In situ spectroscopic ellipsometry as a versatile tool to study atomic layer deposition

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Technische Universiteit
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Where innovation starts

Outline

- **Atomic layer deposition (ALD)**
    - Basics of ALD
    - Materials deposited by ALD
    - Applications for ALD
- ***In situ* spectroscopic ellipsometry as tool to monitor ALD**

Monitoring the film thickness
- ALD growth & growth per cycle
- Self-limiting chemistry
- Initial film growth & substrate dependence
- Nanolaminates

Parametrizing the dielectric function
- Metallic films:
    Electrical properties & electron scattering
- Ultrahigh-*k* dielectrics
    Film composition & microstructure

Thin film materials:
Al_2O_3
Ta_2O_5
Er_2O_3
TiO_2
TiN
TaN
Ta_3N_5
$SrTiO_3$
Pt
Ru

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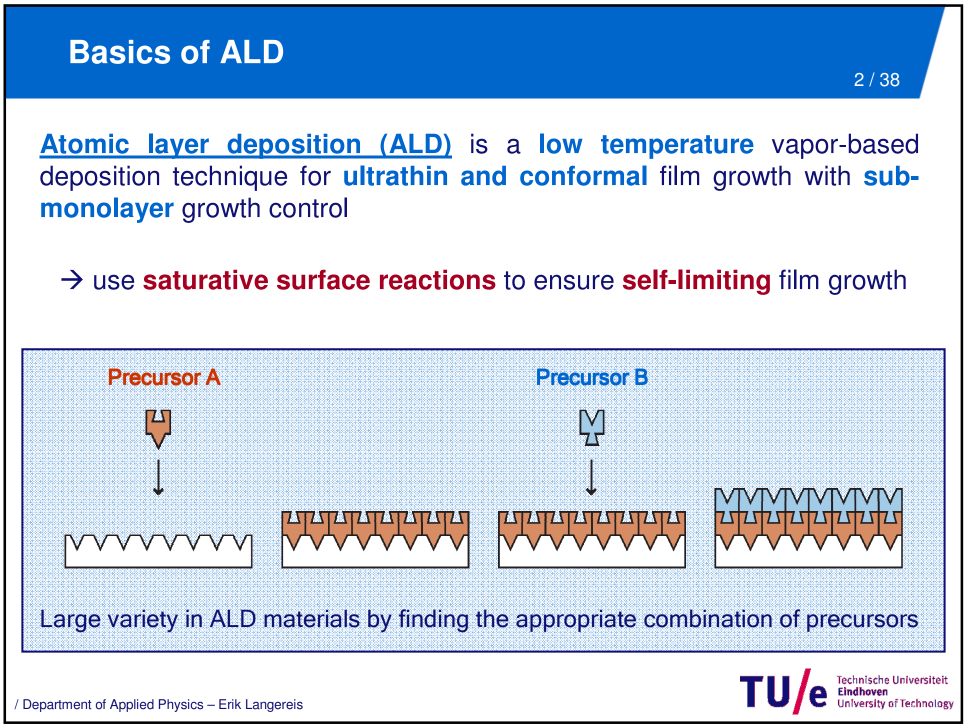

Basics of ALD

Atomic layer deposition (ALD) is a **low temperature** vapor-based deposition technique for **ultrathin and conformal** film growth with **sub-monolayer** growth control

→ use **saturative surface reactions** to ensure **self-limiting** film growth

Large variety in ALD materials by finding the appropriate combination of precursors

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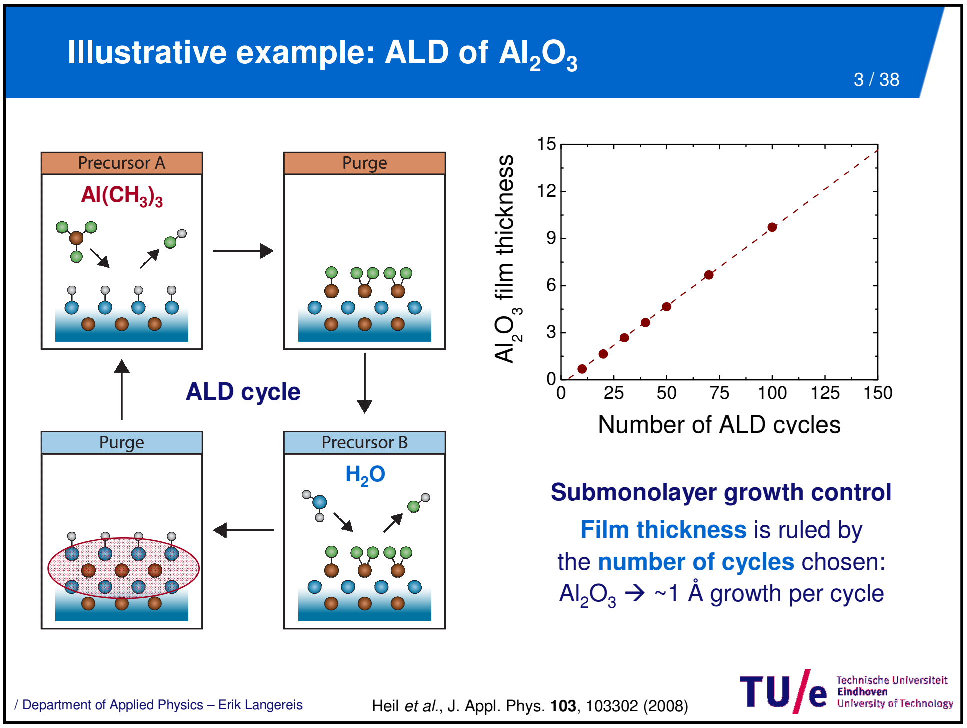
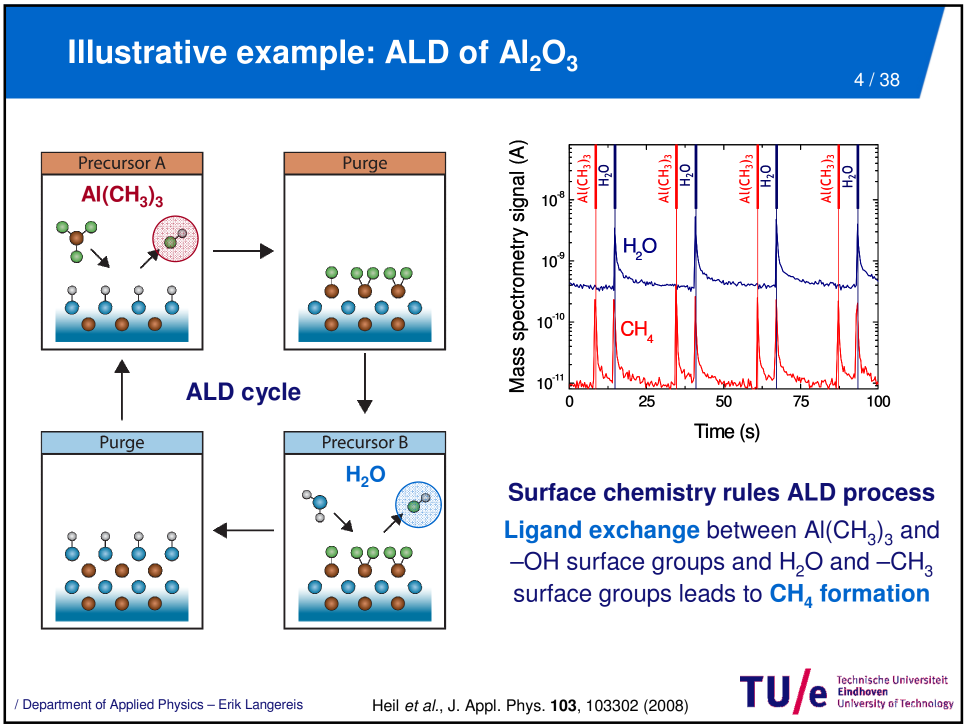


