja501513t

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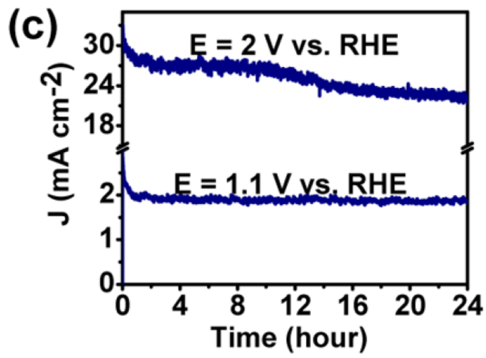
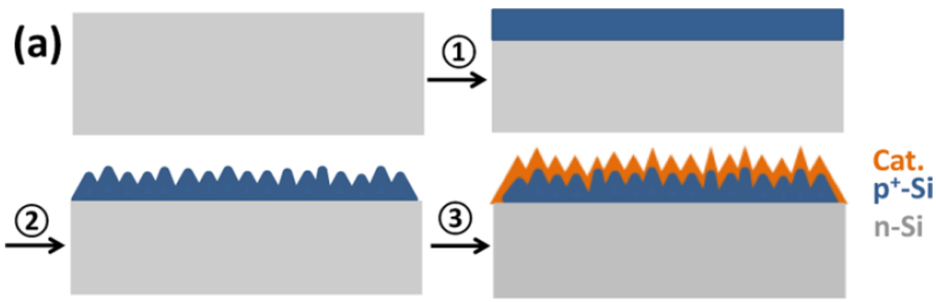


Stable photocurrent over time at 1.1 V with Co_3O_4 ALD on nanostructured surface



Co_3O_4 to serve as catalyst and protection layer of nanotextured Si photoanode

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Ga

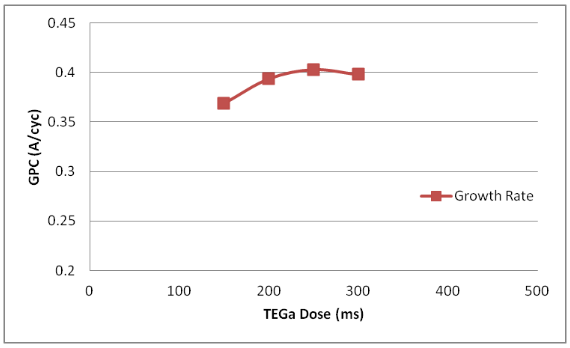
GaN

Precursor - properties	TEGa – $Ga(CH_2CH_3)_3$ - liquid vapour draw @ 30°C
Non-metal precursors	N_2/H_2 plasma
Temperature range	150°C - 350°C
Growth rate per cycle	0.40Å/cycle @ 300°C
Deposition rate	0.12nm/min @ 300°C
Refractive Index	1.90 @ 350°C
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm
Precursor consumption	15.5nm/g

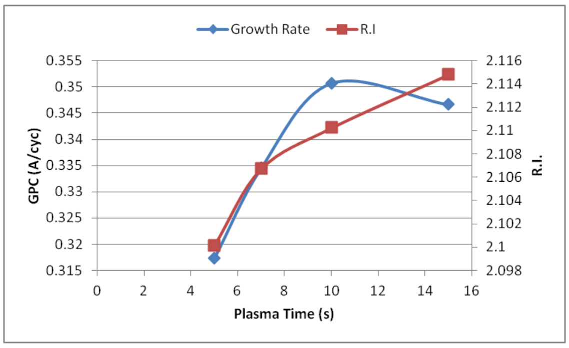
200mm data for FlexAL only

Saturation curves:

Previous literature has demonstrated that the process with NH_3 is not self-saturating. An ideal ALD process has been demonstrated using a mixed N_2/H_2 plasma. Apparent within this is the influence of additional plasma exposure on film quality, with exposures greater than the saturating 10 seconds leading to an assumed densification of the film accompanied with a higher refractive index from both this affect and a reduction in chemical impurities



Growth rate vs TEGa dose time



Growth rate vs plasma exposure time

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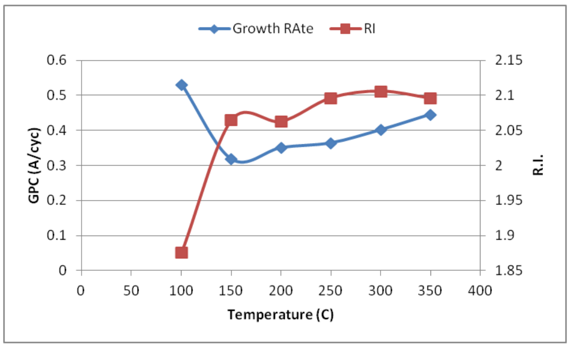
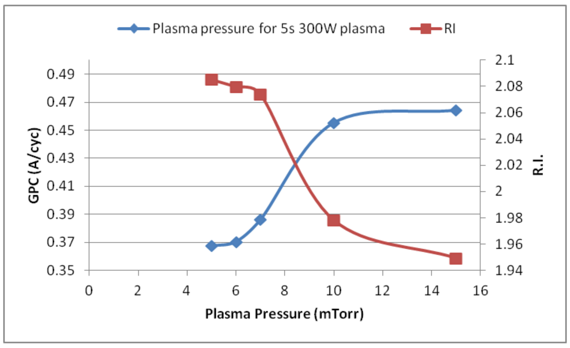
Temperature window and pressure dependence:

ALD window existing between 150 and 350 °C. Temperatures greater than 350 °C have not been tested but the lower bound agrees with previous literature which has stated the same bounds. Verified independently by AES it is observed that there is a defined shift in impurity levels when dropping to low pressures. Refractive Index is often directly comparable to levels of impurity.



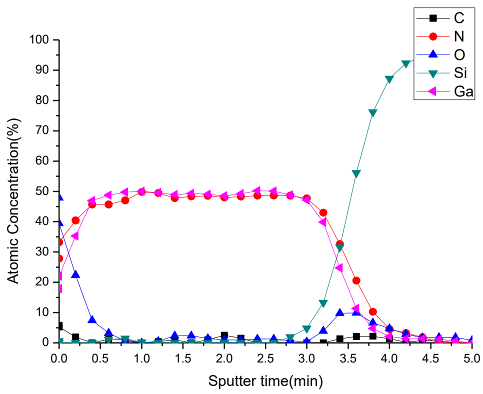
growth rate vs temperature



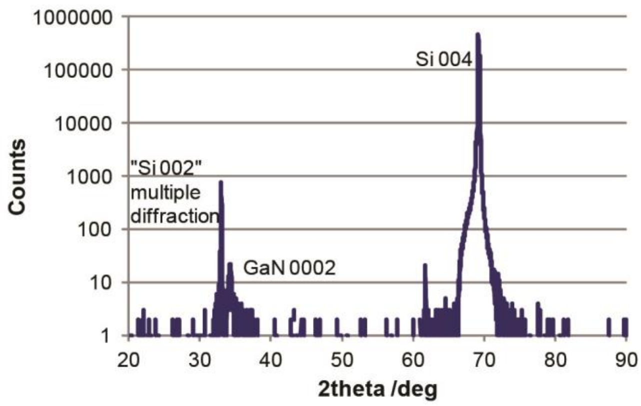
growth rate vs plasma pressure

Film Analysis:

Auger Electron Spectroscopy (AES) analysis of 65nm of ALD GaN film (deposited at 350 °C with low plasma pressure) <3 at% of both C and O are observed in the bulk and the film is shown to be stoichiometric. XRD analysis of this film shows a very small peak attributable to the GaN[0002] phase.



AES analysis of 65nm ALD GaN film



XRD analysis of GaN film

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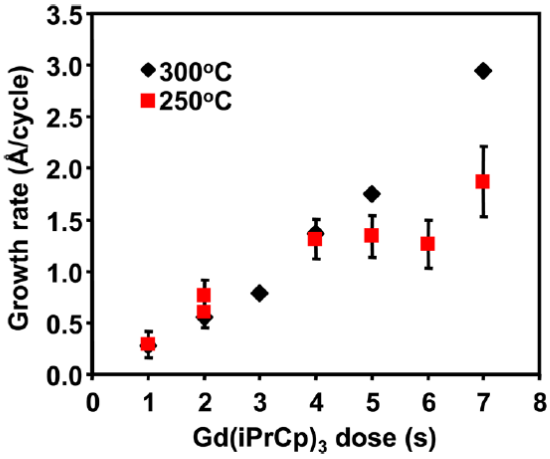
Gd

Gd_2O_3 and GdN

Customer results show that both Gd_2O_3 and GdN can be grown by plasma ALD. Generally the precursors need quite high temperatures (190 °C for Gd(^{i}PrCp)$_3$) and the maximum temperature is also limited by precursor decomposition (max. 250 °C for Gd(^{i}PrCp)$_3$ and some decomposition already occurring at 200 °C for Gd(MeCp)$_3$).

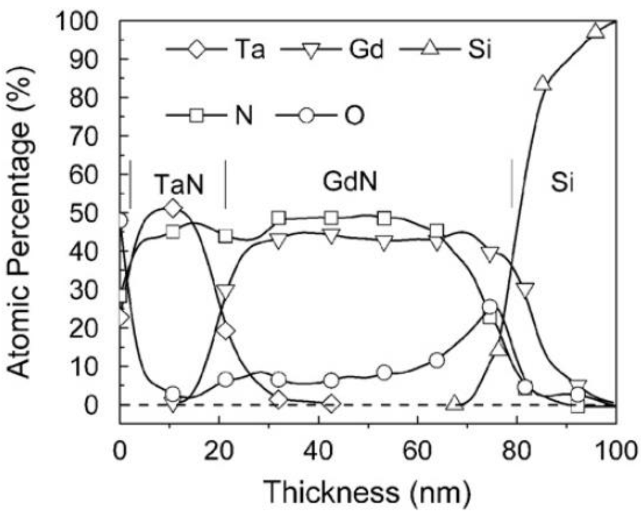
Reported in papers using Oxford Instruments tools

Plasma ALD of Gd_2O_3 using Gd(^{i}PrCp)$_3$ and O_2 plasma in OpAL at Massachusetts Institute of Technology
Vitale et al., *J. Vac. Sci. Technol. A* **30**, 01A130 (2012) http://dx.doi.org/10.1116/1.3664756



Growth rate of Gd_2O_3 PE-ALD films at 250 and 300 °C as a function of precursor dose.

Plasma ALD of GdN using Gd(MeCp)$_3$ and N_2 plasma in OpAL at University of Liverpool
Fang et al., *J. Crystal Growth* **338**, 111 (2012) http://dx.doi.org/10.1016/j.jcrysgro.2011.10.049



AES depth profiling of gadolinium nitride film deposited with N_2 plasma (5s) at 200 °C.

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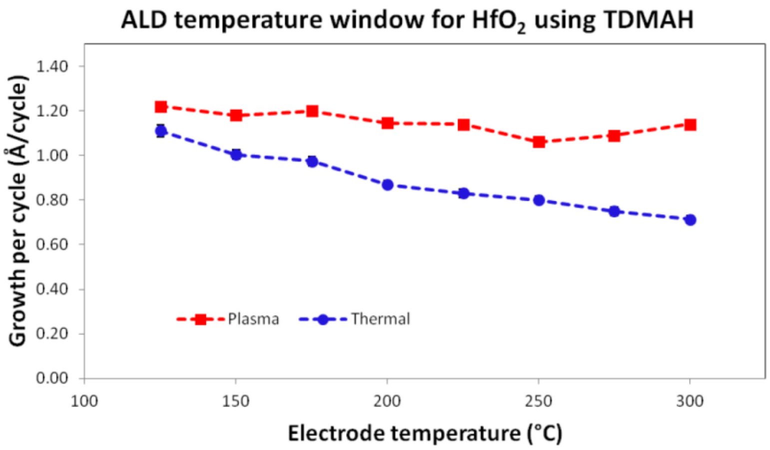
Hf

HfO_2

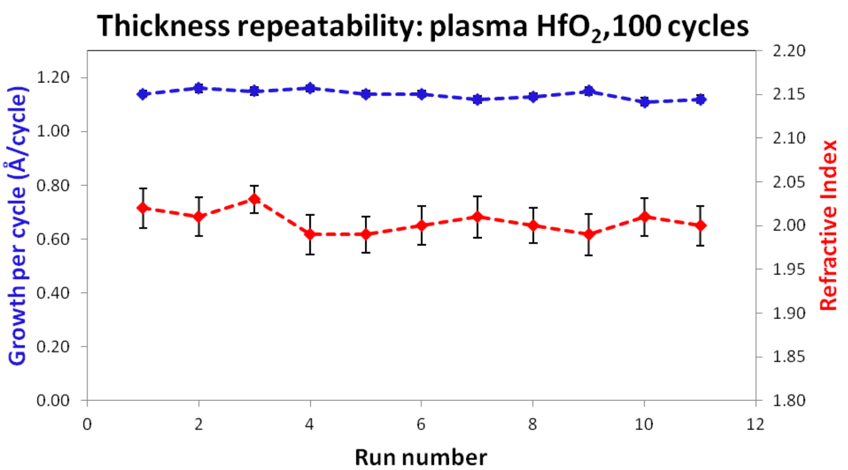
TDMAH precursor – vapour drawn (recommended process)

Precursor - properties	TDMAH – $Hf(N(CH_3)_2)_4$ – liquid vapour draw @ 70°C
Non-metal precursors	H_2O thermal, O_2 plasma
Temperature range	80°C - 300°C
Growth rate per cycle	1.1 Å/cycle @ 275°C (plasma), 0.7 Å/cycle @ 300°C (thermal)
Deposition rate	0.3-0.4 nm/min @ 290°C
Refractive Index	1.98 – 2.06
Breakdown Voltage	> 3.0 MV/cm @ 290 °C
Uniformity	± 1.5% over 100, ± 2.0% over 150mm, ± 3-4% over 200mm

200mm data for FlexAL only



Wide temperature window both for plasma and thermal ALD of HfO2, higher growth per cycle for plasma process



Good repeatability plasma process for both thickness and refractive index (other HfO_2 processes can sometimes be less reproducible)

