Spatial Atomic Layer Deposition a novel very fast atmospheric pressure deposition technique

bringing new possibilities for nano-scaled and nano-designed coatings for a range of large area glass and foil based applications

Prof. Drs. Karel Spee (karel.spee@solliance.eu)

28 June 2017 - GPD Workshop

Holst Centre
Open Innovation by IMEC and TNO

TNO

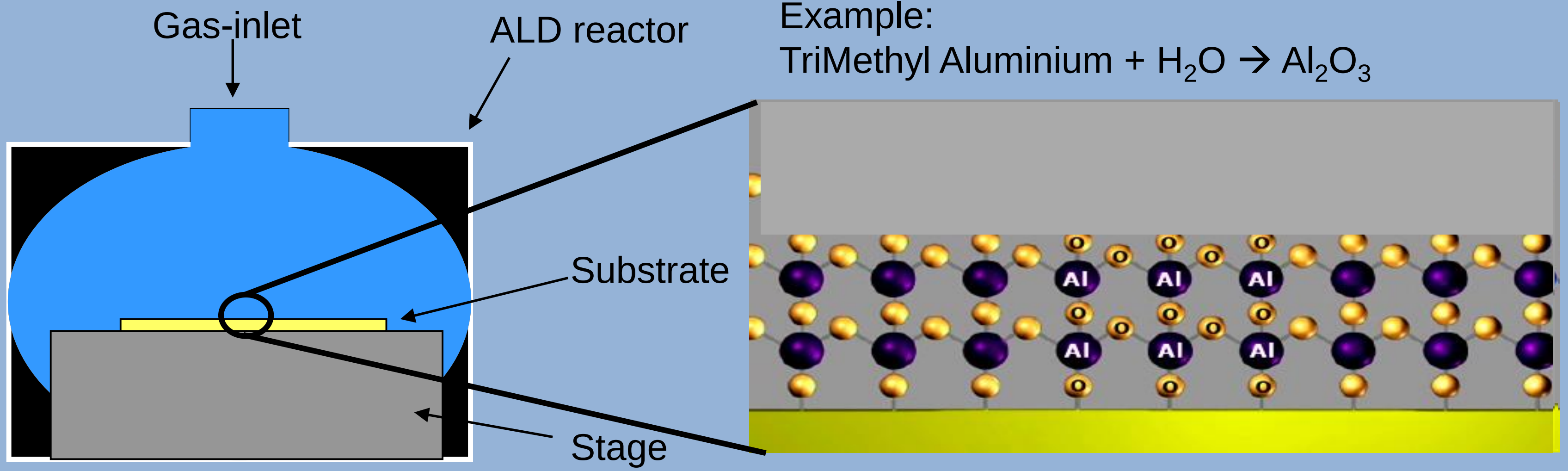
SOLAR RESEARCH
SOLLIANCE
LED BY IMEC - ECN - TNO

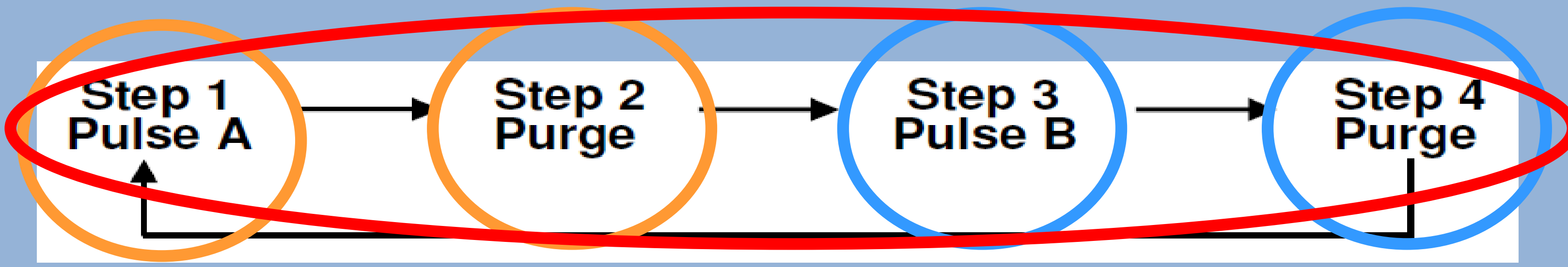
Introduction

- **Intro to spatial ALD**
- **Overview on SALD equipment**
- **Overview on Applications**
  - **Photovoltaics**
  - **Flexible electronics**
  - **Glass based products**
- **Conclusions**