Illustrative example: ALD of Al_2O_3

Submonolayer growth control

Film thickness is ruled by the **number of cycles** chosen: Al_2O_3 → ~1 Å growth per cycle

Heil *et al.*, J. Appl. Phys. **103**, 103302 (2008)

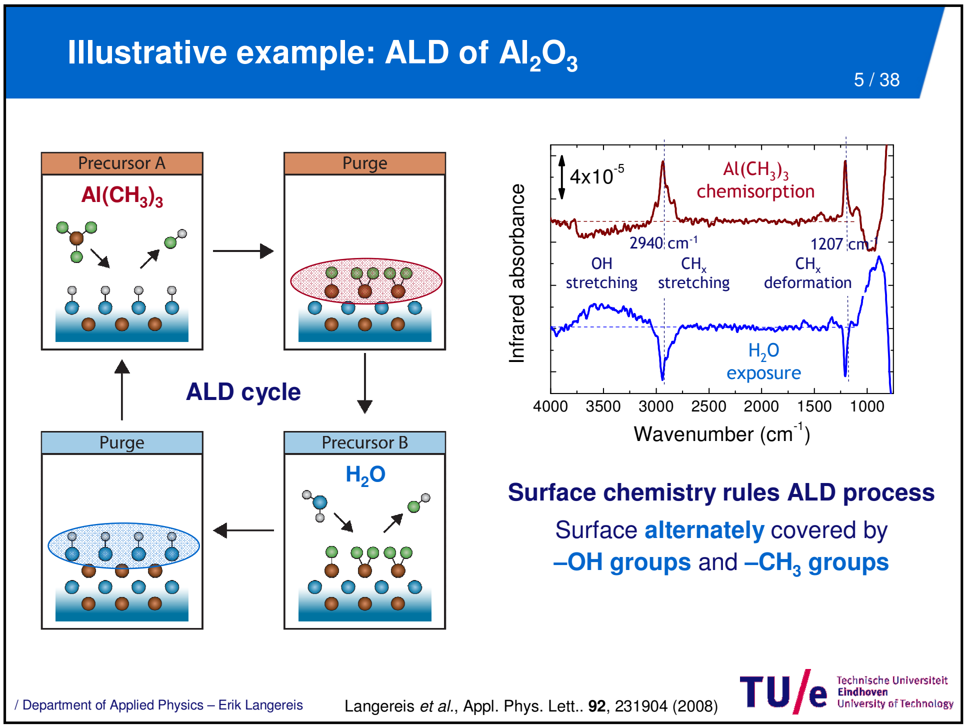


Illustrative example: ALD of Al_2O_3

Surface chemistry rules ALD process

Ligand exchange between $Al(CH_3)_3$ and –OH surface groups and H_2O and $–CH_3$ surface groups leads to **CH_4 formation**

Heil *et al.*, J. Appl. Phys. **103**, 103302 (2008)

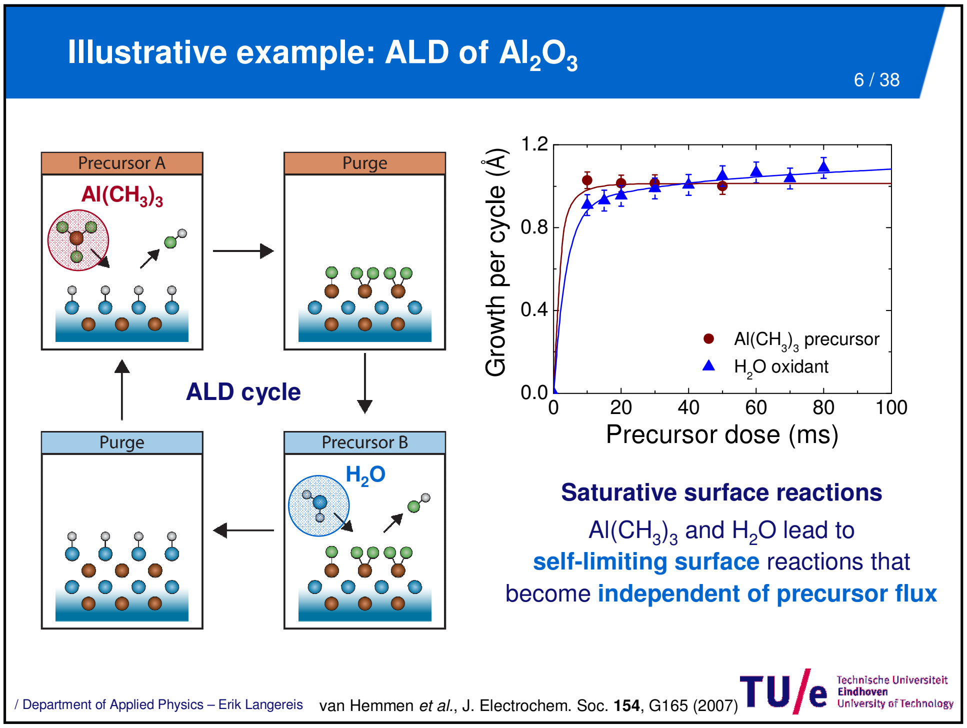


Illustrative example: ALD of Al_2O_3

Surface chemistry rules ALD process

Surface **alternately** covered by **–OH groups** and **$–CH_3$ groups**

Langereis *et al.*, Appl. Phys. Lett.. **92**, 231904 (2008)

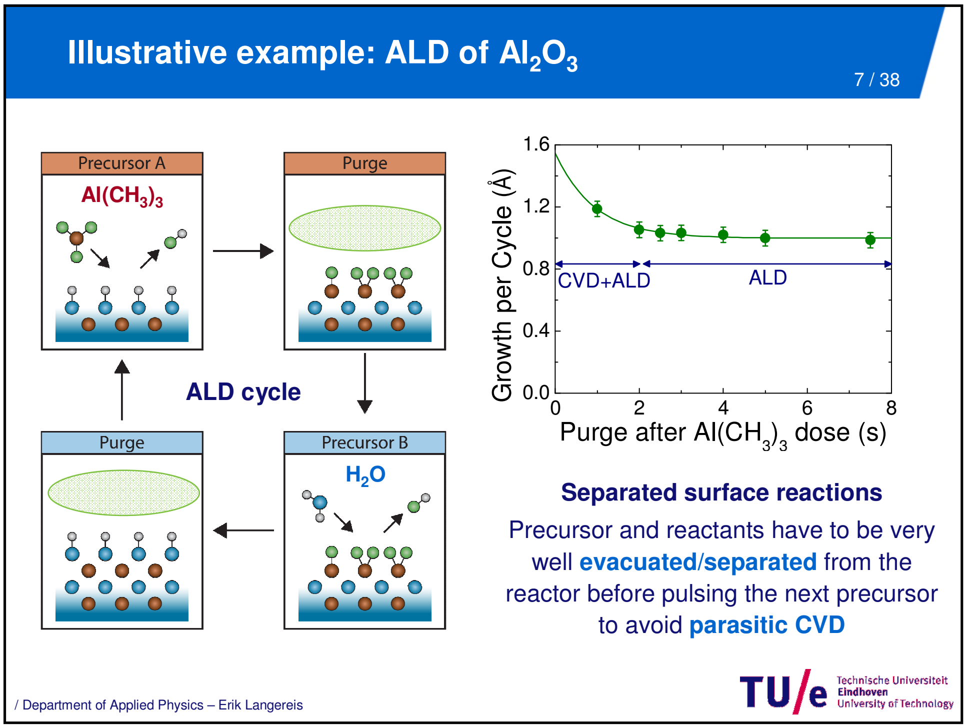


Illustrative example: ALD of Al_2O_3

Saturative surface reactions

$Al(CH_3)_3$ and H_2O lead to **self-limiting surface** reactions that become **independent of precursor flux**