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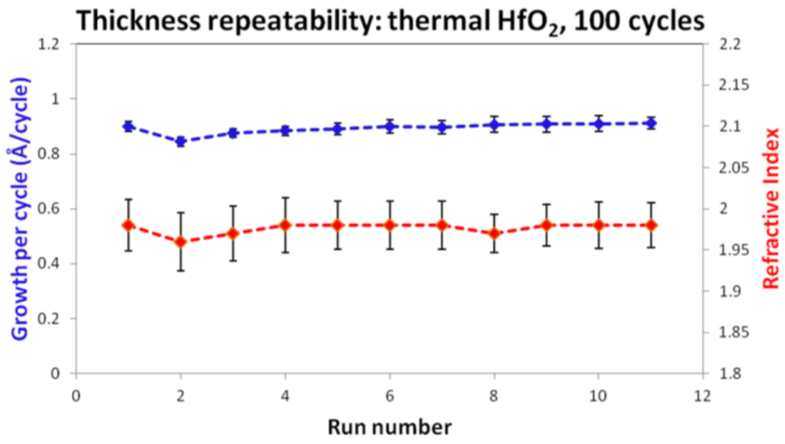


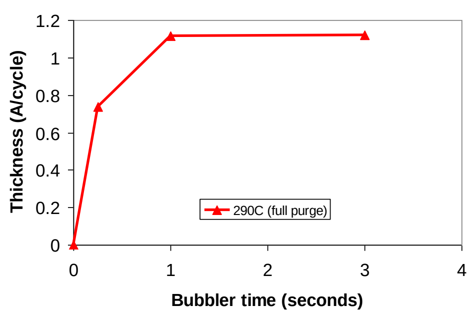
Also good repeatability for thermal process for both thickness and refractive index (other HfO_2 processes can sometimes be less reproducible)

TEMAH precursor – bubbled or carrier gas assisted

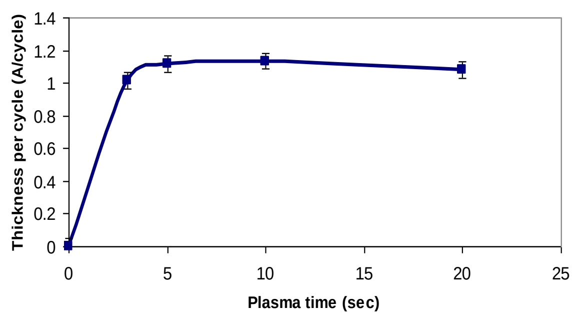
Precursor - properties	TEMAH - $Hf(N(C_2H_5)(CH_3))_4$ - liquid bubbled @ 70°C
Non-metal precursors	H_2O thermal, O_3 thermal, O_2 plasma
Temperature range	80°C - 290°C
Growth rate per cycle	1.1 Å/cycle @ 290°C (plasma), 0.8 Å/cycle @ 290°C (thermal)
Refractive Index	1.95 – 2.05
Breakdown Voltage	> 3.0 MV/cm @ 290 °C
Dielectric Constant	> 17 @ 290 °C (plasma), > 15 @ 290 °C (thermal)
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm
Precursor consumption	70nm/g

200mm data for FlexAL only

Saturation curves:



TEMAH saturation (O_2 process)



O_2 plasma saturation

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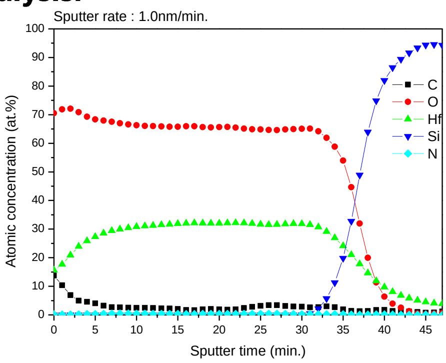
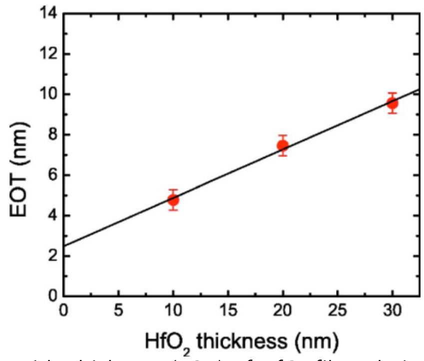
Film analysis:



AES analysis of 25nm of remote plasma ALD HfO_2 deposited at 290 °C, showing a carbon contamination of less than 2%.



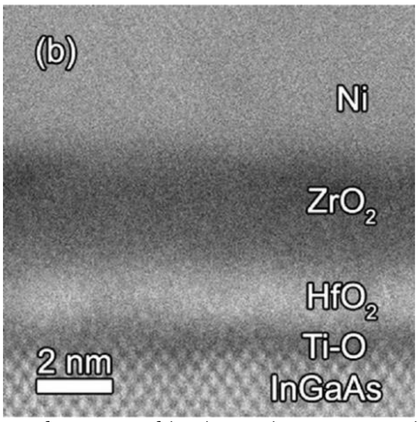
Equivalent oxide thickness (EOT) of HfO_2 films derived from C-V measurements vs physical thickness measured by spectroscopic ellipsometry, the calculated dielectric constant is ~17.

Reported in papers using Oxford Instruments tools

Thermal ALD using TEMAH and H_2O in FlexAL at UC Santa Barbara.

> Chobpattana et al., *J. Appl. Phys* **116**, 124104 (2014) http://dx.doi.org/10.1063/1.4896494
> Elias et al., *Jpn. J. Appl. Phys.* **53**, 065503 (2014) http://dx.doi.org/10.7567/JJAP.53.065503

UCSB



ALD HfO_2 part of high-quality gate stack on InGaAs

Plasma ALD using $HfCp(NMe_2)_3$ (HyALD™) and O_2 plasma in FlexAL at Eindhoven University of Technology.

> Sharma et al., *JVST A* **35**, 01B130 (2017) http://dx.doi.org/10.1116/1.4972210

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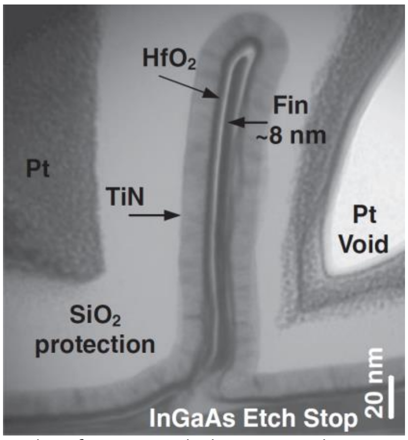
HfO_2 ALD over a temperature range of 150–400 °C at a growth per cycle around 1.1 A/cycle. Increasing the deposition temperature from 200 to 400 °C, reduced the atomic concentrations of residual carbon and hydrogen from 1.0 to <0.5 at.% and 3.4 to 0.8 at.%, respectively.



FinFET with HfO_2 gate dielectric and TiN gate metal done on FlexAL at UCSB

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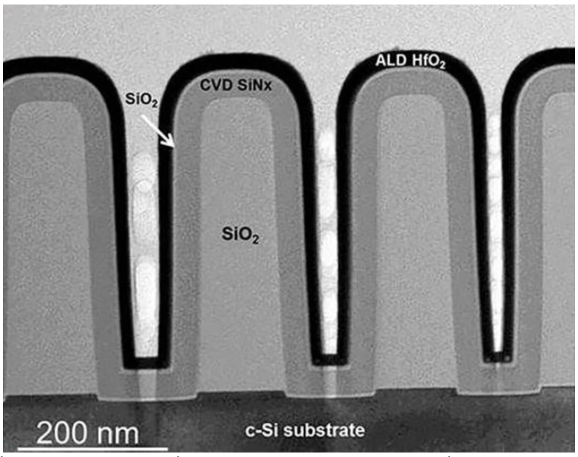
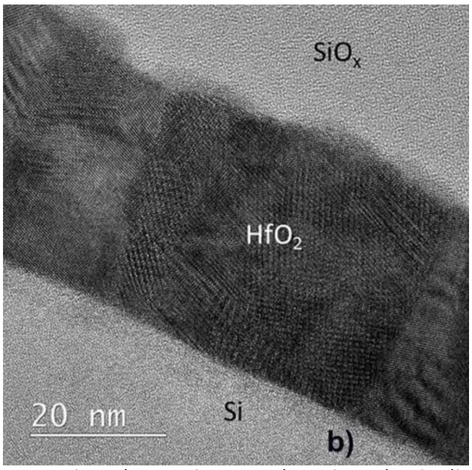


Trench structures with varying aspect ratios showing conformal HfO_2 thin film



Cross-sectional TEM image showing the individual crystalline grains of HfO_2

Other relevant papers:

Heil et al., *J. Vac. Sci. Technol. A* **25**, 1357 (2007)
http://dx.doi.org/10.1116/1.2753846

El-Atab et al., *Nanoscale Research Letters* **10**, 248 (2015)
http://dx.doi.org/10.1186/s11671-015-0957-5

English et al., *J. Vac. Sci. Technol. B* **32**, 03D106 (2014)
http://dx.doi.org/10.1116/1.4831875

Chobpattana et al., *J. Appl. Phys.* **114**, 154108 (2013)
http://dx.doi.org/10.1063/1.4825259

Richter et al., *J. Vac. Sci. Technol. A* **32**, 01A117 (2014)
http://dx.doi.org/10.1116/1.4842675

Mather et al., *Microelectronic Engineering* **109**, 126 (2013)
http://dx.doi.org/10.1016/j.mee.2013.03.032

Colón and Shi, *Solid-State Electronics* **99**, 25 (2014)
http://dx.doi.org/10.1016/j.sse.2014.05.005

Simon et al., *Sol. Energy Mat. & Sol. Cells* **131**, 72 (2014)
http://dx.doi.org/10.1016/j.solmat.2014.06.005

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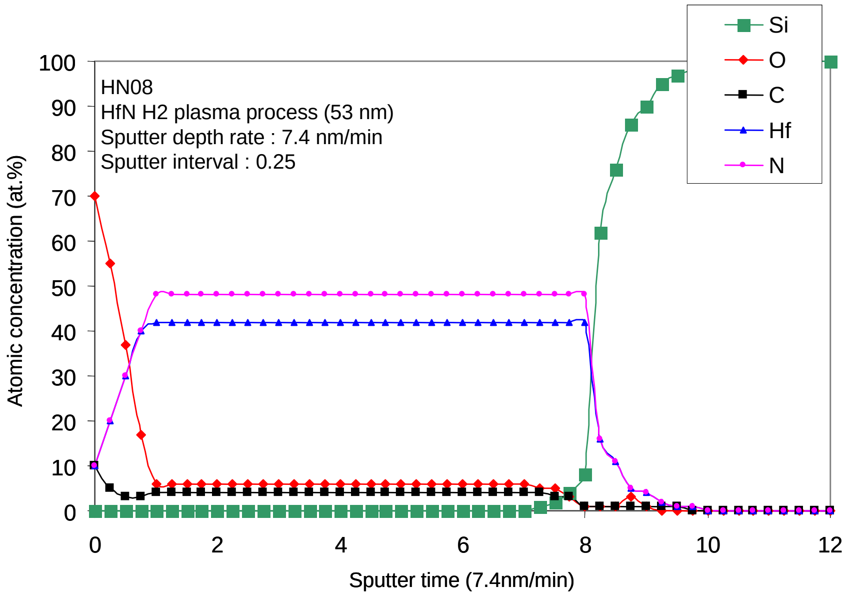
Hf — HfN

Precursor - properties	TEMAH - $Hf(N(C_2H_5)(CH_3))_4$ - liquid bubbled @ 70°C
Non-metal precursors	NH_3 thermal, N_2/H_2 plasma
Temperature range	290°C
Growth rate per cycle	0.9 Å/cycle @ 290°C
Deposition rate	0.45nm/min @ 290°C
Uniformity	± 2.0% over 100, ± 3.0% over 150mm
Precursor consumption	75nm/g



AES showing composition of HfN by plasma ALD.

Reported in papers using Oxford Instruments tools

Plasma ALD using $HfCp(NMe_2)_3$ (HyALD™) and N_2 (insulating HfN_x) or H_2 plasma (conductive HfN_x) in FlexAL at Eindhoven University of Technology.

Karwal et al., *JVST A* **35**, 01B129 (2017)
http://dx.doi.org/10.1116/1.4972208

Technische Universiteit Eindhoven University of Technology

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In

In_2O_3

Based on customer results

Precursor - properties	InCp – solid carrier gas assisted @ 40°C
Non-metal precursors	Both H_2O and O_2 gas
Temperature range	100°C[1]
Growth rate per cycle	~1.2 Å/cycle @ 100°C
Uniformity	Expected values: ± 2.0% over 100, ± 3.0% over 150mm, ± 3.5% over 200mm

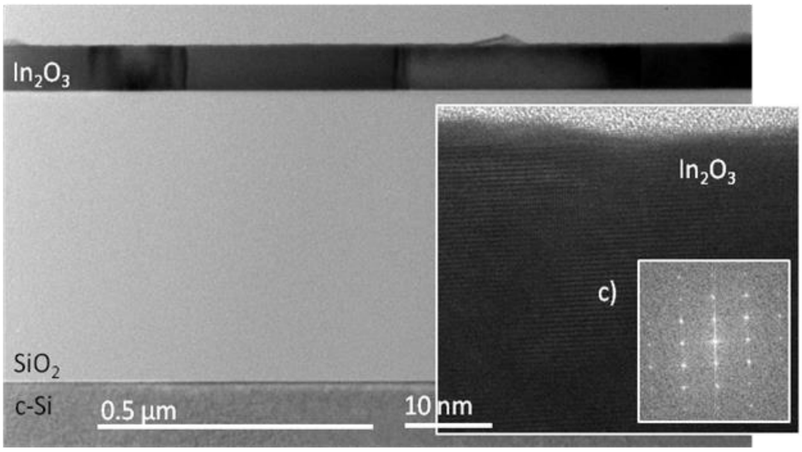
Notes

[1] The films are amorphous in the as-deposited state. The highest mobility is obtained after crystallization at 150-200 °C

Reported in papers using Oxford Instruments tools

Thermal ALD using InCp and a mixture of H_2O and O_2 gas in OpAL at Eindhoven University of Technology (TU/e). Although the ALD process can actually be performed at higher temperatures, the best results are obtained by growing at 100 °C and subsequently annealing at a modest temperature (150-200 °C).

Macco et al., *Phys. Status Solidi RRL* **8**, 987 (2014) http://dx.doi.org/10.1002/pssr.201409426
Macco et al., *ACS Appl. Mater. Interfaces* **7**, 16723 (2015) http://dx.doi.org/10.1021/acsami.5b04420



Crystallisation leads to large grains, but because of minimal volume change still smooth films.