What is Atomic Layer Deposition

Example:
TriMethyl Aluminium + $H_2O \rightarrow Al_2O_3$



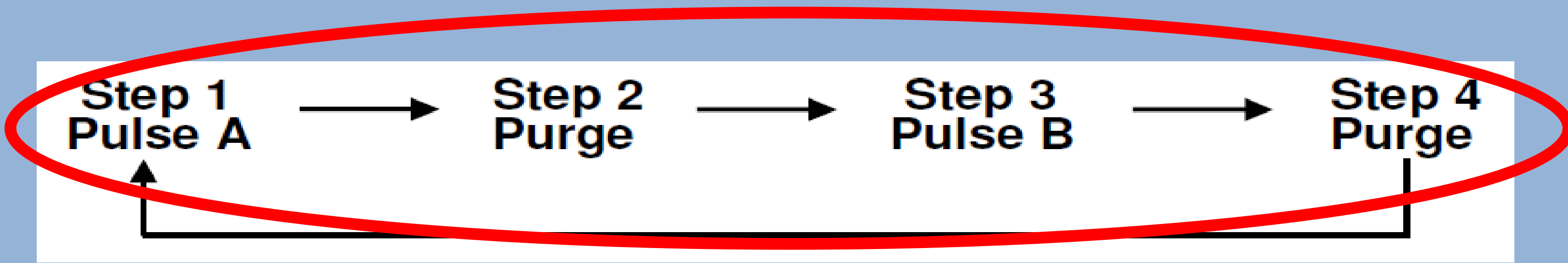


What is Atomic Layer Deposition

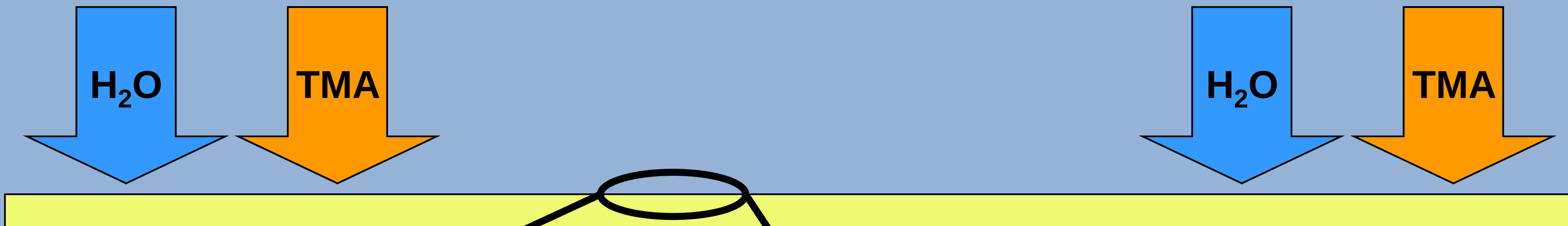
Example:
TriM

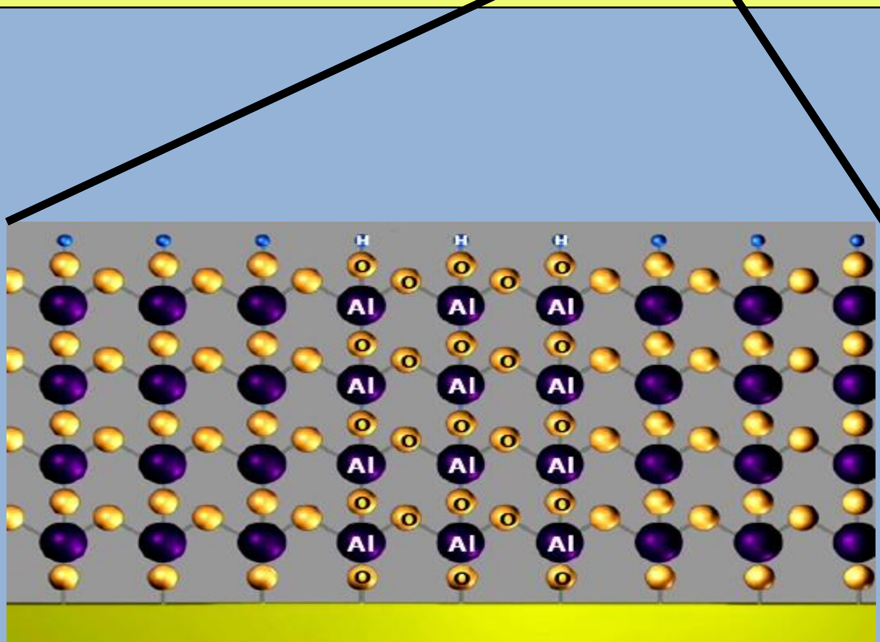
- Excellent conformality
- Extreme layer thickness control
- Wide variety of materials
- Reactor geometry, flow layout & temperature less critical