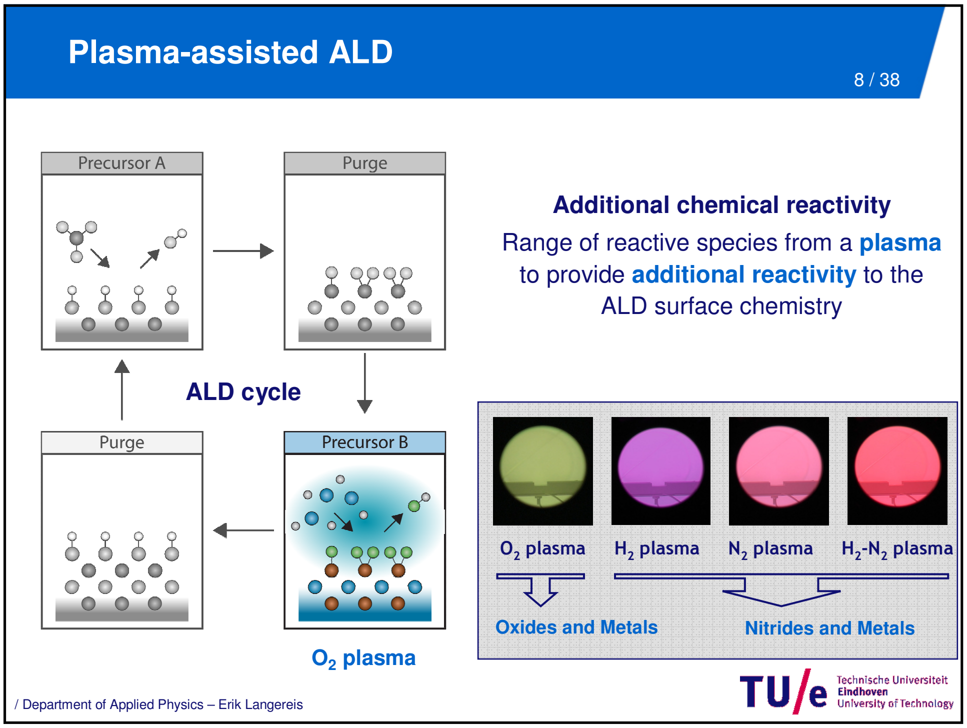
van Hemmen *et al.*, J. Electrochem. Soc. **154**, G165 (2007)



Illustrative example: ALD of Al_2O_3

Separated surface reactions

Precursor and reactants have to be very well **evacuated/separated** from the reactor before pulsing the next precursor to avoid **parasitic CVD**



Plasma-assisted ALD

8 / 38

Precursor A

Purge

ALD cycle

Purge

Precursor B

O_2 plasma

Additional chemical reactivity

Range of reactive species from a **plasma** to provide **additional reactivity** to the ALD surface chemistry

O_2 plasma

H_2 plasma

N_2 plasma

H_2-N_2 plasma

Oxides and Metals

Nitrides and Metals

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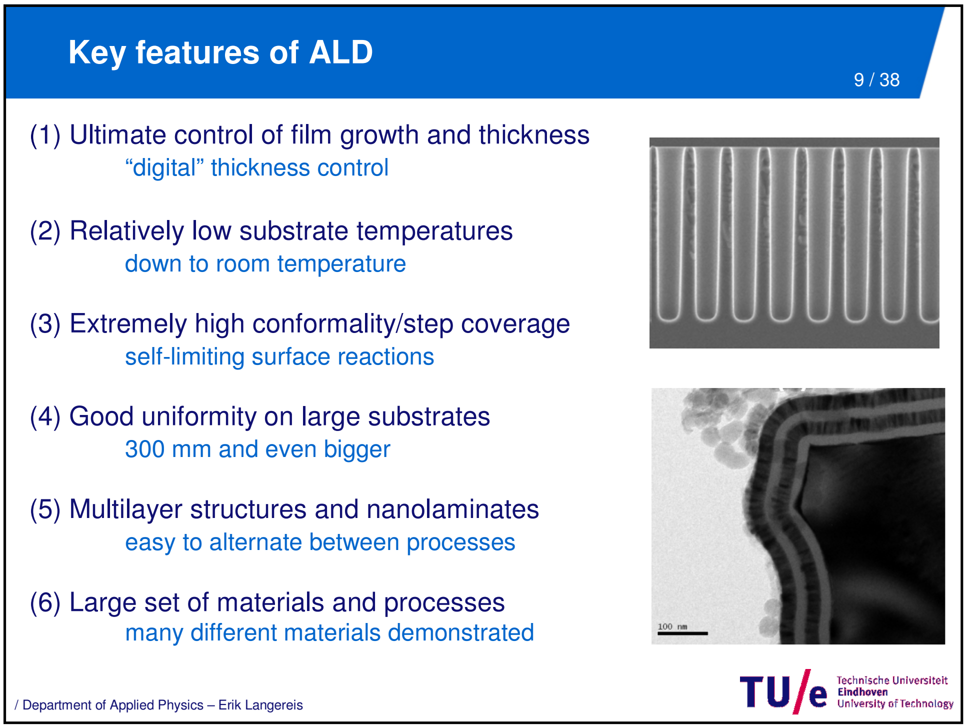

Key features of ALD

9 / 38

(1) Ultimate control of film growth and thickness
“digital” thickness control

(2) Relatively low substrate temperatures
down to room temperature

(3) Extremely high conformality/step coverage
self-limiting surface reactions

(4) Good uniformity on large substrates
300 mm and even bigger

(5) Multilayer structures and nanolaminates
easy to alternate between processes

(6) Large set of materials and processes
many different materials demonstrated

100 nm

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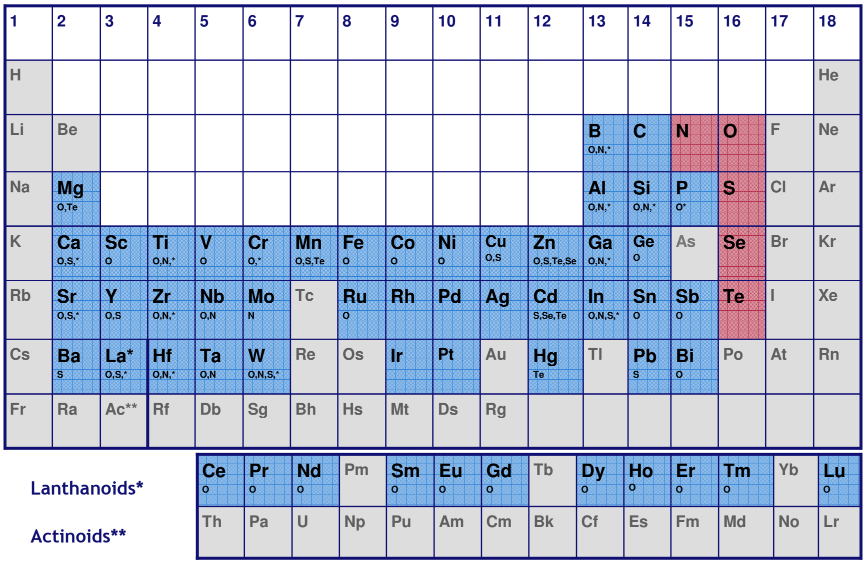
Key features ALD