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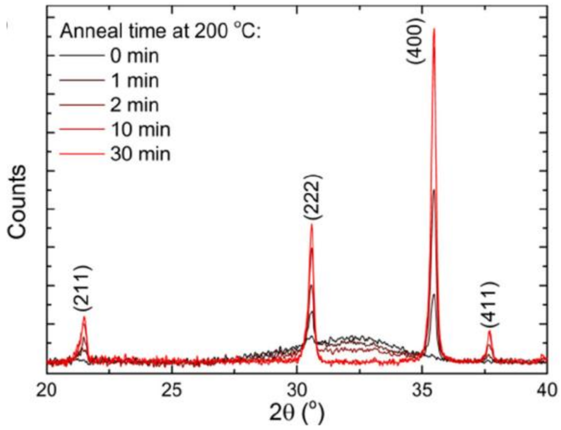
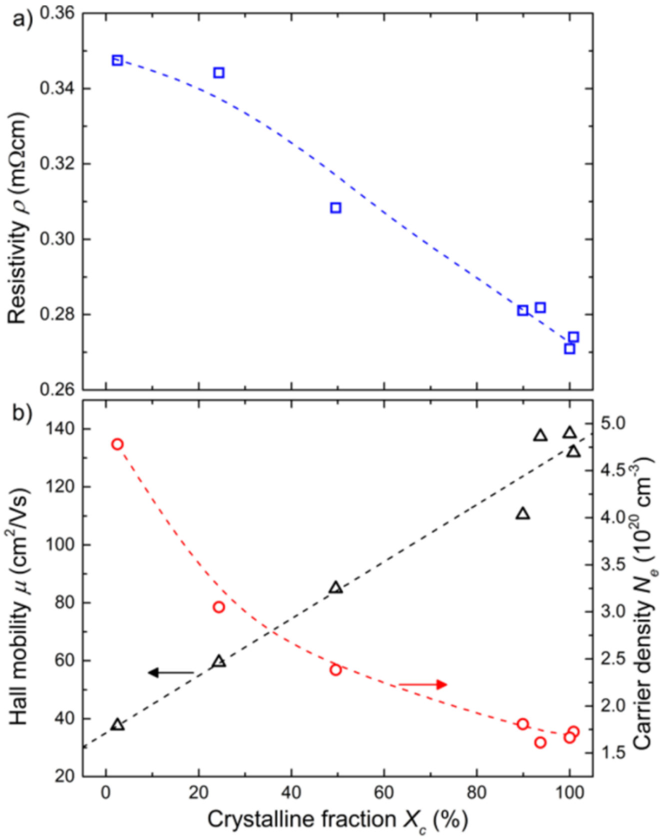


A short anneal provides highly crystalline films



With crystallization a strong increase in mobility occurs leading to lower resistivity values (down to 0.27 mOhm cm)

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Li

Li_2CO_3

Based on customer results

Precursor - properties	LiO^{t}Bu – solid carrier gas assisted @ 140°C
Non-metal precursors	H_2O/CO_2 thermal, O_2 plasma
Temperature range	50 °C - 300 °C
Growth rate per cycle	0.60 Å/cycle (thermal), 0.82 Å/cycle (plasma) @ 150 °C

Reported in papers using Oxford Instruments tools

Thermal and plasma ALD using LiO^{t}Bu and a mixture of H_2O and CO_2 gas for thermal ALD and pure O_2 plasma for plasma ALD in FlexAL at Eindhoven University of Technology (TU/e).

Hornsveld et al., *RSC Adv.* **7**, 41359 (2017)
http://dx.doi.org/10.1039/c7ra07722j

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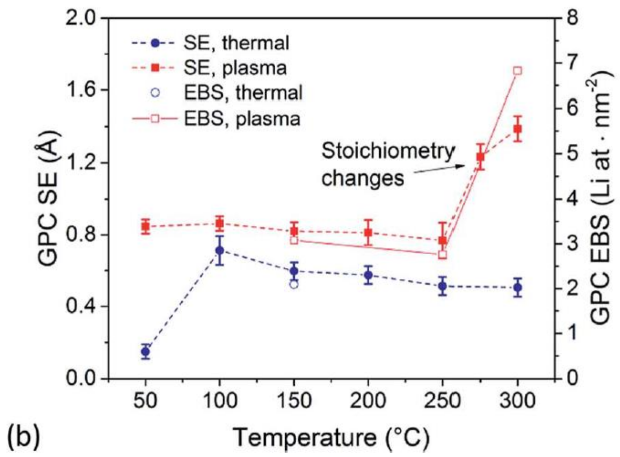
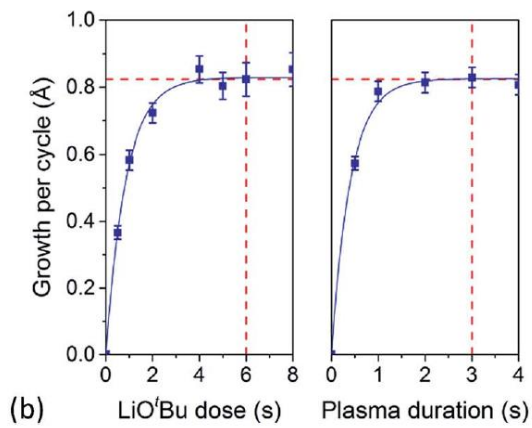


Wide temperature window for both thermal and plasma ALD



ALD behaviour for both precursor and plasma dose

Table 2 Properties of ~50 nm films fabricated using the standard thermal ALD process at 150 °C and plasma ALD process at 150, 250 and 300 °C. The growth per cycle in terms of atoms per nm^2 and the atomic percentages where determined by EBS and ERD. The mass density was obtained by combining EBS and SE results. In the first row the typical error is given for a certain parameter

Sample	GPC (at. per nm^2)	[Li] (at%)	[C] (at%)	[O] (at%)	[H] (at%)	Mass density (g cm^{-3})
Thermal 150 °C	2.09 ± 0.1	33.4 ± 1.7	14.6 ± 0.8	50.7 ± 2.0	1.3 ± 0.2	1.95 ± 0.20
Plasma 150 °C	3.08	32.7	15.1	49.6	2.6	2.06
Plasma 250 °C	2.76	30.5	15.8	50.9	2.8	1.97
Plasma 300 °C	6.83	30.9	13.3	44.7	11.1	n.a.

Li_2CO_3 composition at most temperatures, for plasma ALD at 300 °C material goes towards Li_2O/LiOH

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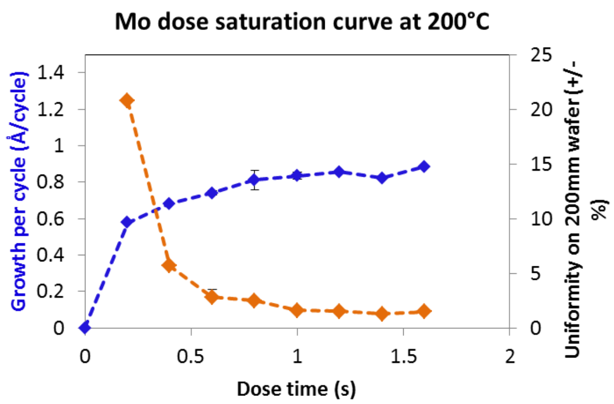
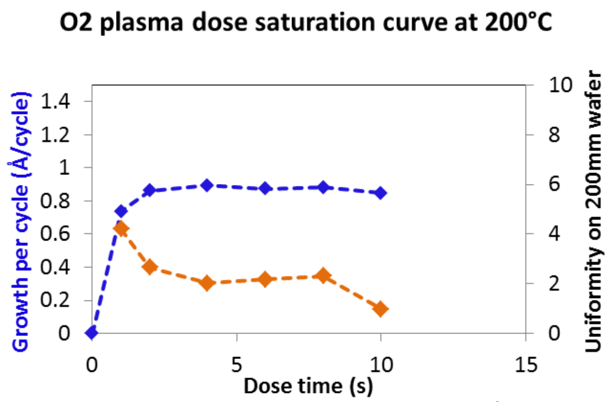
Mo MoO$_3$

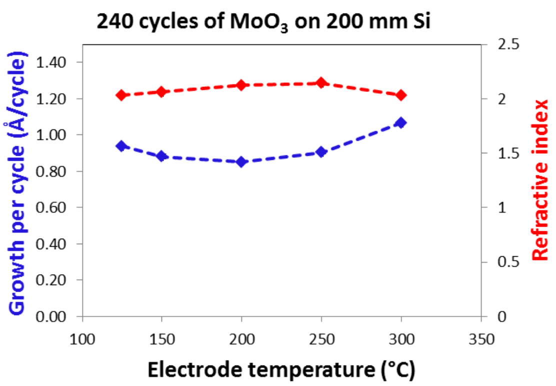
Precursor - properties	$(^tBuN)_2Mo(NMe_2)_2$ – liquid bubbled @ 80°C
Non-metal precursors	O_2 plasma
Temperature range	50 °C - 350 °C
Growth rate per cycle	0.85 Å/cycle @ 200 °C
Deposition rate	0.46 nm/min @ 200°C
Refractive index	>2.03 for >17 nm film measured at 632.8 nm wavelength
Uniformity	± 1.5% over 100, ± 2.0% over 150mm, ± 3.0% over 200mm
RMS Roughness	187 pm for 46 nm film



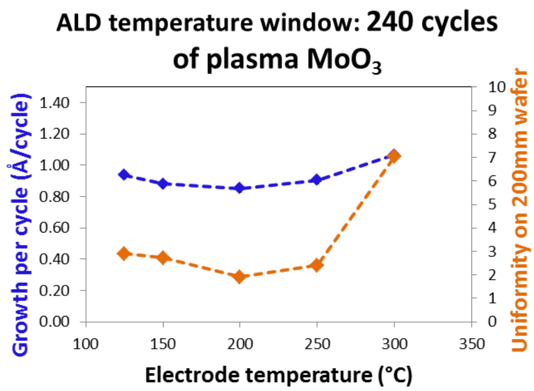
ALD behaviour and good uniformity in saturation



Fast plasma saturation and good uniformity



Wide temperature window



Wide temperature window, possible CVD at high T, although could be crystallization

Reported in papers using Oxford Instruments tools

Ziegler et al., *Appl. Phys. A* **120**, 811 (2015)
http://dx.doi.org/10.1007/s00339-015-9280-3

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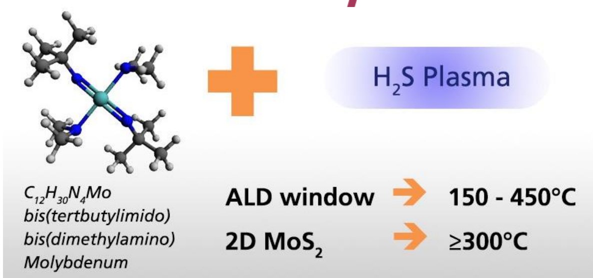
Mo — MoS_2

Based on customer results

Precursor - properties	$(^tBuN)_2Mo(NMe_2)_2$ – liquid bubbled @ 50°C
Non-metal precursors	$H_2S + H_2$ + Ar plasma mixture
Temperature range	150 °C - 450 °C
Growth rate per cycle	1.0 Å/cycle @ 250 °C
Crystallinity	2D MoS_2 material >300 °C, grain size (few to 10s of nm range) and plane orientation depending on conditions
Composition	Negligible oxygen and carbon (<2% by XPS)
Monolayer signature	Confirmed by Raman and photoluminescence for 10 cycles ALD

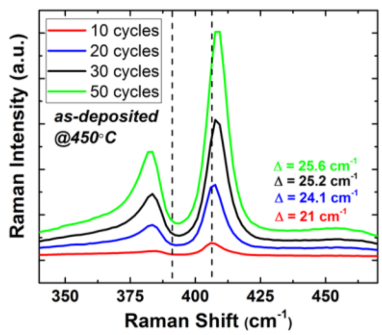
Oxford Instruments' ALD and 2D technical specialists have teamed up with Eindhoven University of Technology research teams to develop the innovative FlexAL-2D for atomic layer deposition (ALD) of 2D transition metal dichalcogenides for nanodevice applications.

TU/e Technische Universiteit Eindhoven University of Technology



The FlexAL-2D ALD system offers a number of benefits for growth of 2D materials:

- 2D materials growth:
  - At CMOS compatible temperatures
  - With precise digital thickness control
  - Over a large area (200mm wafers)
- Growth of ALD dielectrics & other ALD layers on 2D materials in one tool
- H_2S plasma and H_2S gas dosing for ALD and sulfurization and surface treatments
- Load-lock and turbo-pump for clean growth and working conditions
- High temperature table (RT-600 °C)
- Plasma cleaning and conditioning of chamber
- RF substrate biasing option for further process flexibility
- In situ process monitoring option using spectroscopic ellipsometry and mass spectrometry



Increasing Raman peak separation (Δ) as a function of number of layers. At 10 cycles monolayer signature

2D MoS_2 films with tuneable morphologies can be synthesized i.e. in-plane and vertically standing nano-scale architectures. The 2D in-plane morphology has potential applications in nanoelectronics, while the 3D fin structures are ideal for catalysis applications such as water splitting.

Reported in papers using Oxford Instruments tools

Supporting data is submitted for publication.

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Nb

NbN

Based on customer results

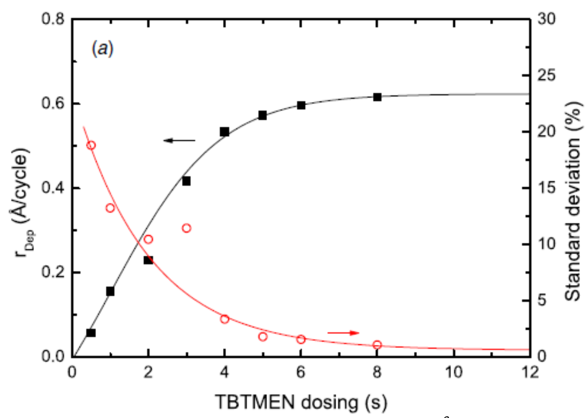
Precursor - properties	TBTDEN or TBTMEN
Non-metal precursors	H_2 plasma
Temperature range	250°C
Growth rate per cycle	0.6 Å/cycle @ 250°C
Deposition rate	0.1nm/min @ 250°C (for low resistivity values)
Resistivity	~ 900μΩcm @ 250 °C (low pressure)

Reported in papers using Oxford Instruments tools

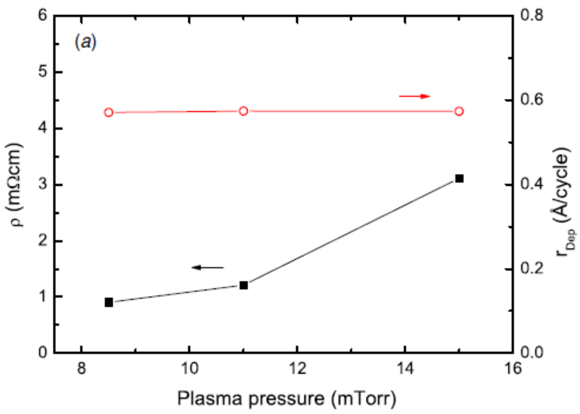
ALD of NbN using TBTMEN precursor and H_2 plasma at 250 °C in FlexAL at Fraunhofer Institute for Integrated Systems and Device Technology (IISB). Stoichiometric carbon-free NbN was obtained.