- Low deposition rate
- Inefficient precursor use
- Backside deposition & coating on walls reactor
- Not economically feasible for many applications



Spatial separation of half-reactions





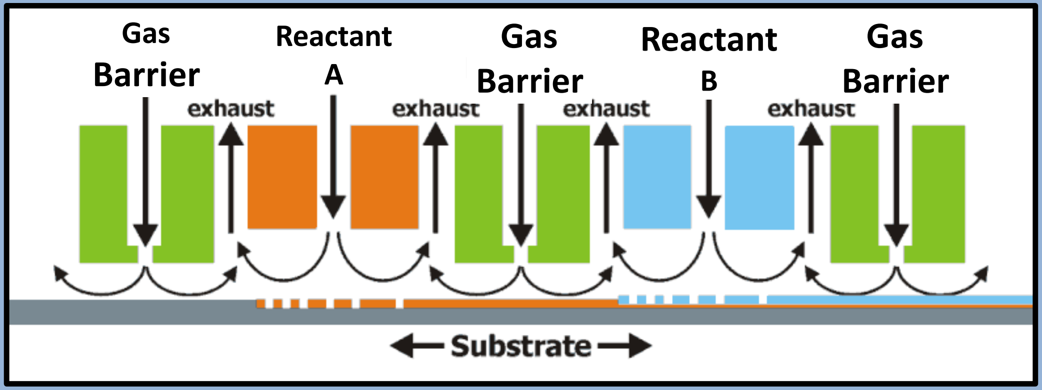
100x speed increase possible

How to keep reactions separated?

How to do the mechanics?

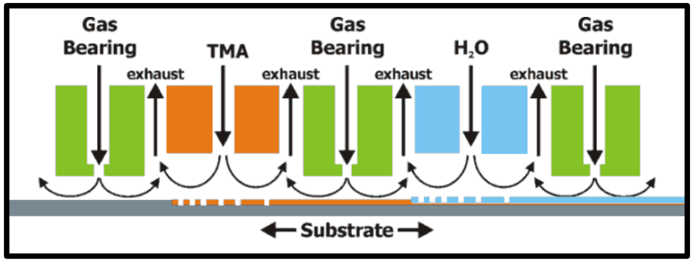
Spatial Atomic Layer Deposition

- TNO solution:
- Atmospheric pressure Spatial Atomic Layer Deposition



- Spatial separation of half reactions instead of time-separated
- Gas bearings maintain very close distance between injector and substrate → Typically 10-20 µm
- No intermixing of precursor and reactant

S-ALD Advantages



- **Atmospheric pressure: no vacuum! → compatible with IJP, slot-die, etc.**
- **Allows roll-to-roll and large area sheet-to-sheet processing**
- **Deposition rates ~nm/s: Hours become minutes!**
- **No parasitic deposition**
- **High precursor yield**
- **Premixing of precursors possible**
- **Many materials deposited so far:**
  - Al_2O_3, TiO_2, SiO_2, HfO_2, ZnO, Al:ZnO, In:ZnO, InZnO, InGaZnO, $ZnSnO_x$, Ag, Alucone (MLD) and many more