Thin films synthesized by ALD



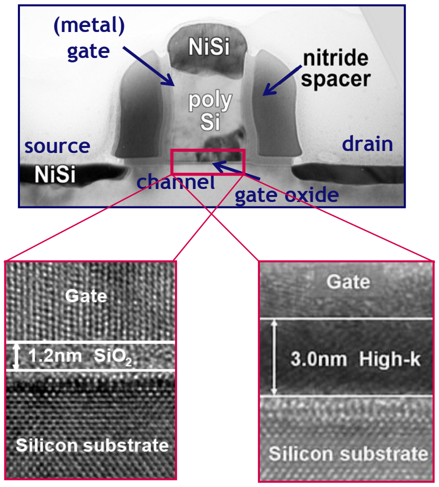
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											**B** O,N,*	**C**	**N**	**O**	F	Ne
Na	**Mg** O,Te											**Al** O,N,*	**Si** O,N,*	**P** O*	**S**	Cl	Ar
K	**Ca** O,S,*	**Sc** O	**Ti** O,N,*	**V** O	**Cr** O,*	**Mn** O,S,Te	**Fe** O	**Co** O	**Ni** O	**Cu** O,S	**Zn** O,S,Te,Se	**Ga** O,N,*	**Ge** O	As	**Se**	Br	Kr
Rb	**Sr** O,S,*	**Y** O,S	**Zr** O,N,*	**Nb** O,N	**Mo** N	Tc	**Ru** O	**Rh**	**Pd**	**Ag**	**Cd** S,Se,Te	**In** O,N,S,*	**Sn** O	**Sb** O	**Te**	I	Xe
Cs	**Ba** S	**La*** O,S,*	**Hf** O,N,*	**Ta** O,N	**W** O,N,S,*	Re	Os	**Ir**	**Pt**	Au	**Hg** Te	Tl	**Pb** S	**Bi** O	Po	At	Rn
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Lanthanoids*	**Ce** O	**Pr** O	**Nd** O	Pm	**Sm** O	**Eu** O	**Gd** O	Tb	**Dy** O	**Ho** O	**Er** O	**Tm** O	Yb	**Lu** O
Actinoids**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Puurunen, J. Appl. Phys. **97,** 121301 (2005)

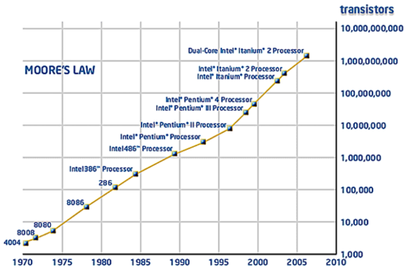
ALD applications:
Semiconductor industry (= key driver)

Metal-oxide-semiconductor field effect transistor (**MOSFET**)

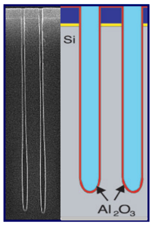


Thermally grown SiO_2

Deposited high-k oxide

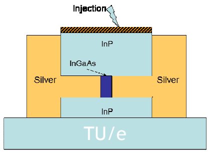


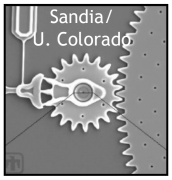
DRAM deep trench capacitors
(aspect ratio up to 70)

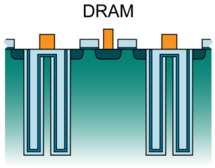


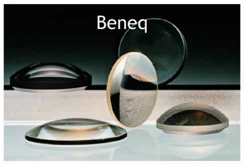
ALD applications:
Overview

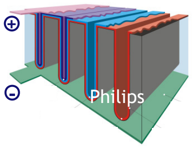
- Transistor gates stacks
- Deep trench DRAM
- High density capacitors
- Hard disks
- Interconnect technology
- MEMS/Microsystems
- Corrosion protection
- Thin film encapsulation
- Li^+-batteries
- Photonics
- Photovoltaics
- Displays
- Solid-state lighting
- Optical coatings
- Nanotechnology
- …







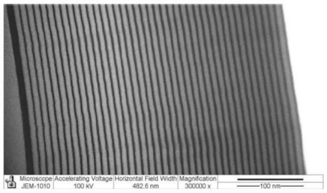




ALD applications:
Ultrathin films – conformal growth – high material quality

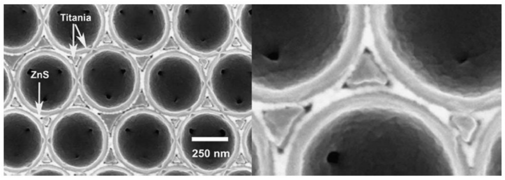
Al_2O_3/Ta_2O_5: **x-ray mirror**

Szeghalmi *et al.*, Appl. Phys. Lett. **94,** 133111 (2009)

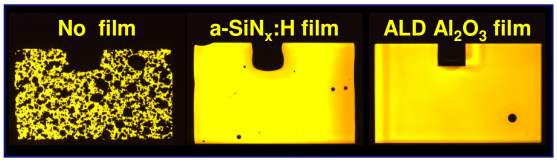


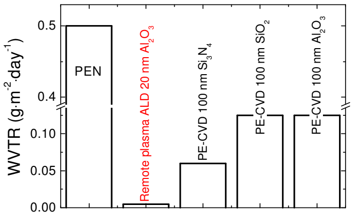
TiO_2/ZnS:Mn/TiO_2 and TiO_2: **inverse opals**

King *et al.*, Adv. Mater. **17,** 1010 (2005)



Al_2O_3: **encapsulation of organic LED**





Langereis *et al.*, Appl. Phys. Lett. **89**, 081915 (2006)
Groner *et al.*, Appl. Phys. Lett. **88**, 051907 (2006)
Garcia *et al.*, Appl. Phys. Lett. **89**, 031915 (2006).

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  - \- Materials deposited by ALD
  - \- Applications for ALD

- ***In situ* spectroscopic ellipsometry as tool to monitor ALD**

Monitoring the film thickness
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Parametrizing the dielectric function
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  Electrical properties & electron scattering
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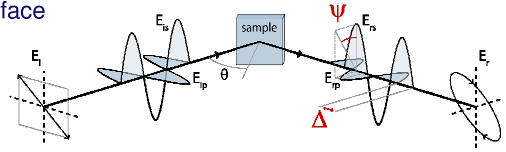
  Film composition & microstructure

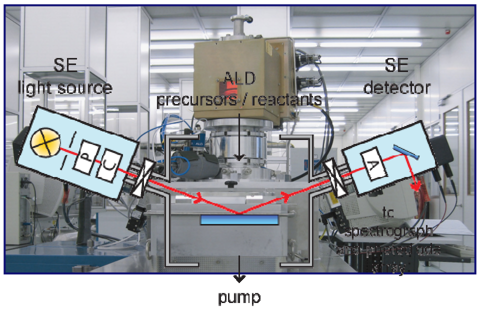
Thin film materials:
Al_2O_3
Ta_2O_5
Er_2O_3
TiO_2
TiN
TaN
Ta_3N_5
$SrTiO_3$
Pt
Ru

In situ spectroscopic ellipsometry during ALD

Measurement of the **change in polarization** of a light beam (at different wavelengths) upon reflection from a surface



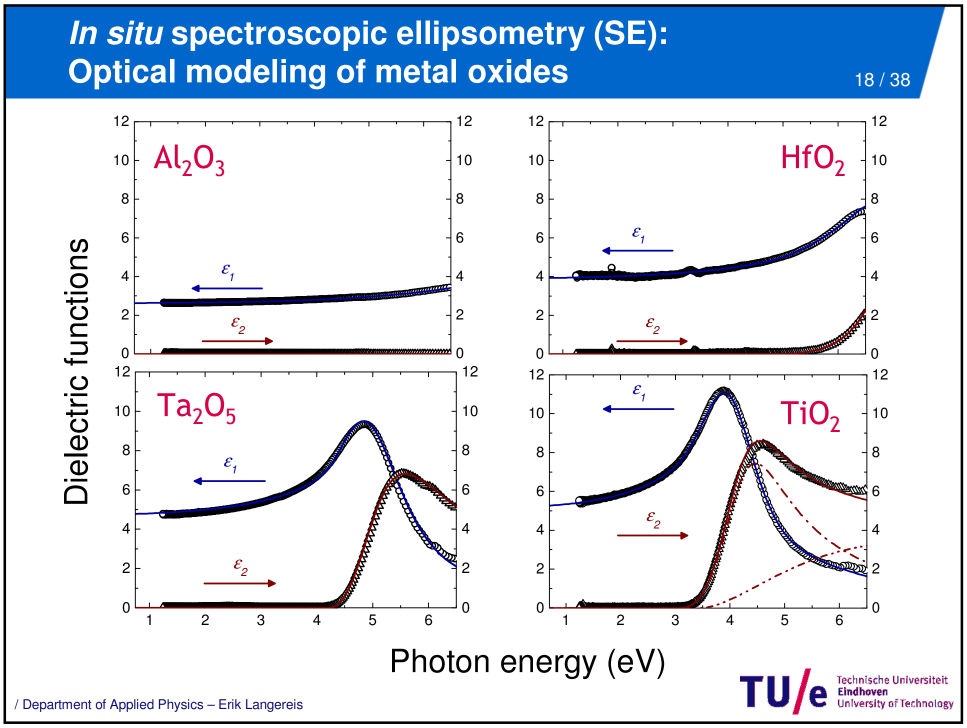
→ Film thickness and optical dielectric function extracted by **model-based analysis**