Hinz et al., *Semicond. Sci. Technol.* **25**, 075009 (2010) http://dx.doi.org/10.1088/0268-1242/25/7/075009

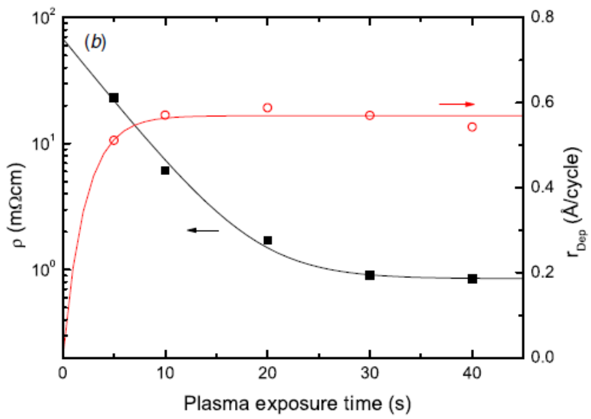
Fraunhofer
IISB



TBTMEN dose saturation at 0.6Å/cyc



Influence of plasma pressure on resistivity. The minimum resistivity value of 905 μΩcm was achieved at a pressure of 8.5mTorr.



Saturation with respect to plasma exposure time

Other relevant papers:

Ziegler et al., *Supercond. Sci. Technol.* **26**, 025008 (2013)
http://dx.doi.org/10.1088/0953-2048/26/2/025008

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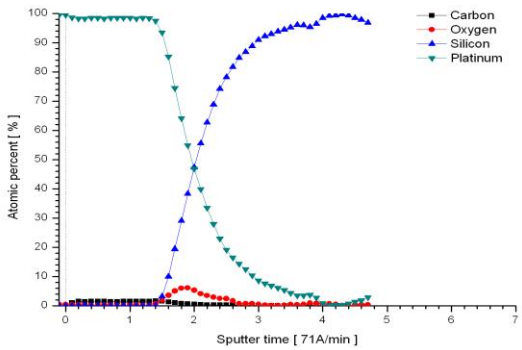
Pt

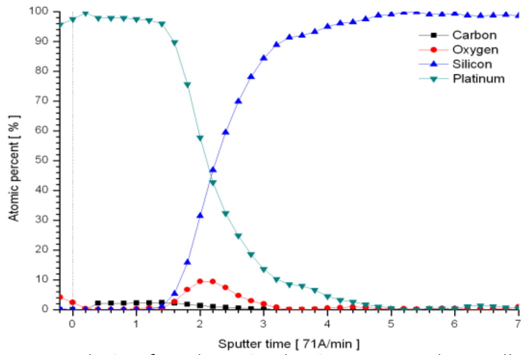
Precursor - properties	MeCp-Pt-Me3 – liquid vapour draw @ 70°C
Non-metal precursors	O_2 (thermal and plasma)
Temperature range	30°C* - 300°C (plasma), 225°C - 300°C (thermal) *below 200°C by adding H_2 gas step in cycle, below 100°C by H_2 plasma step in cycle (80°C - 300°C for OpAL)
Growth rate per cycle	0.45 Å/cycle @ 300°C
Deposition rate	0.18nm/min @ 300°C
Resistivity	< 20 μΩcm @ 300°C (for 20nm)
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm

200mm data for FlexAL only

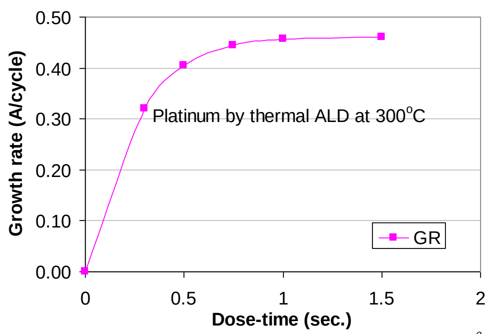
Thermal Pt nucleation difficult at temperatures below 300 °C, at these temperatures plasma ALD which nucleates easily can be used to grow a seed layer for subsequent thermal process. At lower temperatures, PtO_2 formation becomes the energetically favourable process. H_2 gas/plasma can reduce PtO_2 and lowers achievable temperature range of Pt deposition down to room temperature.



AES analysis of Pt deposited using O_2 plasma



AES analysis of Pt deposited using O_2 gas thermally



MeCpPtMe$_3$ saturation for thermal Pt at 0.45 Å/cyc

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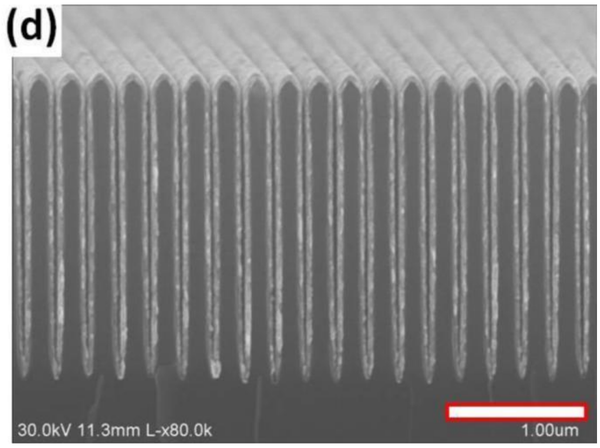
Reported in papers using Oxford Instruments tools

Thermal ALD using $MeCpPtMe_3$ and O_2 gas in FlexAL at NIST Center for Nanoscale Science and Technology.

Kaplan et al., *ACS Photonics* **1**, 554 (2014) http://dx.doi.org/10.1021/ph500018b

Vaish et al., *J. Vac. Sci. Technol. A* **33**, 01A148 (2015) http://dx.doi.org/10.1116/1.4904398

NIST
National Institute of Standards and Technology



Conformal coating of 20 nm Pt in 75 nm by 2.5 mm trench (AR 33 to 71 after coating)

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Ru

Recommended precursor: $Ru(EtCp)_2$

Best results are expected either by using an ABC process doing an O_2 plasma dose followed by a dose of H_2 plasma or gas in the cycle, or by following the approach from KAUST below, where a small continuous diluted flow of O_2 is present.

Reported in papers using Oxford Instruments tools

Plasma ALD using $CpRu(CO)_2Et$ and O_2 plasma in FlexAL at Eindhoven University of Technology (TU/e).

Leick et al., *J. Vac. Sci. Technol. A* **29**, 021016 (2011) http://dx.doi.org/10.1116/1.3554691
Leick et al., *Chem. Mater.* **24**, 3696 (2012) http://dx.doi.org/10.1021/cm301115s

TU/e Technische Universiteit Eindhoven University of Technology

RuO_2

Plasma ALD using $Ru(EtCp)_2$ and O_2 plasma in FlexAL at King Abdullah University of Science and Technology (KAUST)

Xia et al., *Adv. Energy Mater.* **5**, 1401805 (2015) http://dx.doi.org/10.1002/aenm.201401805

KAUST

The temperature of precursor was maintained at 75 °C. Substrate table at 180 °C. An optimization of an early reported modified ALD process was adopted in which a continuous Ar gas diluted oxygen exposure was maintained through all the steps of a standard ALD deposition cycle.

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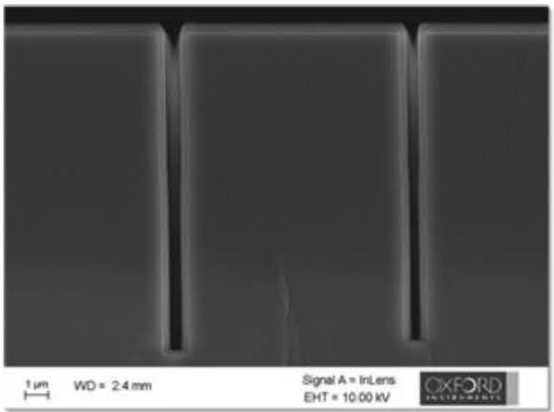
Si

SiO_2

Precursor - properties	BTBAS, BDEAS or 3DMAS
Non-metal precursors	O_2 plasma
Temperature range	30°C - 400°C (50°C - 400°C for OpAL)
Growth rate per cycle	~1.4 Å/cycle @ 300°C
Deposition rate	1.2nm/min @ 300°C
Refractive Index	1.42 – 1.46
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm
Precursor consumption	15nm/g

High-rate process: A higher rate process has been developed (requiring a pressure gauge range up to 1 Torr instead of the standard 250 mTorr) where the speed has increased but most important while maintaining good electrical properties and good uniformity. The process works with Bis(tert-butylimino)silane (BTBAS) and O_2 plasma and yields deposition rate of 1.3 nm/min, see also the table below. Also the conformality is still good (conformal coating of high aspect ratio (15:1) structure) with SiO_2 deposited using the high rate process, see image below.

High Rate SiO_2 PEALD Process	
V_{BD}	>10 MV/cm at 200°C dep. temp.
Cycle time (PEALD)	1.3 nm/min
Thickness uniformity (200mm, 3 mm EE)	< ± 2.6%
Thickness Repeatability	< ± 1.6%
Conformality	> 90% >30:1 AR substrate at 300◦C dep. temp.



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Reported in papers using Oxford Instruments tools

SiO_2 grown by plasma ALD using BDEAS and O_2 plasma at Eindhoven University of Technology.

In OpAL:
Dingemans et al., *J. Electrochem. Soc.* **159**, H277 (2012) http://dx.doi.org/10.1149/2.067203jes
In FlexAL:
Potts et al., *Chem. Vap. Deposition*, **19**, 125 (2013) http://dx.doi.org/10.1002/cvde.201207033

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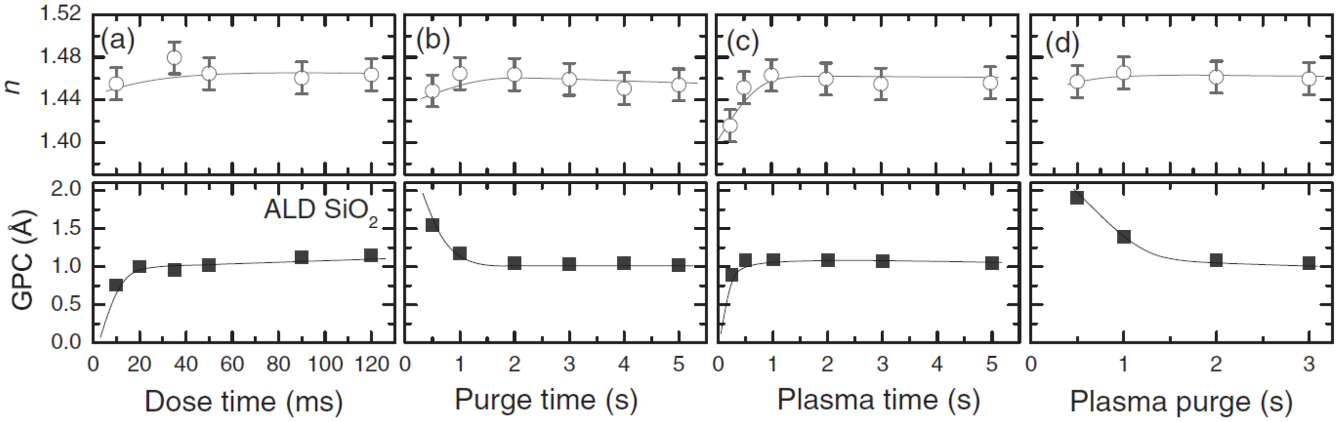
Substrate temperature (°C)	Si atoms per cycle (10^{14} cm^{-2})	[H] (at.%)	O/Si Ratio	Mass density (g/cm^3)
RT*	2.8	8	2.0	1.9
100	2.8	10	2.1	2.0
200	2.3	7	2.1	2.0
300	1.9	8	2.1	2.1

* Oxford FlexAL and longer plasma instead of OpAL reactor

- Similar properties down to room temperature.
- Carbon below detection limit (<5 at.%).



Fast saturation of refractive index and growth per cycle for both precursor and plasma at 250 °C (OpAL).

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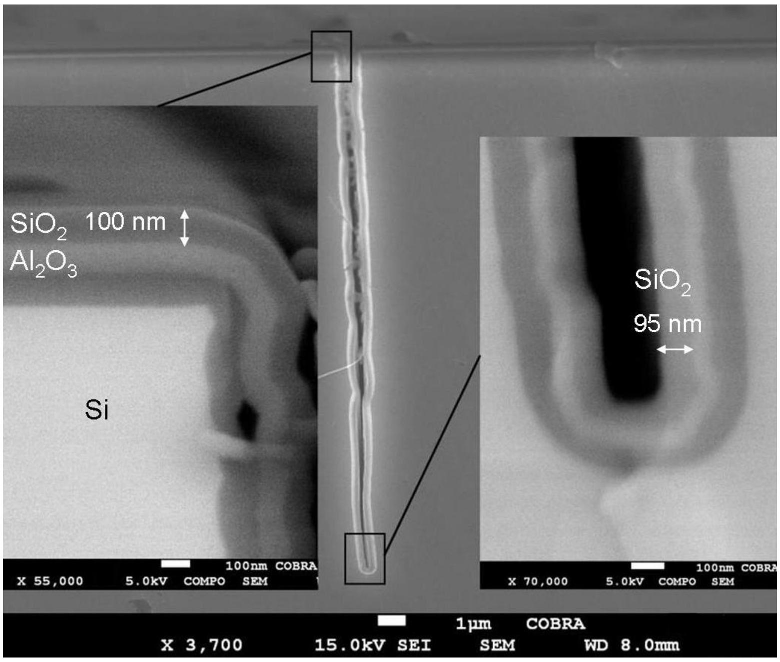
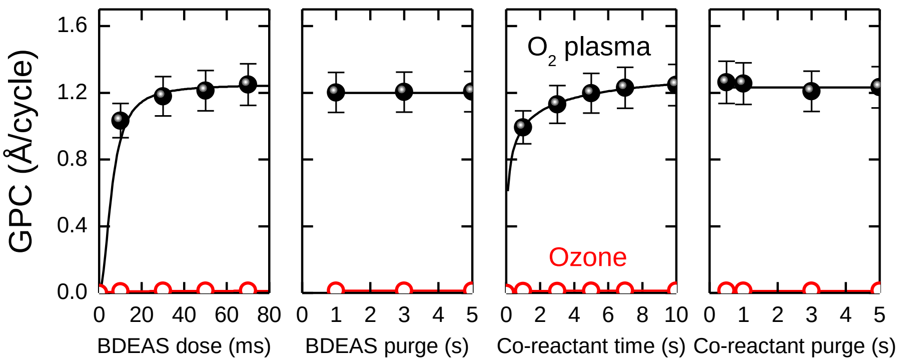


Very high conformality with short cycle time
(90 ms prec. and 4.5 s plasma)



Even fast saturation and short purging at room temperature on FlexAL using O_2 plasma. At these low temperatures ozone is not reactive enough to provide growth.