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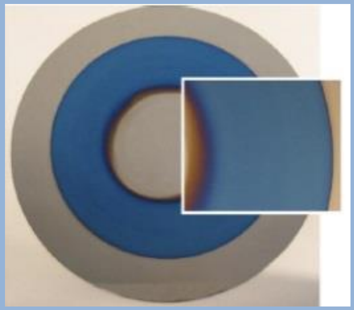
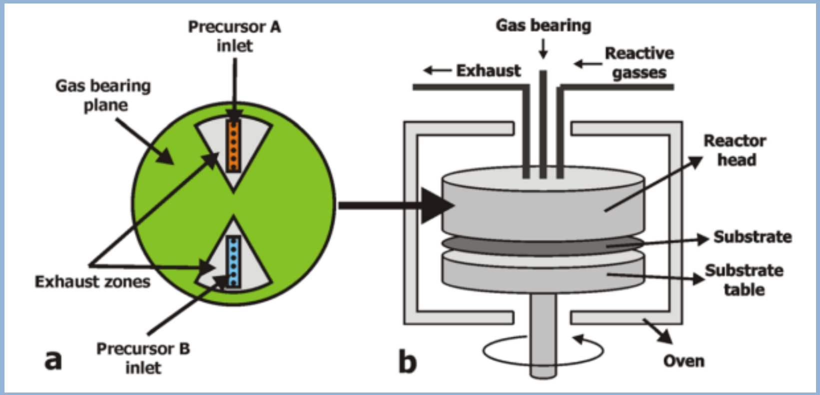
TNO Lab reactor(s)

- Rotating reactor
- Head floating on substrate/substrate table by a gas bearing plane → Proximity 20 µm
- Total reactor placed in furnace