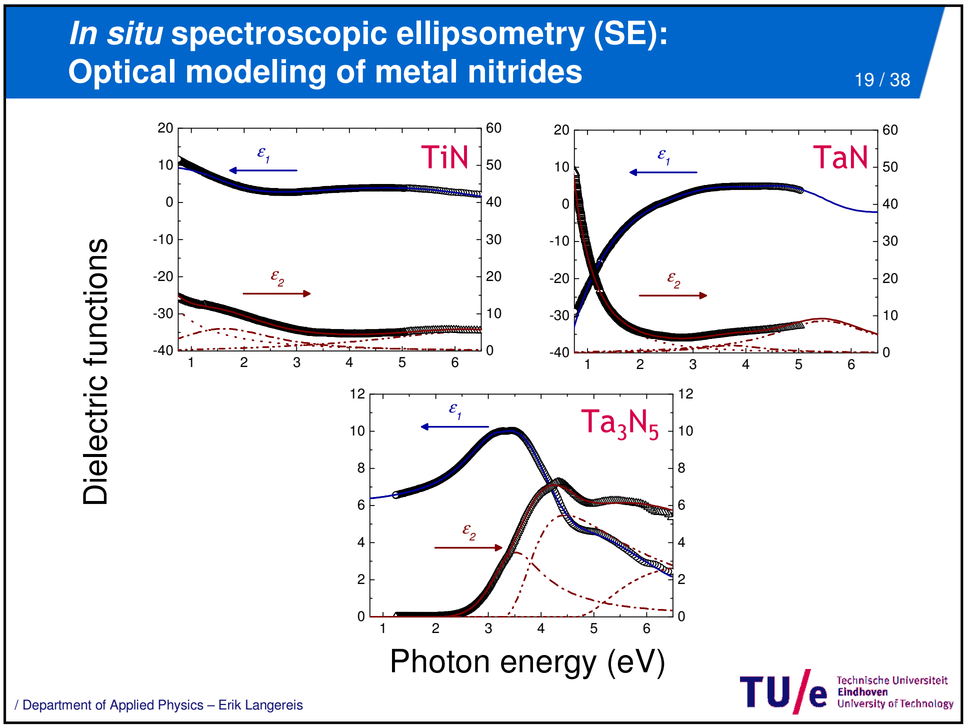
J.A. Woollam Co. M2000-series:
VIS + IR: **0.75 – 5.0 eV**
VIS + UV: **1.2 – 6.5 eV**

ALD materials investigated
→ Metal oxides – Metal nitrides - Metals

Material	Precursor gas	Reducing/ Oxidizing agent	Cycle time (s)	Temperature (ºC)
Al_2O_3	$Al(CH_3)_3$	H_2O/O_2 plasma	4	100 (25–300)
HfO_2	$Hf[N(CH_3)(C_2H_5)]_4$	O_2 plasma	11	290 (230–350)
Er_2O_3	$Er(thd)_3$	O_2 plasma	50	300 (150–300)
TiO_2	$Ti[OCH(CH_3)_2]_4$	O_2 plasma	20	300 (25–300)
Ta_2O_5	$Ta[N(CH_3)_2]_5$	O_2 plasma	15	225 (100–225)
$SrTiO_3$	Star-Ti and Hyper-Sr	O_2 plasma	>60	250 (150-350)
TiN	$TiCl_4$	H_2-N_2 (10:1) plasma	40	400 (100–400)
$TaN_{x, x\leq 1}$	$Ta[N(CH_3)_2]_5$	H_2 plasma	37	225 (150–250)
Ta_3N_5	$Ta[N(CH_3)_2]_5$	NH_3 plasma	37	225 (150–250)
Pt	$(CpCH_3)Pt(CH_3)_3$	O_2/O_2 plasma	17	300 (100-300)
Ru	$CpRu(CO)_2C_2H_5$	O_2/O_2 plasma	8	400 (300-400)



In situ spectroscopic ellipsometry (SE): Optical modeling of metal oxides



In situ spectroscopic ellipsometry (SE): Optical modeling of metal nitrides

In situ spectroscopic ellipsometry (SE): Overview optical model parameters

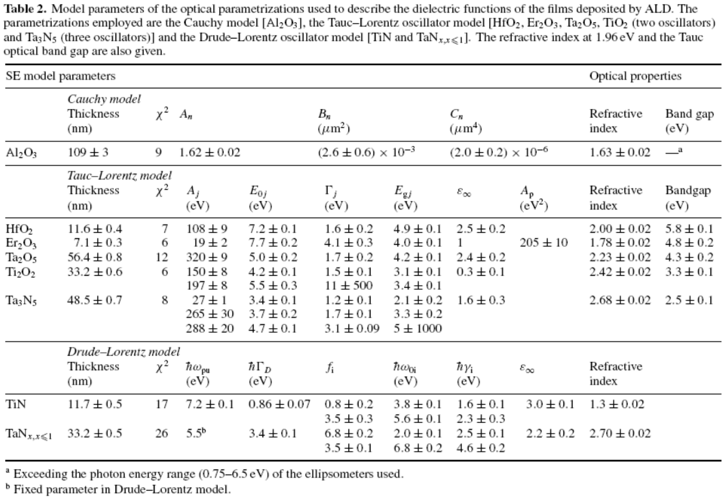


Table 2. Model parameters of the optical parametrizations used to describe the dielectric functions of the films deposited by ALD. The parametrizations employed are the Cauchy model [Al_2O_3], the Tauc–Lorentz oscillator model [HfO_2, Er_2O_3, Ta_2O_5, TiO_2 (two oscillators) and Ta_3N_5 (three oscillators)] and the Drude–Lorentz oscillator model [TiN and $TaN_{x,x\leqslant 1}$]. The refractive index at 1.96 eV and the Tauc optical band gap are also given.