Other relevant papers:

Usui et al., *Acta Materialia* **61**, 7660 (2013)
http://dx.doi.org/10.1016/j.actamat.2013.09.003

Ratzsch et al., *Optics Express* **23**, 17955 (2015)
http://dx.doi.org/10.1364/OE.23.017955

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Si — Si_3N_4

Precursor - properties	BTBAS, BDEAS, or 3DMAS
Non-metal precursors	N_2 plasma
Temperature range	100°C - 400°C
Growth rate per cycle	0.16 Å/cycle @ 400°C
Deposition rate	0.05 nm/min @ 400°C
Refractive Index	>1.80 @ 100°C >1.90 @ 200°C >1.95 @ 400°C
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm
Precursor consumption	15 nm/g

The literature data has shown Si_3N_4 to be a notoriously difficult ALD process due to the ease of forming Si-O bonds. Oxford Instruments has developed a SiN process with very low oxygen impurities for a SiN film deposited using ALD – this is reflected in the refractive index measurement which is very sensitive to oxygen contamination (lower refractive index means more oxygen contamination in the film).

Special note: the preferential reaction of silicon precursors is always with residual oxygen containing species such as OH groups from background moisture in the system. Consequently this process requires a load lock or nitrogen purged glove box option on the OpAL reactor.

Reported in papers using Oxford Instruments tools

Si_3N_4 grown by plasma ALD using BTBAS and N_2 plasma in FlexAL at Eindhoven University of Technology.

Knoops et al., *Appl. Phys. Lett.* **107**, 014102 (2015) http://dx.doi.org/10.1063/1.4926366
Knoops et al., *ACS Appl. Mater. Interfaces* (2015) http://dx.doi.org/10.1021/acsami.5b06833

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The growth per cycle (GPC), refractive index at 2 eV, and composition of SiN_x films of ~40 nm thickness deposited at various substrate table temperatures and plasma conditions. Typical error margins are indicated for the first value in each column. A dash indicates "not measured". A change in used parameters compared to the first line is indicated in bold.

Table temperature (°C)	Plasma pressure (mTorr)	Plasma time (s)	GPC (Å)	Refractive index	N/Si ratio	XPS [C] at. %	XPS [O] at. %	ERD [H] at. %
200	40	10	0.32 ± 0.02	1.83 ± 0.03	1.7 ± 0.1	9 ± 1	5 ± 1	10.9 ± 0.5
200	40	**15**	0.28	1.86	1.7	8	5	9.6
200	**13**	10	0.24	1.91	1.6	6	5	-
400	40	10	0.16	1.96	1.5	2	4	5.4

Best material properties at higher temperatures, lower plasma pressures and longer plasma times.

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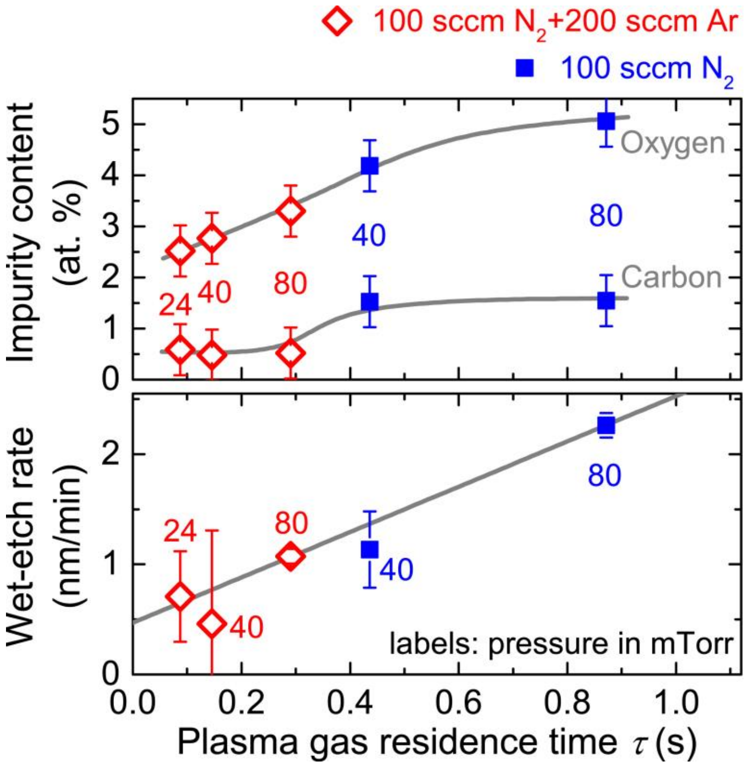
Better material can be achieved by using conditions with short residence time (high gas flows and low pressures). Gas residence time ***τ*** is the time that species reside in the reactor.

Shorter residence times (figure on the right):
→ lower O and C levels
→ lower wet-etch rates



Plasma ALD of SiN_x using TSA and N_2 plasma and 3DMAS and N_2 plasma at 250 °C and also studies of post-deposition anneals in H_2 plasma.

Provine et al., *AIP Advances* **6**, 065012 (2016)
http://dx.doi.org/10.1063/1.4954238

Stanford University

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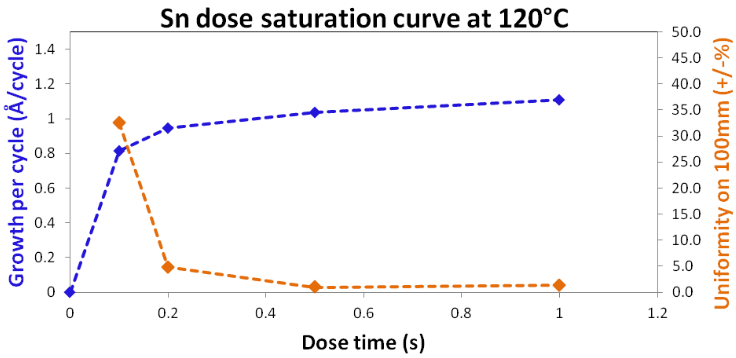
Sn

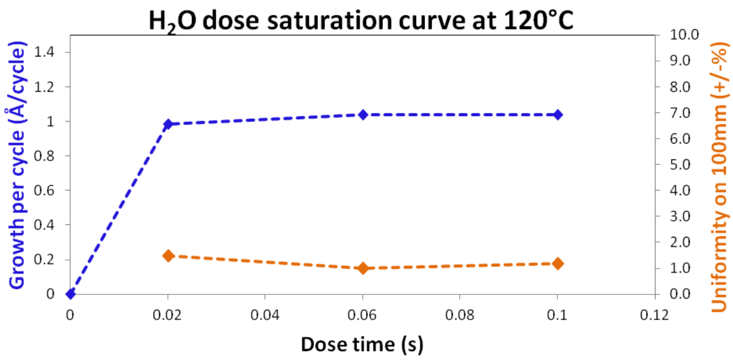
SnO_2

Precursor - properties	TDMASn - liquid vapour draw @ 60°C
Non-metal precursors	H_2O thermal, O_2 plasma
Temperature range	120°C - 200°C
Growth rate per cycle	1.0 Å/cycle @ 120°C
Deposition rate	0.29nm/min @ 120°C
Refractive Index	>1.80 @ 120 °C for 10 nm thick film
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm

Tin oxide (SnO_2) ALD has been developed at 120 °C on the OpAL system and an optimized recipe was established. SnO_2 can be off interest as a transparent conductive oxide for optoelectronic applications (e.g., solar cells) or as dopant in such layers.



Fast saturation of precursor dose and good uniformity achieved.



Fast saturation of water dose and good uniformity achieved.

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Sr SrTiO$_3$

Precursor - properties	StarTi, HyperSr
Non-metal precursors	O_2 (plasma)
Temperature range	300°C
Growth rate per cycle	0.45 Å/cycle @ 300°C

Strontium titanate is an ultra-high-k dielectric (k=80 – 100). Ru is commonly used as a compatible electrode.

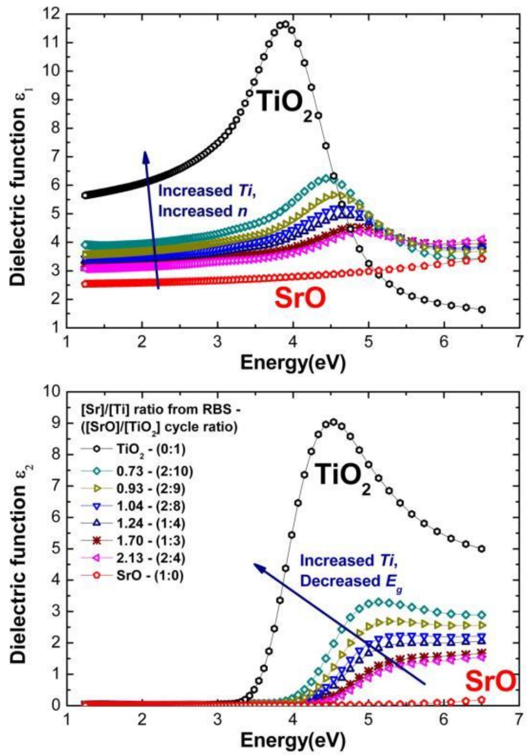
Reported in papers using Oxford Instruments tools

STO grown by plasma ALD using StarTi, HyperSr and O_2 plasma in FlexAL at Eindhoven University of Technology.

Longo et al., *ECS J. Solid State Sci. Technol.* **2**, N15 (2013) http://dx.doi.org/10.1149/2.024301jss
Longo et al., *ECS J. Solid State Sci. Technol.* **2**, N120 (2013) http://dx.doi.org/10.1149/2.016305jss
Aslam et al., *Phys. Status Solidi A* **211**, 389 (2014) http://dx.doi.org/10.1002/pssa.201330101
Aslam et al., *J. Appl. Phys.* **116**, 064503 (2014) http://dx.doi.org/10.1063/1.4891831

Technische Universiteit Eindhoven University of Technology

- STO composition tuned by [SrO]/[TiO$_2$] ALD cycle ratio.
- Stoichiometry determined by Spectroscopic Ellipsometry.
- Pt/STO/Pt capacitors for high-k demonstrated (CET ~ 0.7 nm) by FZ Juelich.



In situ ellipsometry can be used to monitor the change in optical properties

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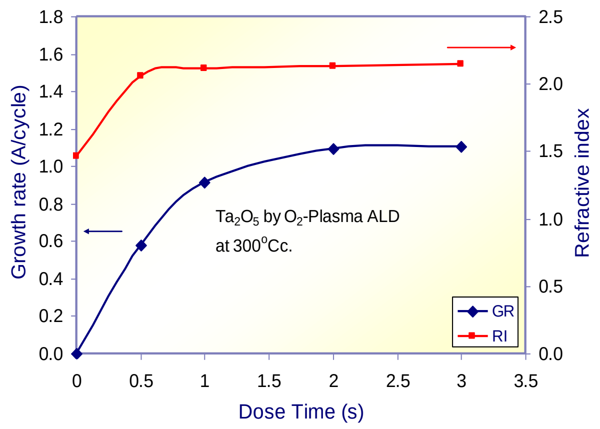
Ta — Ta_2O_5

Precursor - properties	TBTDMT - *t-butylimido tris(dimethylamido)tantalum* - liquid bubbled @ 50°C
Non-metal precursors	O_2 plasma or H_2O thermal
Temperature range	100°C - 300°C
Growth rate per cycle	1 Å/cycle @ 300°C
Deposition rate	0.6nm/min @ 300°C
Refractive Index	1.95 - 2.15
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm

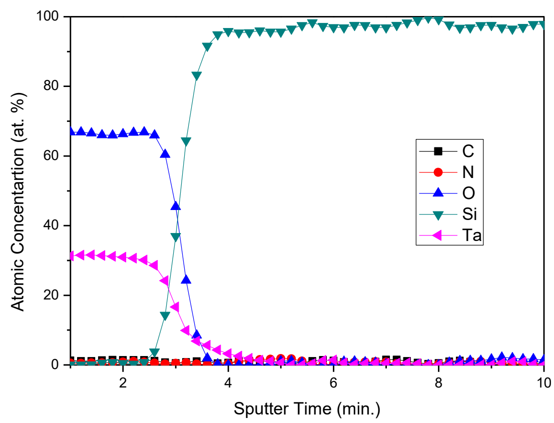
200mm data for FlexAL only

Results:

- Low impurities < 2%@ 300°C



Precursor saturation



AES analysis of Ta_2O_5 film with impurities below detection limit

Reported in papers using Oxford Instruments tools

Plasma ALD using TBTDMT and O_2 plasma at 300 °C in FlexAL at OIPT.
Fang et al., *Physics Procedia* **32**, 379 (2012)
http://dx.doi.org/10.1016/j.phpro.2012.03.572

Plasma ALD using PDMAT and O_2 plasma at 25–250 °C in FlexAL at Eindhoven University of Technology.
Potts et al., *J. Electrochem. Soc.* **157**, P66 (2010)
http://dx.doi.org/10.1149/1.3428705