Poodt et al, Adv. Mat. 22(32) 2010, p. 3564–3567

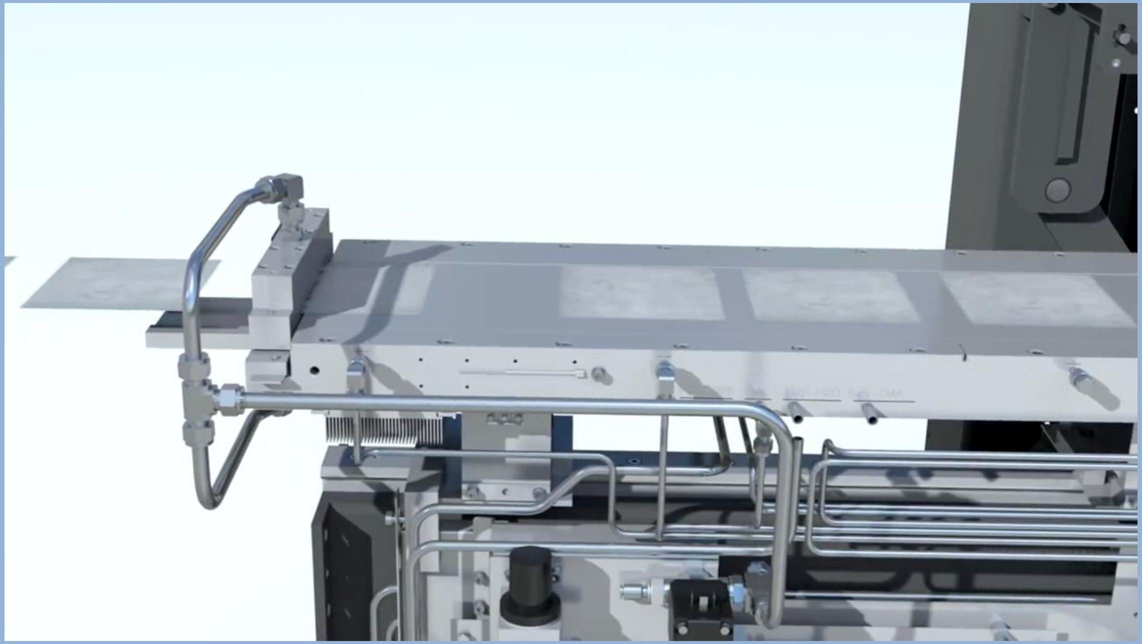
SoLayTec

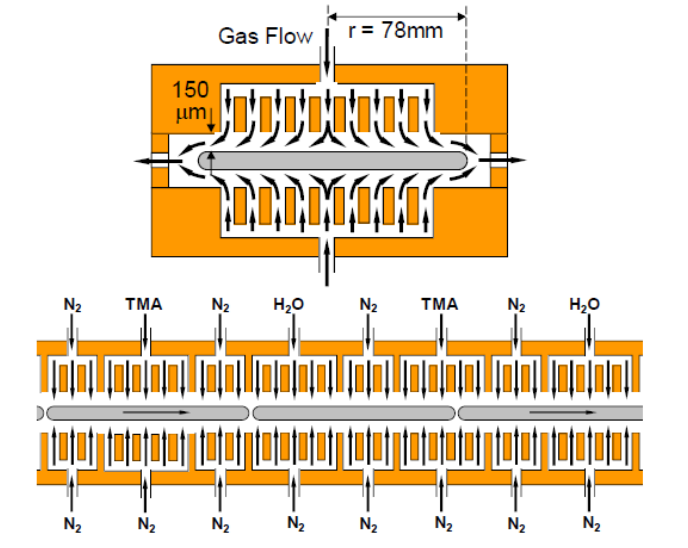
- **Deposition of Al_2O_3 passivation layers on c-Si solar cells**
- **Up to 4800 wph; Dep. Rate 4, 6 or 8 nm/s; T_{dep} 180-225 °C**

https://www.youtube.com/watch?v=juXHYLfaGVU

Levitech

- Deposition of Al_2O_3 passivation layers on c-Si solar cells
- Up to 3600 wafers/hr; 6 nm at 1nm/meter; CoO 0.025 €/wafer
- Independent from TNO development

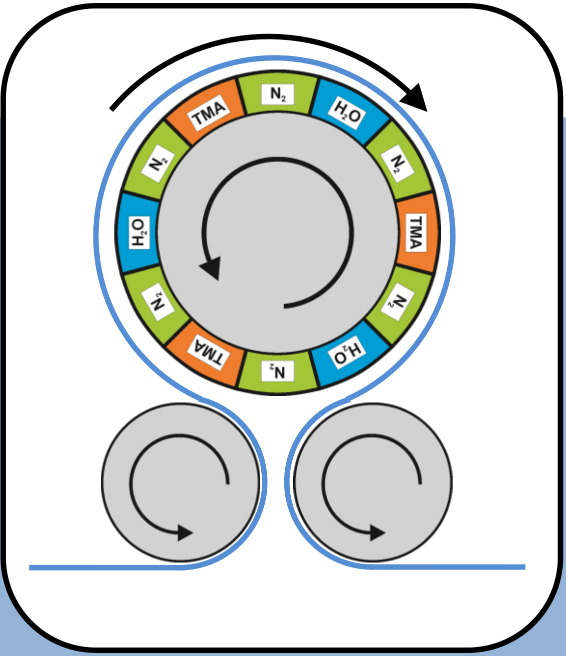


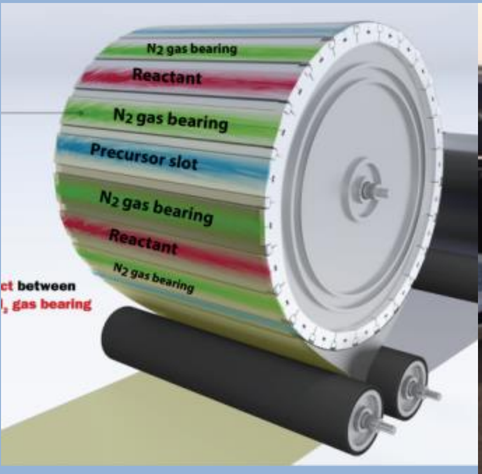


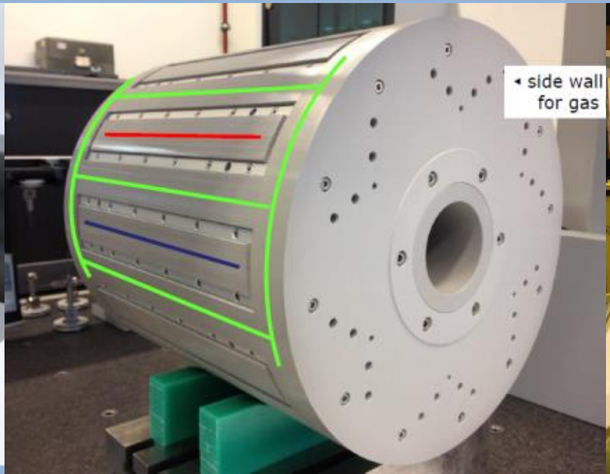
https://www.youtube.com/watch?v=ywBd9K8yJX0