SE model parameters									Optical properties	
	Cauchy model Thickness (nm)	χ^2	A_n		B_n (μm^2)		C_n (μm^4)		Refractive index	Band gap (eV)
Al_2O_3	109 ± 3	9	1.62 ± 0.02		$(2.6 \pm 0.6) \times 10^{-3}$		$(2.0 \pm 0.2) \times 10^{-6}$		1.63 ± 0.02	—[a]
	Tauc–Lorentz model Thickness (nm)	χ^2	A_j (eV)	E_{0j} (eV)	Γ_j (eV)	E_{gj} (eV)	ε_∞	A_p (eV^2)	Refractive index	Bandgap (eV)
HfO_2	11.6 ± 0.4	7	108 ± 9	7.2 ± 0.1	1.6 ± 0.2	4.9 ± 0.1	2.5 ± 0.2		2.00 ± 0.02	5.8 ± 0.1
Er_2O_3	7.1 ± 0.3	6	19 ± 2	7.7 ± 0.2	4.1 ± 0.3	4.0 ± 0.1	1	205 ± 10	1.78 ± 0.02	4.8 ± 0.2
Ta_2O_5	56.4 ± 0.8	12	320 ± 9	5.0 ± 0.2	1.7 ± 0.2	4.2 ± 0.1	2.4 ± 0.2		2.23 ± 0.02	4.3 ± 0.2
Ti_2O_2	33.2 ± 0.6	6	150 ± 8	4.2 ± 0.1	1.5 ± 0.1	3.1 ± 0.1	0.3 ± 0.1		2.42 ± 0.02	3.3 ± 0.1
			197 ± 8	5.5 ± 0.3	11 ± 500	3.4 ± 0.1				
Ta_3N_5	48.5 ± 0.7	8	27 ± 1	3.4 ± 0.1	1.2 ± 0.1	2.1 ± 0.2	1.6 ± 0.3		2.68 ± 0.02	2.5 ± 0.1
			265 ± 30	3.7 ± 0.2	1.7 ± 0.1	3.3 ± 0.2				
			288 ± 20	4.7 ± 0.1	3.1 ± 0.09	5 ± 1000				
	Drude–Lorentz model Thickness (nm)	χ^2	$\hbar\omega_{pu}$ (eV)	$\hbar\Gamma_D$ (eV)	f_i	$\hbar\omega_{0i}$ (eV)	$\hbar\gamma_i$ (eV)	ε_∞	Refractive index	
TiN	11.7 ± 0.5	17	7.2 ± 0.1	0.86 ± 0.07	0.8 ± 0.2	3.8 ± 0.1	1.6 ± 0.1	3.0 ± 0.1	1.3 ± 0.02	
					3.5 ± 0.3	5.6 ± 0.1	2.3 ± 0.3			
$TaN_{x,x\leqslant 1}$	33.2 ± 0.5	26	5.5[b]	3.4 ± 0.1	6.8 ± 0.2	2.0 ± 0.1	2.5 ± 0.1	2.2 ± 0.2	2.70 ± 0.02	
					3.5 ± 0.1	6.8 ± 0.2	4.6 ± 0.2			

[a] Exceeding the photon energy range (0.75–6.5 eV) of the ellipsometers used.

[b] Fixed parameter in Drude–Lorentz model.

See Topical Review: Langereis *et al.*, J. Phys. D: Appl. Phys. 42, 073001 (2009)

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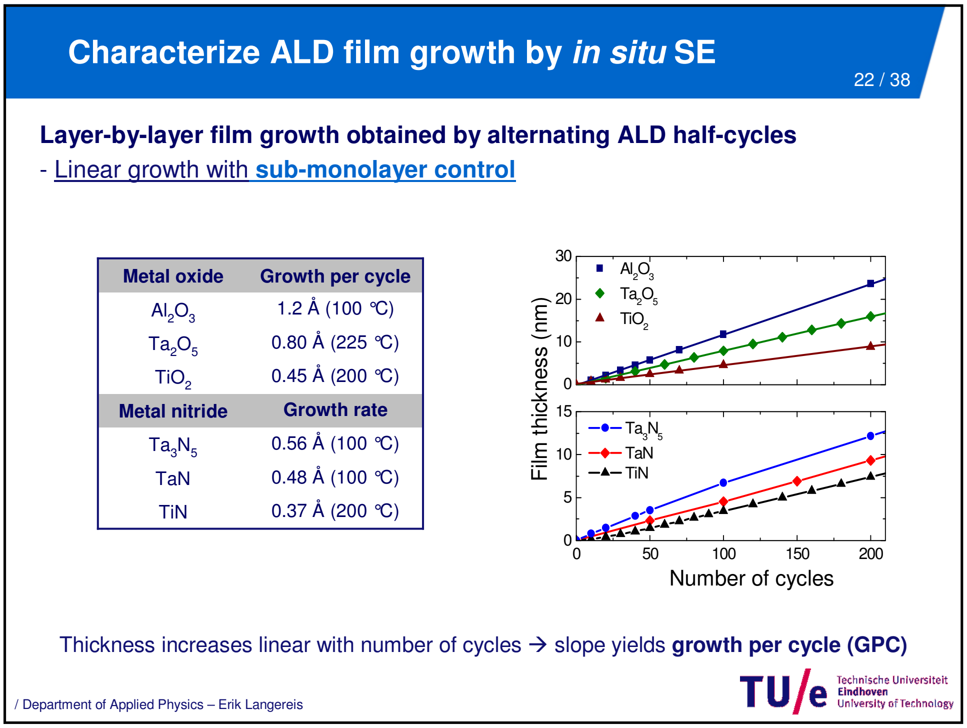


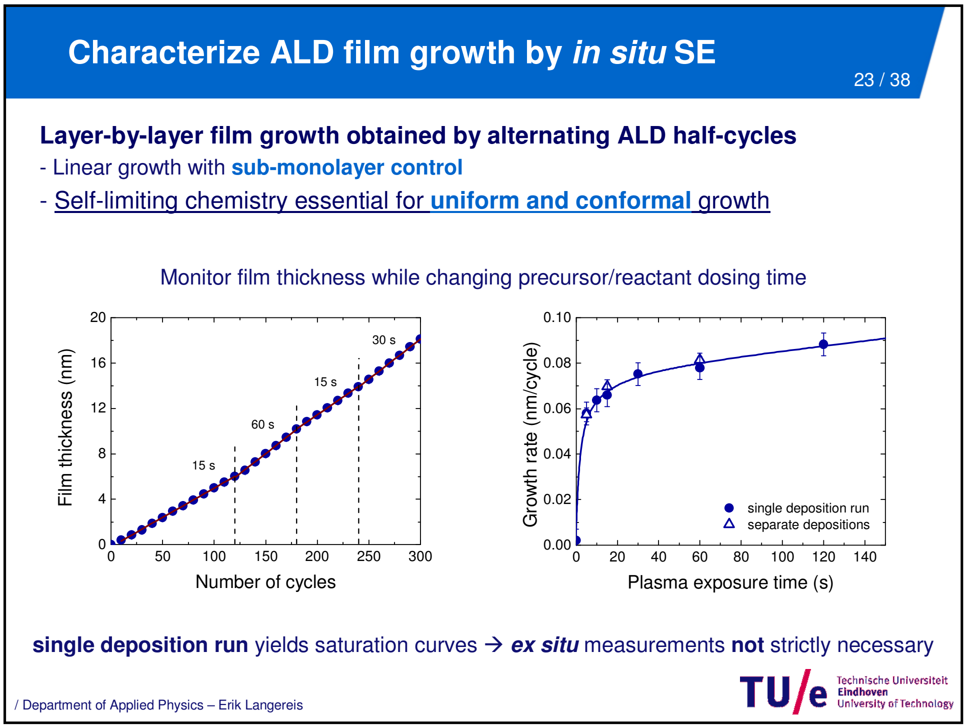
Characterize ALD film growth by *in situ* SE

Layer-by-layer film growth obtained by alternating ALD half-cycles

- Linear growth with **sub-monolayer control**

Metal oxide	Growth per cycle
Al_2O_3	1.2 Å (100 ℃)
Ta_2O_5	0.80 Å (225 ℃)
TiO_2	0.45 Å (200 ℃)
Metal nitride	**Growth rate**
Ta_3N_5	0.56 Å (100 ℃)
TaN	0.48 Å (100 ℃)
TiN	0.37 Å (200 ℃)

Thickness increases linear with number of cycles → slope yields **growth per cycle (GPC)**