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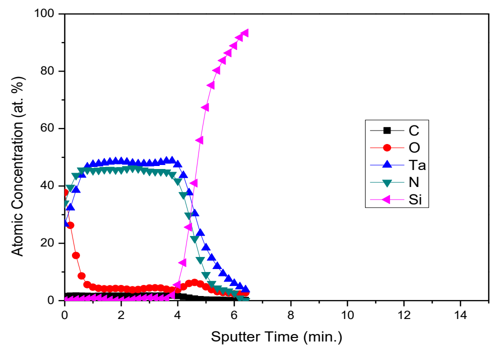
Ta TaN

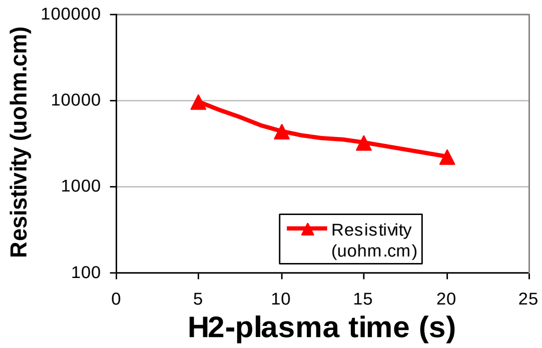
Precursor - properties	TBTDMT - *t-butylimido tris(dimethylamido)tantalum* - liquid bubbled @ 60°C
Non-metal precursors	H_2 plasma, N_2/H_2 plasma or NH_3 plasma
Temperature range	250 - 350°C
Growth rate per cycle	0.42 Å/cycle @ 350°C
Deposition rate	0.25nm/min @ 350°C for insulating phase
Resistivity	< 1000μΩcm @ 350°C (for long and low pressure plasma) < 300 μΩcm (with a RF biased electrode)
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm

200mm data for FlexAL only

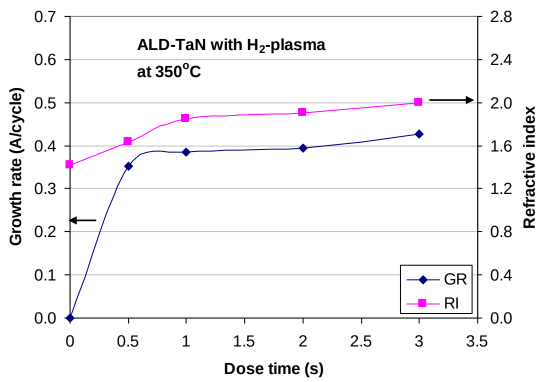
Pure H_2 plasma gives TaN conductive phase, all others give Ta_3N_5 insulating phase.



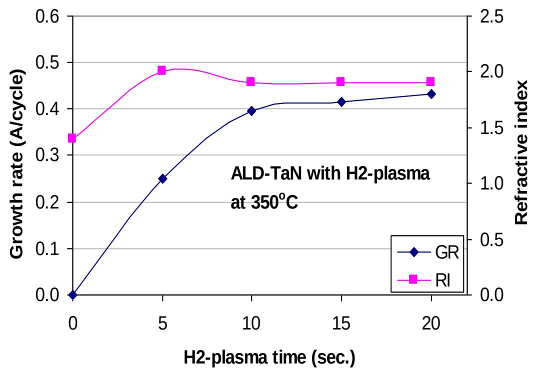
AES analysis of TaN deposited using H_2 plasma



Resistivity versus hydrogen plasma exposure time



GPC and RI against TBTMET dose time



GPC and RI against H_2 plasma time

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Reported in papers using Oxford Instruments tools

Precursor adsorption study using PDMAT in FlexAL at Cornell NanoScale Facility.

Hughes et al., *J. Phys. Chem. C* **116**, 21948 (2012)
http://dx.doi.org/10.1021/jp3086232

Thermal ALD using PDMAT and ammonia or monomethylhydrazine in OpAL at University of Liverpool.

Fang et al., *Journal of Crystal Growth* **331**, 33 (2011)
http://dx.doi.org/10.1016/j.jcrysgro.2011.07.012

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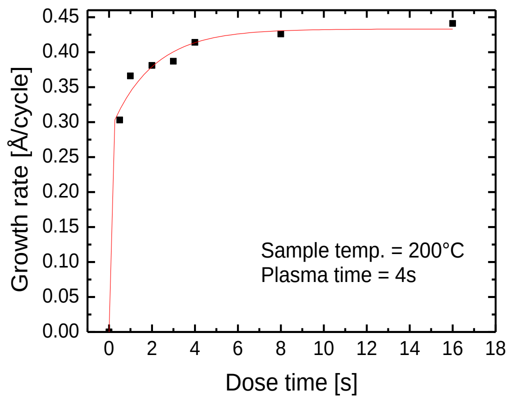
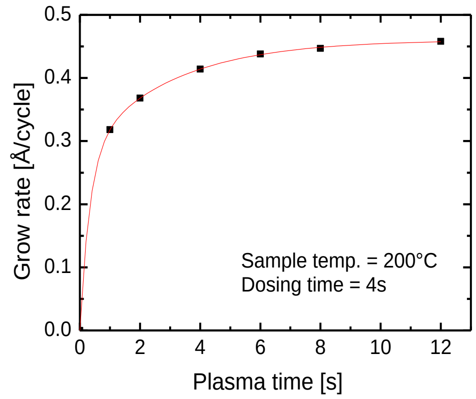
Ti — TiO_2

Precursor - properties	TTIP or TDMAT
Non-metal precursors	H_2O thermal, O_2 plasma
Temperature range	30°C - 300°C (80°C - 300°C for OpAL)
Growth rate per cycle	~0.55 Å/cycle @ 200°C
Deposition rate	0.35nm/min @ 200°C
Refractive Index	2.2 – 2.4
Uniformity	± 1.5% over 100, ± 2.0% over 150mm, ± 3.0% over 200mm

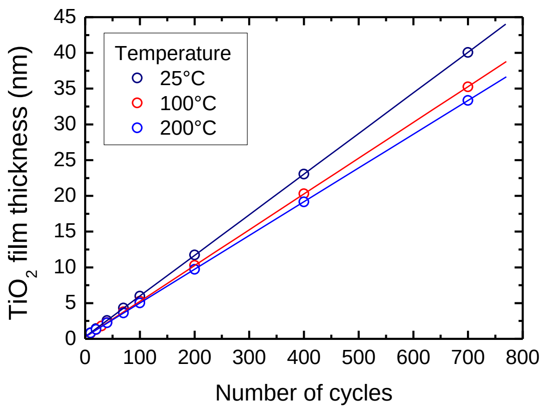
Saturation curves:



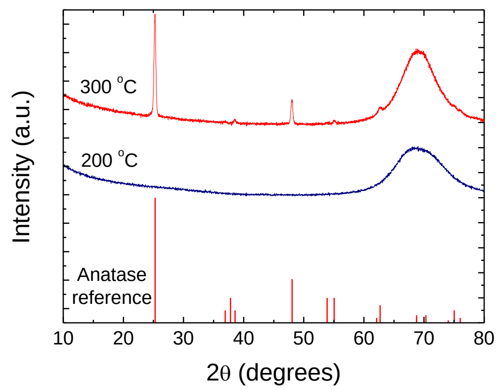
saturation curve for TTIP @ 200°C



saturation curve for O_2 plasma



linear growth regime down to room temperature



XRD analysis showing TiO_2 is amorphous @ 200°C and anatase @ 300°C.

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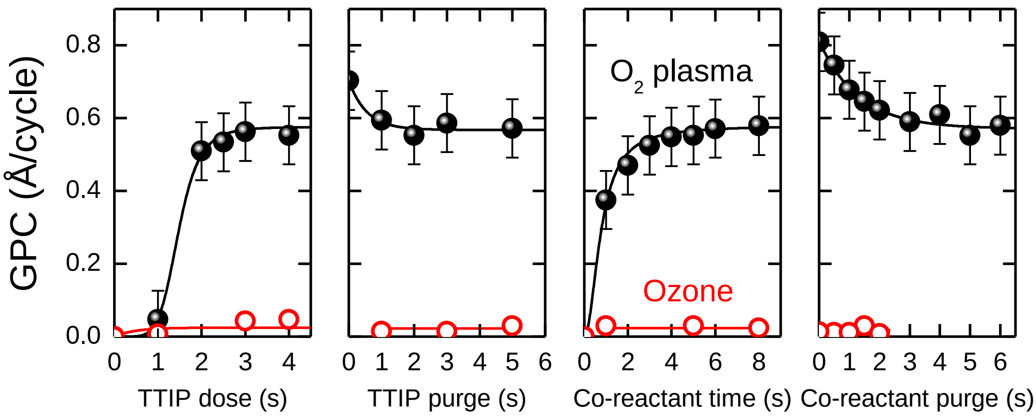
Reported in papers using Oxford Instruments tools

Plasma ALD using TTIP, $Ti(Cp^{Me})O^iPr_3$, $TiCp^*(OMe)_3$ and O_2 plasma at 25–400 °C in FlexAL at Eindhoven University of Technology.

Potts et al., *J. Electrochem. Soc.* **157**, P66 (2010) http://dx.doi.org/10.1149/1.3428705
Potts et al., *Chem. Vap. Deposition*, **19**, 125 (2013) http://dx.doi.org/10.1002/cvde.201207033

Technische Universiteit Eindhoven University of Technology

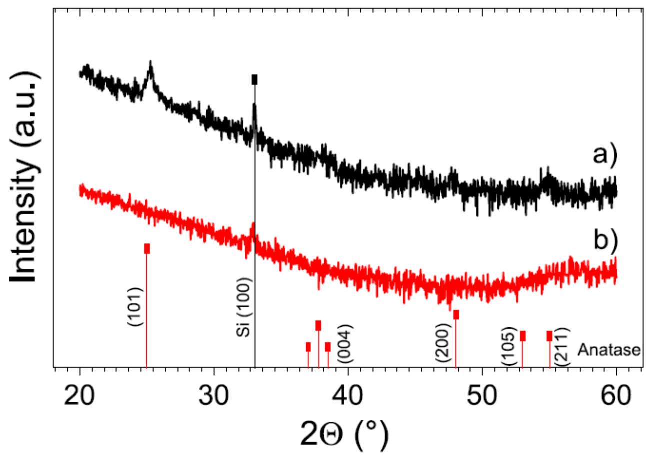


Fast saturation of plasma process in FlexAL even at room temperature.

Thermal ALD using TDMAT and H_2O at 200 °C on gold nanorods in FlexAL at UC Santa Barbara. As a pretreatment, prior to ALD deposition, the gold nanorods were subjected to an O_2 plasma treatment for 2 min at 100 W.

Mubeen et al. *ACS Nano*, **8**, 6066 (2014) http://dx.doi.org/10.1021/nn501379r

UCSB



Control of crystallinity at 100 °C by changing ion energy via the plasma pressure. TiO_2 films grown at ~40 mTorr (a) and ~140 mTorr (b) plasma pressures at 300W.

Plasma and thermal ALD using TTIP and O_2 plasma or H_2O in OpAL in Jena.

Ratzsch et al., *Nanotechnology* **26,** 024003 (2015) http://dx.doi.org/10.1088/0957-4484/26/2/024003

Friedrich-Schiller-Universität

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Ti

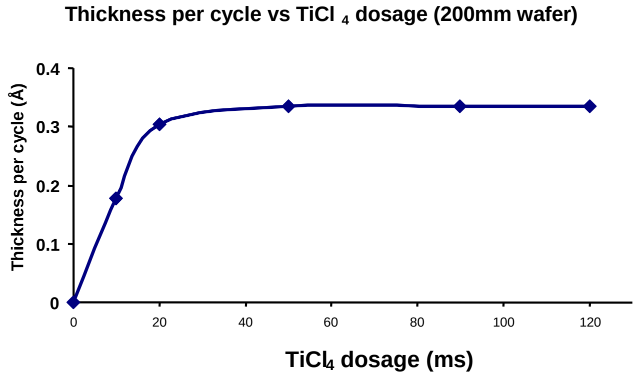
TiN

Recommended precursor $TiCl_4$ for lowest resistivity or TDMAT for low resistivity and best compatibility with metal-organic precursors.

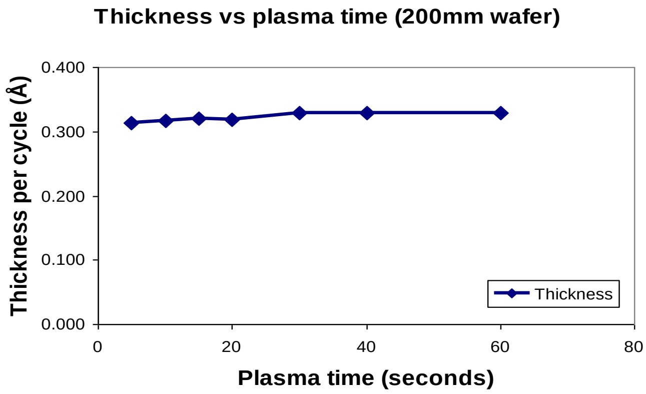
Precursor - properties	$TiCl_4$ – liquid vapour draw @ 30°C
Non-metal precursors	N_2/H_2 plasma, NH_3 thermal
Temperature range	100 - 350°C (plasma) – 550°C (thermal)
Growth rate per cycle	0.35 Å/cycle @ 350°C
Deposition rate	0.13nm/min @ 350°C
Resistivity	< 150 µΩcm @ 350 °C (for long and low pressure plasma) < 100 µΩcm @ 550 °C (for long and low pressure plasma)
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm

200mm data for FlexAL only

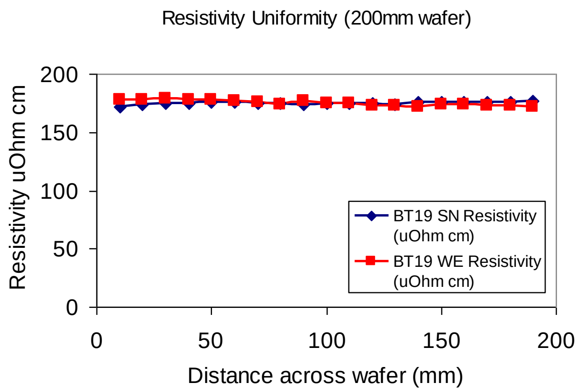
Saturation curves:



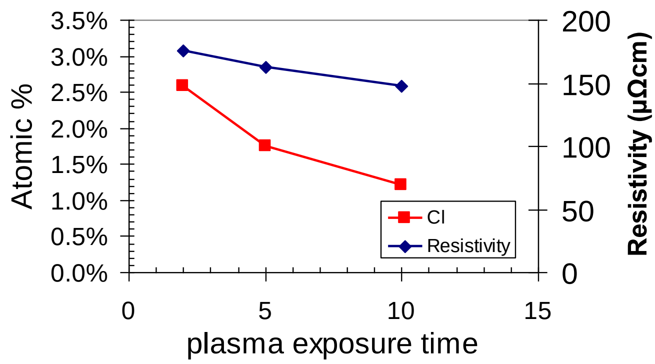
$TiCl_4$ saturation curve.



N_2/H_2 plasma exposure saturation curve for 350°C deposition temperature.



Excellent resistivity uniformity of ±1.8% over a 200mm wafer (<±4% specification).



RBS measurement of chlorine contamination as a function of plasma exposure time plotted on the same graph as resistivity. Deposition temperature was 350°C.

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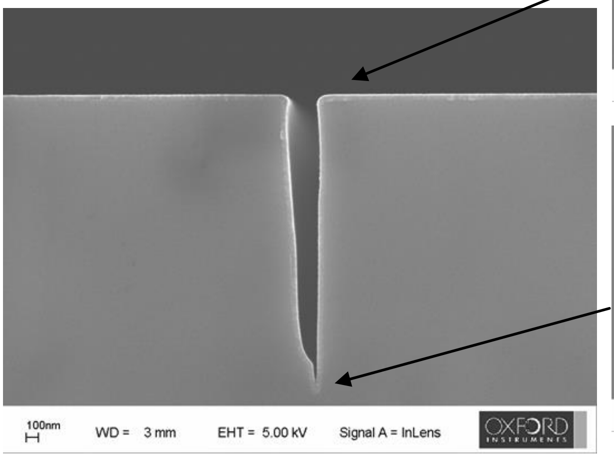
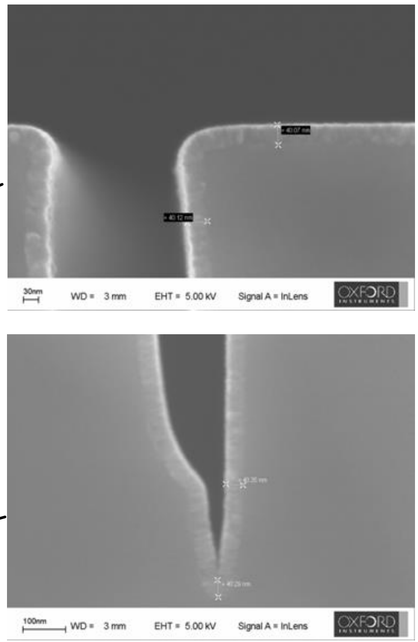
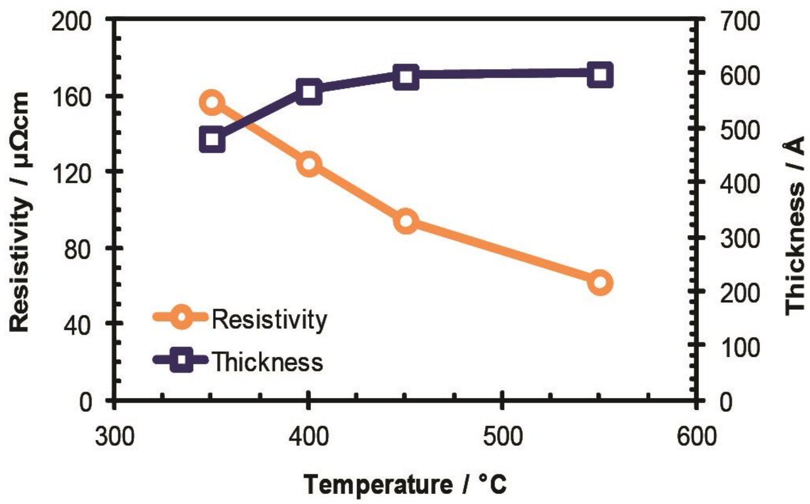
The main impurity in TiN films deposited by $TiCl_4$ is chlorine. By increasing the plasma exposure time the H_2 plasma more effectively removes the chlorine impurities as HCl. This reduction in chlorine impurities results in a corresponding drop in resistivity. The resistivity at 350°C is approximately 175μΩcm, and in order to achieve such low resistivity using thermal ALD would require a deposition temperature in excess of 550°C.

Conformal TiN coating of 40nm in deep trench with increasing aspect ratio by remote plasma ALD.







62 μΩcm achieved at 550 °C for 60 nm film. Higher degree of crystallinity (surface roughness of 3.3 nm).

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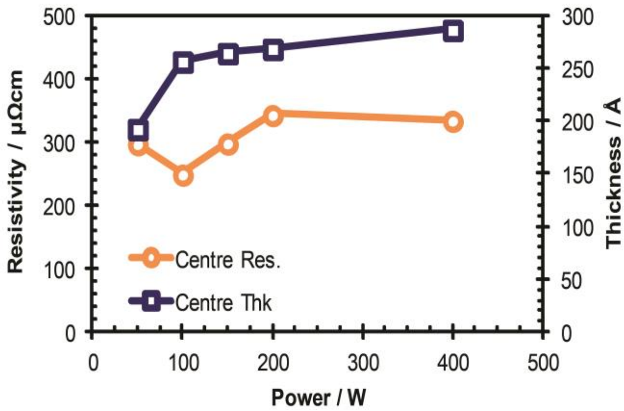
Non-chlorine alternative

Precursor - properties	TDMAT – liquid bubbled @ 60°C
Non-metal precursors	N_2/H_2 plasma, NH_3 thermal
Temperature range	100 - 350°C
Growth rate per cycle	~0.5 Å/cycle @ 200°C
Deposition rate	0.23nm/min @ 200°C
Resistivity	< 300 µΩcm @ >200 °C (for long and low pressure plasma)
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm

200mm data for FlexAL only

Note that even though 350 °C is reportedly above the decomposition temperature of TDMAT, the process results in uniform high-quality films. For thick film (74 nm) also low resistivity of 184 µΩcm obtained at 200 °C.



Plasma properties for low resistivity TiN are optimal at 100 W plasma power. Even though the ion flux would be lower at this power, the ion energy is higher and could be essential in achieving high conductivity.

Reported in papers using Oxford Instruments tools

Plasma ALD using $TiCl_4$ and H_2/N_2 plasma at 150–400 °C in FlexAL at Eindhoven University of Technology.
Heil et al., *J. Vac. Sci. Technol. A* **25**, 1357 (2007) http://dx.doi.org/10.1116/1.2753846
Hoogeland et al., *J. Appl. Phys.* **106**, 114107 (2009) http://dx.doi.org/10.1063/1.3267299

Plasma ALD using $TiCl_4$ and H_2/N_2 plasma at 140 °C in OpAL at Jet Propulsion Laboratory.
Jang et al., *Nature Materials* **12**, 893 (2013) http://dx.doi.org/10.1038/nmat3738

Plasma ALD using TDMAT and H_2/N_2 plasma at 200-300 °C in OpAL at Massachusetts Institute of Technology.
Brennan et al., *J. Appl. Phys.* **118**, 045307 (2015) http://dx.doi.org/10.1063/1.4927517

Other relevant papers:

Knoops et al., *J. Electrochem. Soc.* **155**, G287 (2008) http://dx.doi.org/10.1149/1.2988651
Nelson-Fitzpatrick et al., *J. Vac. Sci. Technol. A* **31**, 021503 (2013) http://dx.doi.org/10.1116/1.4790132
Coumou et al., IEEE Trans. Appl. Supercon. **23**, 7500404 (2013) http://dx.doi.org/10.1109/TASC.2012.2236603

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W — WO_3

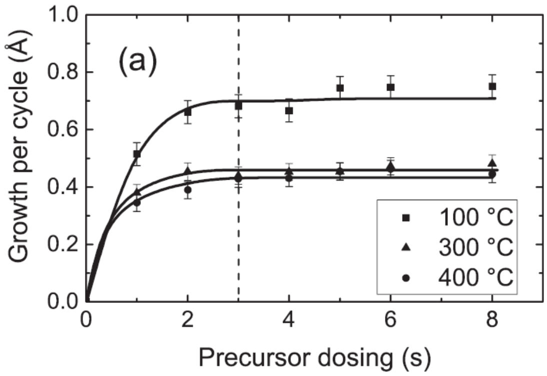
Precursor - properties	WNBURE $(^tBuN)_2W(NMe_2)_2$ – liquid bubbled @ 50°C
Non-metal precursors	O_2 plasma
Temperature range	50 °C - 350 °C
Growth rate per cycle	0.47 Å/cycle @ 300°C
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm

Reported in papers using Oxford Instruments tools

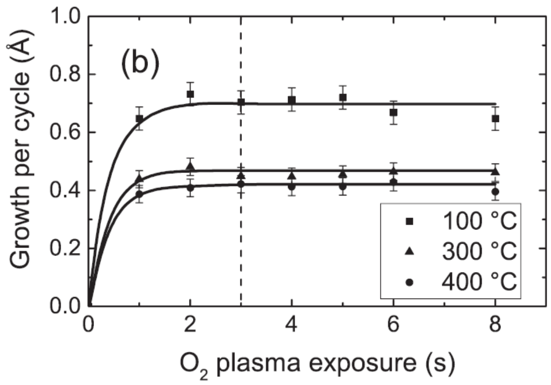
ALD using $(^tBuN)_2W(NMe_2)_2$ and O_2 plasma in FlexAL at Eindhoven University of Technology.

Technische Universiteit Eindhoven University of Technology

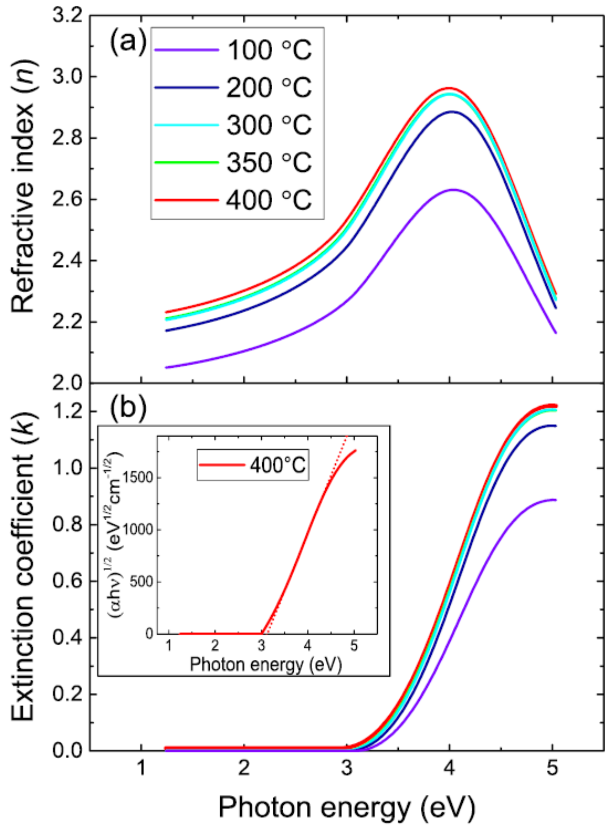
Balasubramanyam et al., *J. Vac. Sci. Technol. A* 36, 01B103 (2018)
http://dx.doi.org/10.1116/1.4986202



Growth per cycle (GPC) as a function of precursor dosing time showing fast saturation even at low temperature.



Growth per cycle (GPC) as a function of plasma exposure time showing saturation at all temperatures.



Optical properties of WO_3 films showing high refractive index and low absorption.

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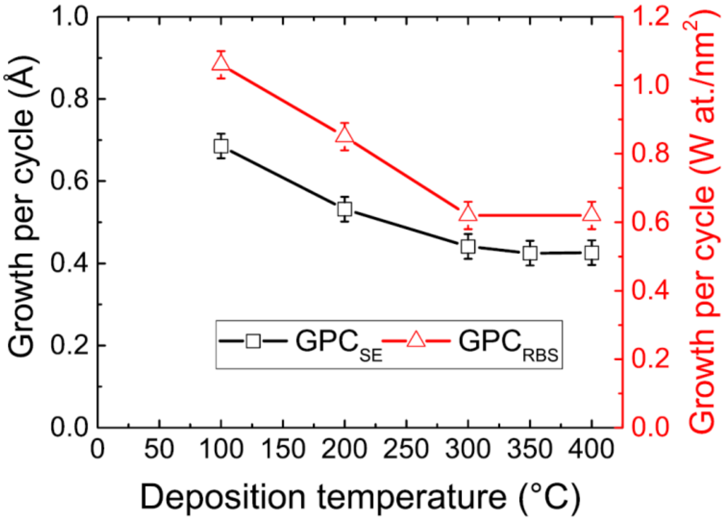
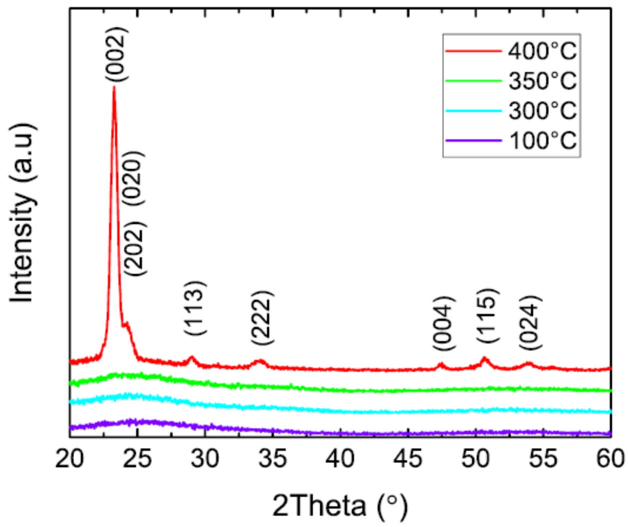


GPC as a function of temperature both in terms of thickness and number of W atoms per cycles both showing a wide temperature window.



GI-XRD diffractogram. For the WO_3 film deposited at 400 °C, shows the respective peaks for monoclinic WO_3.

A composition close to WO_3 and a high mass density are obtained over the entire temperature range.

Deposition temperature (°C)	GPC (Å)	W (at nm^{-2} cycle^{-1})	O/W	[H] (at. %)	Mass density (g cm^{-3})
100	0.68 ± 0.03	1.06 ± 0.08	2.9 ± 0.1	11.3 ± 0.8	5.8 ± 0.1
200	0.53	0.85	2.9	2.5	5.9
300	0.44	0.62	2.9	2.5	5.9
350	0.43	—	—	—	—
400	0.43	0.62	2.9	6.2	5.9

Refractive index and band gap information over entire temperature window.