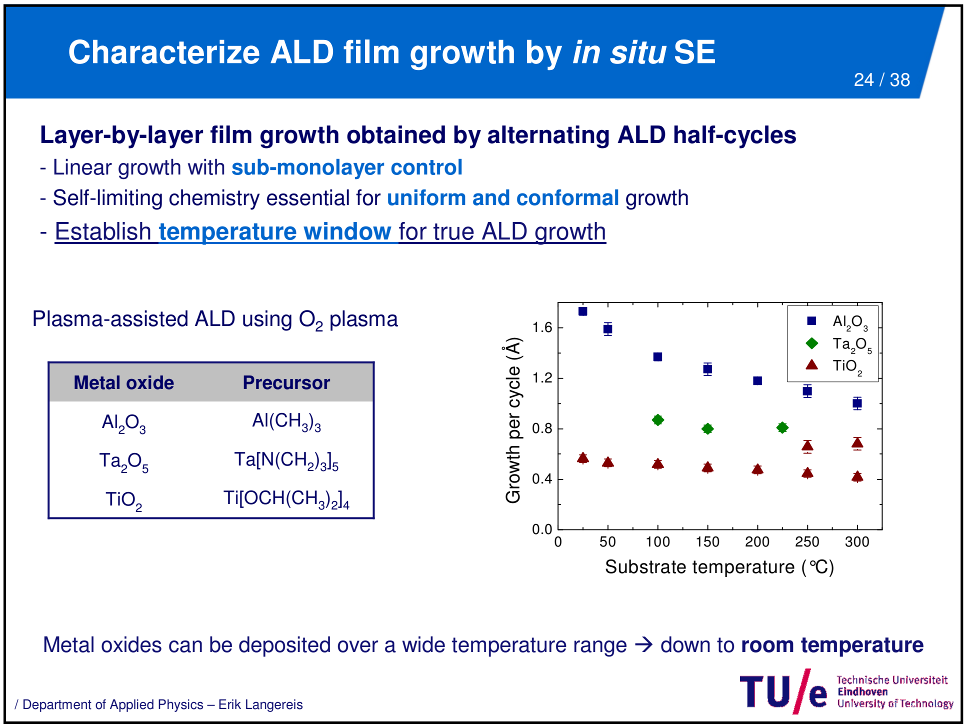
Characterize ALD film growth by *in situ* SE

Layer-by-layer film growth obtained by alternating ALD half-cycles

- Linear growth with **sub-monolayer control**
- Self-limiting chemistry essential for **uniform and conformal** growth

Monitor film thickness while changing precursor/reactant dosing time

single deposition run yields saturation curves → ***ex situ*** measurements **not** strictly necessary



Characterize ALD film growth by *in situ* SE

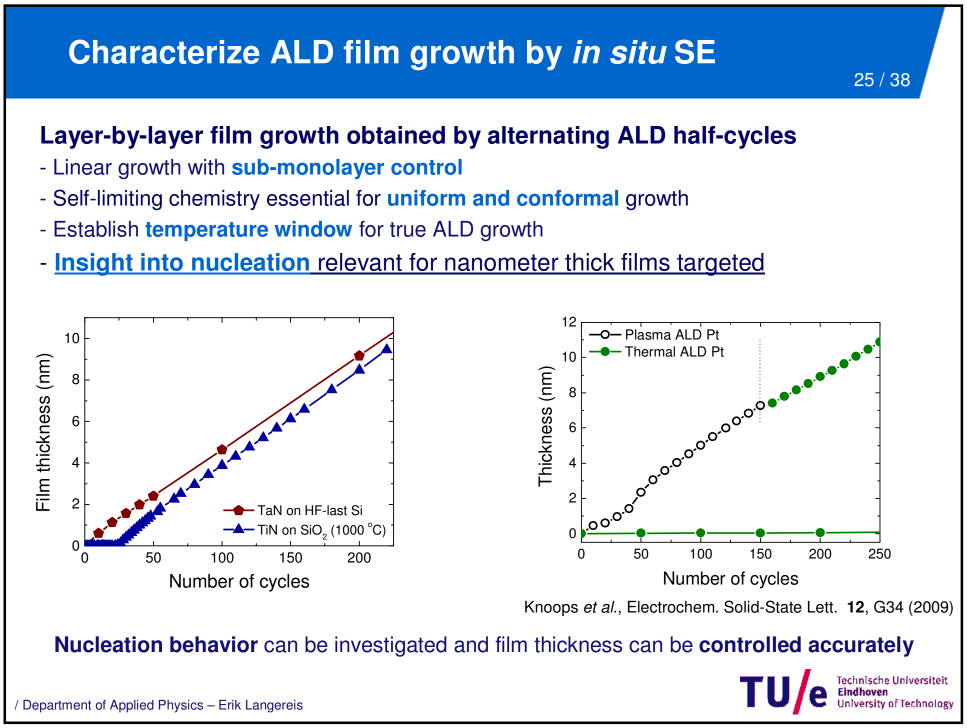
Layer-by-layer film growth obtained by alternating ALD half-cycles

- Linear growth with **sub-monolayer control**
- Self-limiting chemistry essential for **uniform and conformal** growth
- Establish **temperature window** for true ALD growth

Plasma-assisted ALD using O_2 plasma

Metal oxide	Precursor
Al_2O_3	$Al(CH_3)_3$
Ta_2O_5	$Ta[N(CH_2)_3]_5$
TiO_2	$Ti[OCH(CH_3)_2]_4$

Metal oxides can be deposited over a wide temperature range → down to **room temperature**



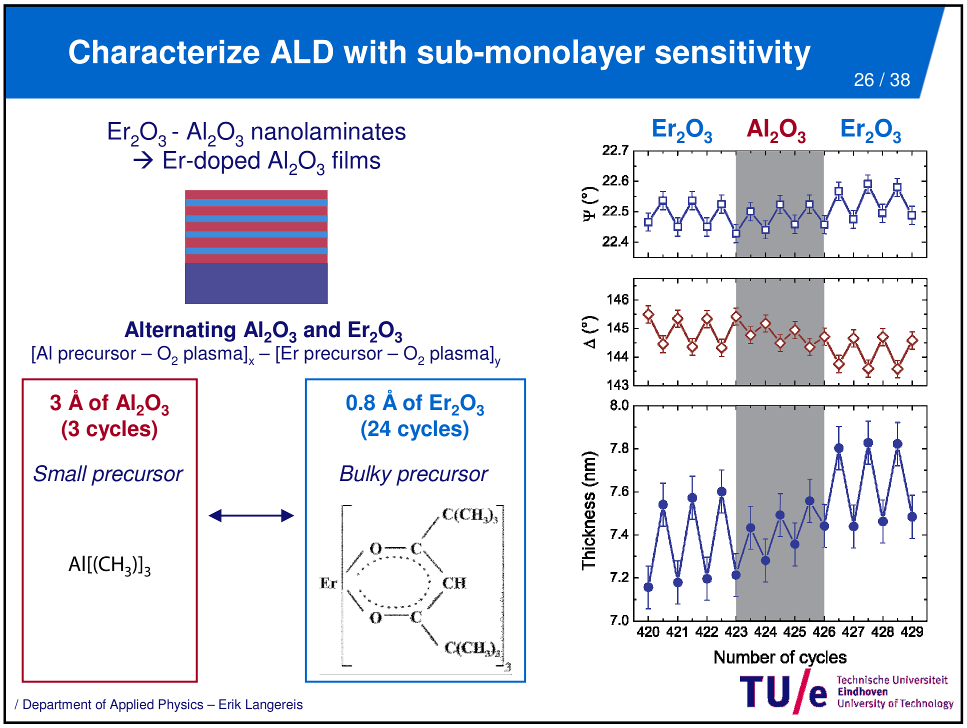
Characterize ALD film growth by *in situ* SE

Layer-by-layer film growth obtained by alternating ALD half-cycles

- Linear growth with **sub-monolayer control**
- Self-limiting chemistry essential for **uniform and conformal** growth
- Establish **temperature window** for true ALD growth
- **Insight into nucleation** relevant for nanometer thick films targeted

Knoops *et al.*, Electrochem. Solid-State Lett. **12**, G34 (2009)

Nucleation behavior can be investigated and film thickness can be **controlled accurately**



Characterize ALD with sub-monolayer sensitivity

Er_2O_3 - Al_2O_3 nanolaminates
→ Er-doped Al_2O_3 films

Alternating Al_2O_3 and Er_2O_3
[Al precursor – O_2 plasma]$_x$ – [Er precursor – O_2 plasma]$_y$

3 Å of Al_2O_3 (3 cycles)

Small precursor

$Al[(CH_3)]_3$

0.8 Å of Er_2O_3 (24 cycles)

Bulky precursor

Outline

- **Atomic layer deposition (ALD)**
  - Basics of ALD
  - Materials deposited by ALD
  - Applications for ALD
- ***In situ* spectroscopic ellipsometry as tool to monitor ALD**

Monitoring the film thickness
- ALD growth & growth per cycle
- Self-limiting chemistry
- Initial film growth & substrate dependence
- Nanolaminates

Parametrizing the dielectric function
- Metallic films:
  Electrical properties & electron scattering
- Ultrahigh *k* dielectrics
  Film composition & microstructure

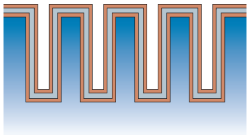
Thin film materials:
Al_2O_3
Ta_2O_5
Er_2O_3
TiO_2
TiN
TaN
Ta_3N_5
$SrTiO_3$
Pt
Ru

ALD for high-density capacitors

Specifications for DRAM and decoupling capacitors:

- **High capacity density: > 500 nF/mm^2**
  - Dielectric thickness: ~10-50 nm
  - High step coverage: > 95% for AR 20-30
  - Electrode thickness: 5-30 nm
  - Electrode conductivity: < 300 μΩcm

$$C = \varepsilon_0 k \frac{A}{d}$$

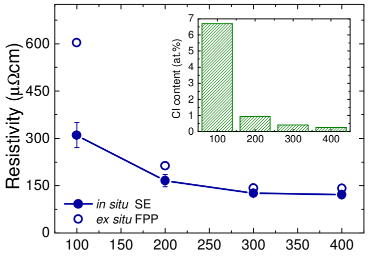


- **Low leakage current (A/cm^2)**
  - Specs: ≤ 10^{-8} @ 1 V (DRAM)
    ≤ 10^{-6} @ 3 V (Decap)

- **Low thermal budget**
  - Specs: 400-600 ℃

Metallic films — resistivity & electron MFP in TiN

Resistivity increases with Cl-content



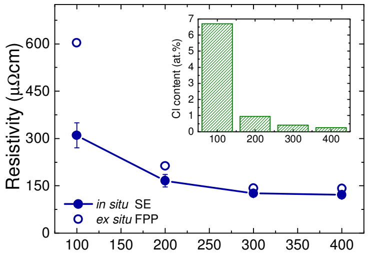
Resistivity:

$$\rho = \left(\frac{1}{\varepsilon_0}\right)\frac{\Gamma_D}{\omega_{pu}^2}$$

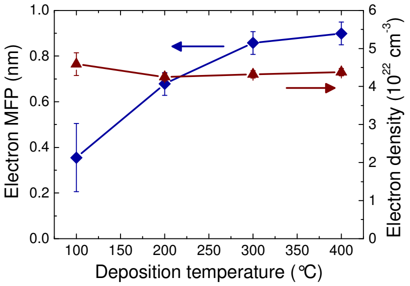
Langereis *et al.*, J. Appl. Phys. **100,** 023534 (2006)

Metallic films — resistivity & electron MFP in TiN

Resistivity increases with Cl-content



Especially electron mean-free-path is affected, electron density remains constant



Resistivity:

$$\rho = \left(\frac{1}{\varepsilon_0}\right)\frac{\Gamma_D}{\omega_{pu}^2}$$

Electron mean free path:

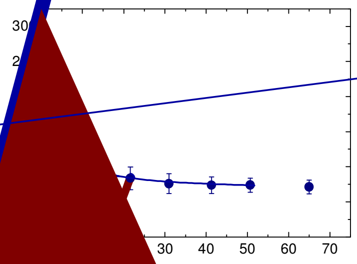
$$\mathrm{MFP} = \hbar\left(\frac{3\pi^2\varepsilon_0}{\left(m^* e\right)^2}\right)^{1/3}\frac{\omega_{pu}^{2/3}}{\Gamma_D}$$

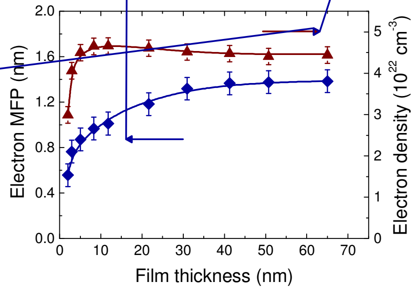
Electron density:

$$N_e = \left(\frac{m^*\varepsilon_0}{e^2}\right)\omega_{pu}^2$$

Langereis *et al.*, J. Appl. Phys. **100**, 023534 (2006)

Finite size effects in ultrathin metallic films





320

- **Composition control to optimize film properties**

  ALD $SrTiO_3$ = x cycles ALD TiO_2 + y cycles ALD SrO

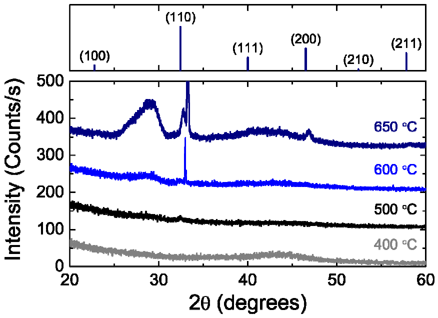
Star Ti:
$[Me_5Cp]Ti(OMe)_3$ =
$[(CH_3)_5C_5]Ti(OCH_3$

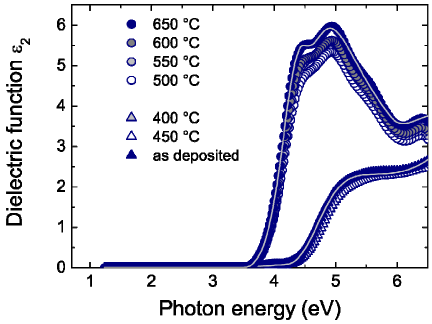
- **Crystalline films yield ultrahigh *k* values**

  Post-deposition anneal required for crystallization

ALD of $SrTiO_3$ - crystallization

Post-deposition anneal of 30 nm thick $SrTiO_3$ films ([Sr]/[Ti] = 1.3)





Film crystallization probed by *in situ* spectroscopic ellipsometry

→ Changing microstructure probed by dielectric function for $T_{RTA} \geq 500$ °C

→ Planar capacitors: *k* > 80 and leakage < 10^{-7} A/cm^2 at 1 V

Summary

Atomic layer deposition is an enabling technology for ultrathin film growth:

- **sub-monolayer growth** control with **excellent conformality**
- **variety of materials** at **low deposition temperatures**

***In situ* spectroscopic ellipsometry during ALD provides many merits:**

- By **monitoring the film thickness** as a function of the number of cycles the **growth rate per cycle** can be calculated ***during*** the ALD process
- **ALD saturation curves** can be obtained in a ***single*** **deposition run**
- **Nucleation behavior** can be studied on various substrates
- **Sub-monolayer level** surface changes can be probed
- **Optical film properties** can be obtained from the **dispersion relation**
- **Electrical properties** can be calculated from the **Drude absorption** in metallic films
- Insight into **crystalline phase** and **composition** of the films can be derived from the “shape” of the energy dispersion

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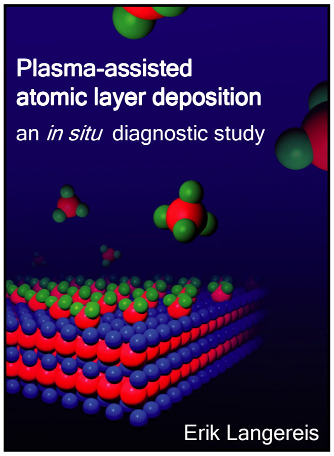
Dutch technology foundation

PhD thesis



Plasma-assisted atomic layer deposition

an *in situ* diagnostic study

Erik Langereis

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