Deposition temperature (°C)	Refractive index (n)	Band gap (eV)
100	2.10 ± 0.03	3.23 ± 0.04
200	2.22	3.17
300	2.27	3.15
350	2.27	3.13
400	2.28	3.12

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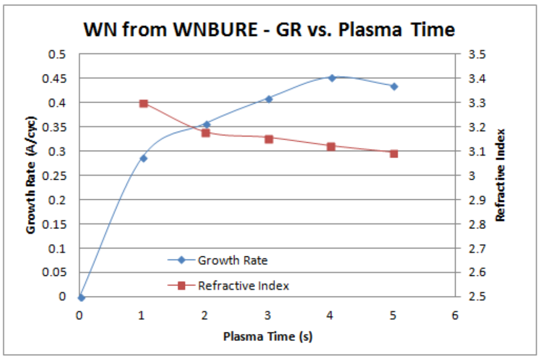
W

WN_x

WN_x based on customer results

Precursor - properties	WNBURE $(^tBuN)_2W(NMe_2)_2$ – liquid bubbled @ 50°C
Non-metal precursors	NH_3 plasma or H_2 plasma
Temperature range	300 °C
Growth rate per cycle	0.45 Å/cycle @ 300°C
Deposition rate	0.22nm/min @ 300°C
Refractive Index	3.10 @ 300°C
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm



GPC against plasma time for WN for 1 second WNBURE dose time

Similar to TaN_x process, the lowest resistivity is expected when using a pure H_2 plasma at low plasma pressure. The usage of biasing should allow further improvement of the conductivity.

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Zn

ZnO

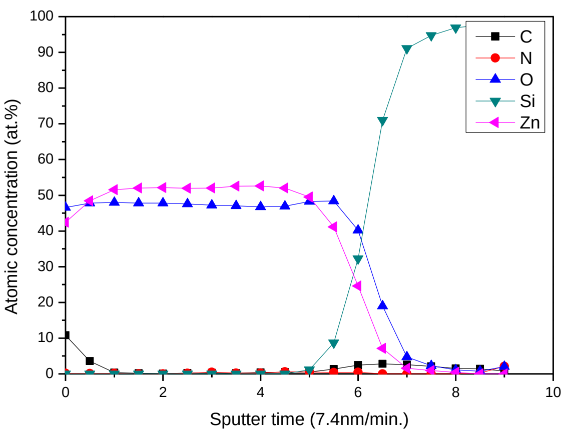
Precursor - properties	DEZ - liquid vapour draw @ 30˚C
Non-metal precursors	H_2O thermal, O_2 plasma, O_2 and H_2 plasma
Temperature range	30°C - 200°C (50°C - 200°C for OpAL)
Growth rate per cycle	1.85 Å/cycle @ 200°C (thermal)
Deposition rate	2.2nm/min @ 200°C
Refractive Index	1.95 @ 200°C
Uniformity	± 1.5% over 100, ± 2.5% over 150mm, ± 3.5% over 200mm
Precursor consumption	100nm/g

200mm data for FlexAL only

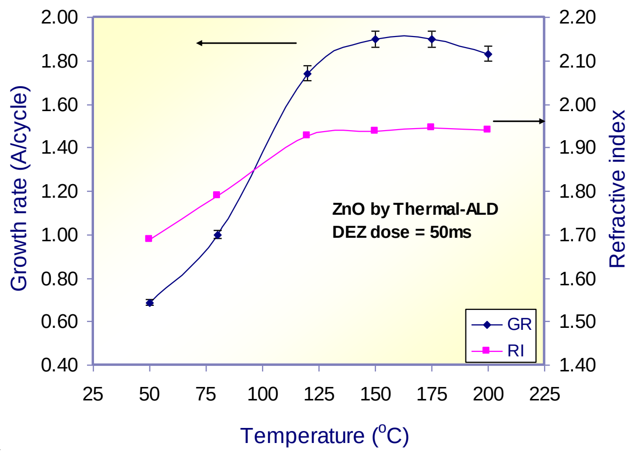
For conductive ZnO films typically thermal ALD is best used to not fully oxidize the films. Doping using Al or B can be used to increase the carrier density. Using O_2 plasma, semiconducting films can be grown which can be good for transistor applications. Due to the low reactivity of H_2O at low temperatures (e.g. ≤100 °C) a recipe with O_2 plasma with occasional H_2 plasma exposures can be used to deposit conductive films.

Results:

- Transparent conductive oxide (TCO)
- Resistivity ~9.0 x10^{-4} ohm cm (Al doped) to 5x10^{-3} ohm cm



AES of ZnO deposited by thermal ALD



Growth rate and refractive index versus temperature for ZnO thermal process.

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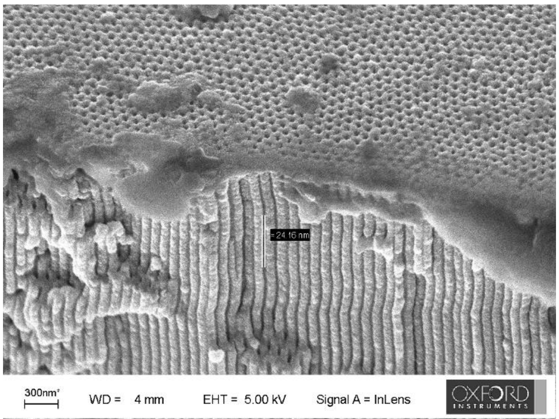
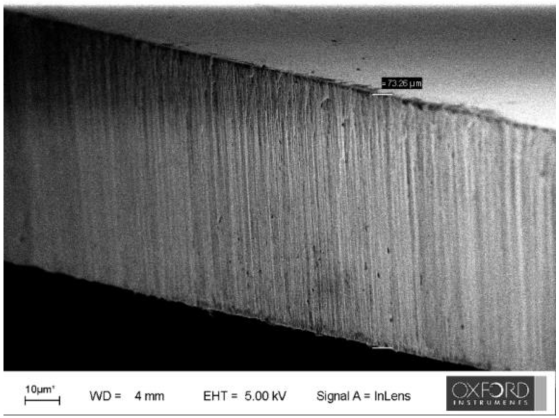
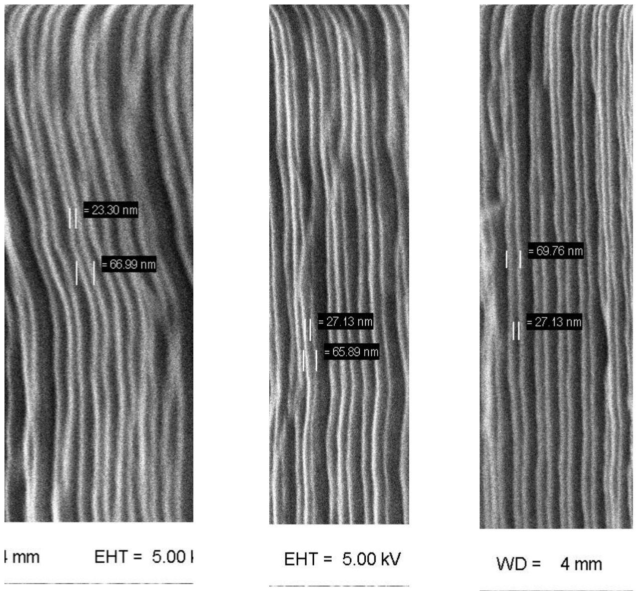
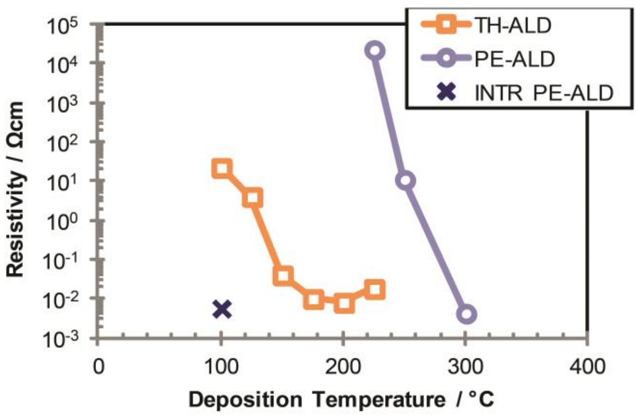






ZnO deposited in AAO template. 70nm wide tube, 100µm long, ~22nm ZnO deposition, ~26nm gap left. From left to right is top, middle and bottom of the tube.



Film resistivity for thermal ALD using H_2O (TH-ALD), plasma ALD using O_2 plasma (PE-ALD), and plasma ALD using O_2 plasma and interleaved H_2 plasma exposures (INTR PE-ALD). Due to the low reactivity of H_2O at low temperatures a plasma process is needed at 100 °C to obtain a low resistivity.

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Reported in papers using Oxford Instruments tools

Thermal ALD using DEZ and H_2O in OpAL at Eindhoven University of Technology.

Al-doped ZnO using TMA and DMAI:
Wu et al., *J. Appl. Phys.* **114**, 024308 (2013)
http://dx.doi.org/10.1063/1.4813136
Wu et al., *Chem. Mater.* **25**, 4619 (2013)
http://dx.doi.org/10.1021/cm402974j
B-doped ZnO using TIB:
Garcia-Alonso et al., *J. Mater. Chem. C* **3**, 3095 (2015)
http://dx.doi.org/10.1039/C4TC02707H
Plasma treatments before and after ZnO grown at 120 °C for CIGS solar cells.
Williams et al., *Sol. Ener. Mat. & Sol. Cells* **157**, 798 (2016)
http://dx.doi.org/10.1016/j.solmat.2016.07.049

Plasma ALD using DEZ and O_2 plasma in FlexAL at University of Southampton.

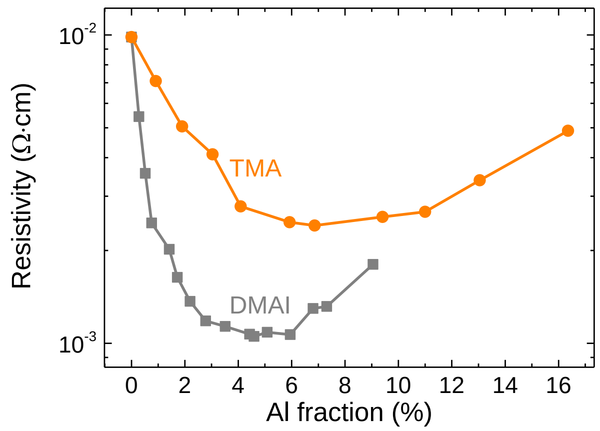
Sultan et al., *IEEE Elec. Dev. Lett.* **33**, 203 (2012)
http://dx.doi.org/10.1109/LED.2011.2174607
Ditshego et al., *Microelectronic Engineering* **145**, 91 (2015)
http://dx.doi.org/10.1016/j.mee.2015.03.013
ZnO nanowire sensors by ALD and ion beam etching for healthcare applications:
Sun et al., *Microelectronic Engineering* **153**, 96 (2016)
http://dx.doi.org/10.1016/j.mee.2016.02.016

Thermal ALD using DEZ and H_2O in OpAL at University of Freiburg for ALD treated storage layer in drug release device.

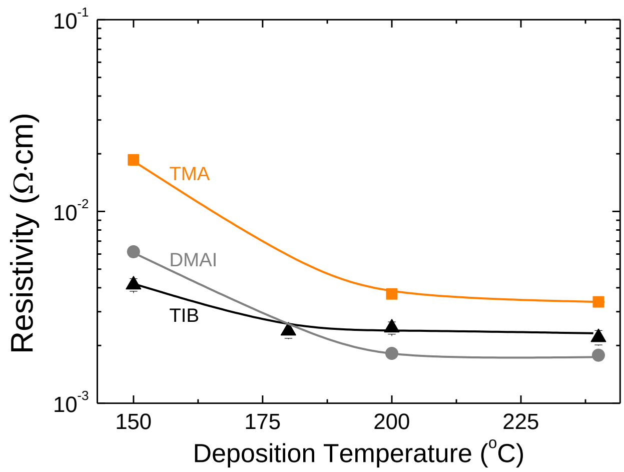
Boehler et al., *Scientific Reports* **6**, 19574 (2016)
http://dx.doi.org/10.1038/srep19574

Other relevant papers:

Demaurex et al., *IEEE J. Photovoltaics* **4**, 1387 (2014) http://dx.doi.org/10.1109/JPHOTOV.2014.2344771
Macco et al., *Semicond. Sci. Technol.* **29**, 122001 (2014) http://dx.doi.org/10.1088/0268-1242/29/12/122001
Pollock et al., *J. Vac. Sci. Technol. A* **32**, 041516 (2014) http://dx.doi.org/10.1116/1.4885063



Lower resistivity with larger dopant precursor DMAI.



At 150 °C lower ρ, for ZnO:B. Also for low temperature better doping with larger ligand precursor (DMAI vs TMA). B better dopant (less easily oxidized) at low temperature.

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Zr — ZrO_2

Precursor - properties	ZrCMMM $(MeCp)_2Zr(OMe)(Me)$ – liquid bubbled @ 70°C
Non-metal precursors	O_2 plasma or H_2O thermal
Temperature range	300°C[1]
Growth rate per cycle	~0.5 Å/cycle @ 300°C
Uniformity	± 2.0% over 100, ± 3.0% over 150mm, ± 3.5% over 200mm

Notes

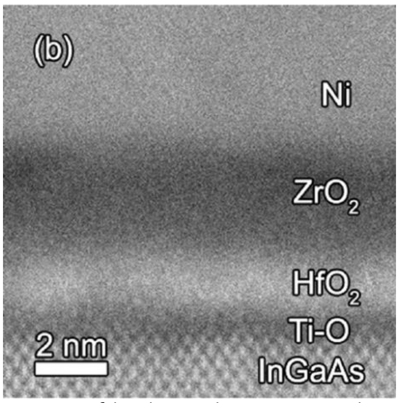
[1] It is anticipated that this can be extended to lower temperatures

Reported in papers using Oxford Instruments tools

Thermal ALD using TEMAZr and H_2O in FlexAL at UC Santa Barbara.

Chobpattana et al., *J. Appl. Phys* **116**, 124104 (2014) http://dx.doi.org/10.1063/1.4896494
Chobpattana et al., *Appl. Phys. Lett.* **104**, 182912 (2014) http://dx.doi.org/10.1063/1.4875977

UCSB



ALD ZrO_2 part of high-quality gate stack on InGaAs

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