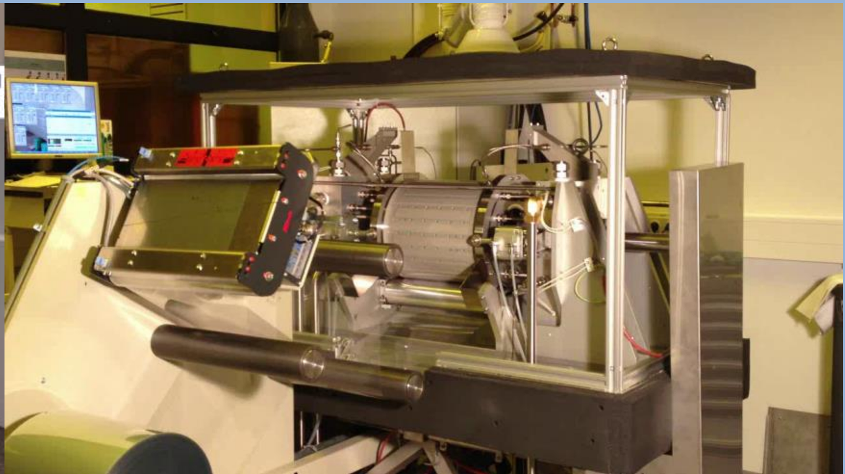
TNO R2R S-ALD

- **Gas bearings prevent foil touching Drum**
- **Roll moves opposite foil direction**
  - Foil clockwise slowly; Drum anti-clockwise fast
- **Nr of cycles depends on Nr of precursor slots, speed of foil and speed of Drum**









TNO R2R S-ALD

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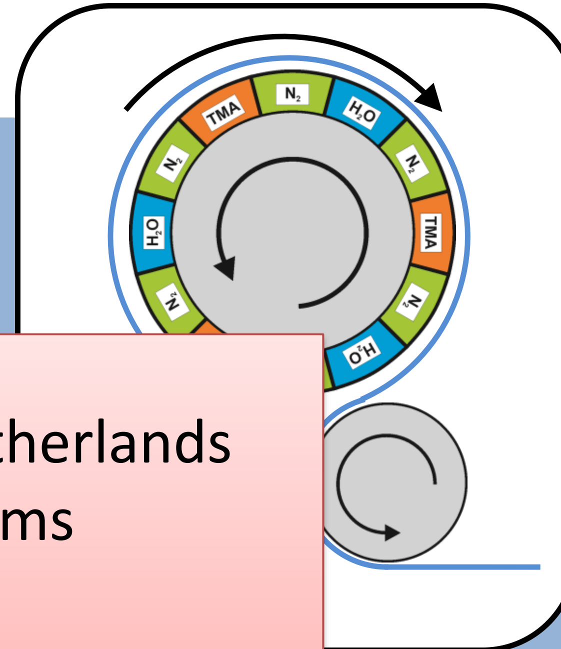
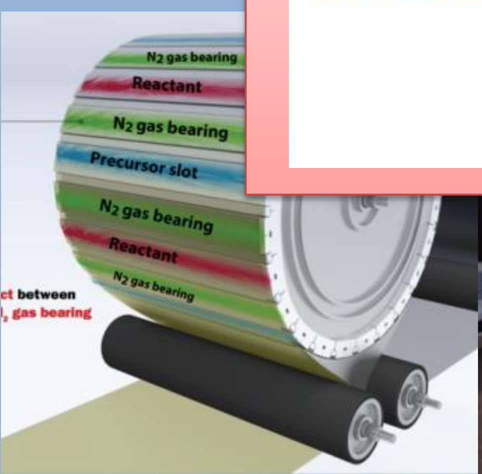
  -
- Nr
  sl

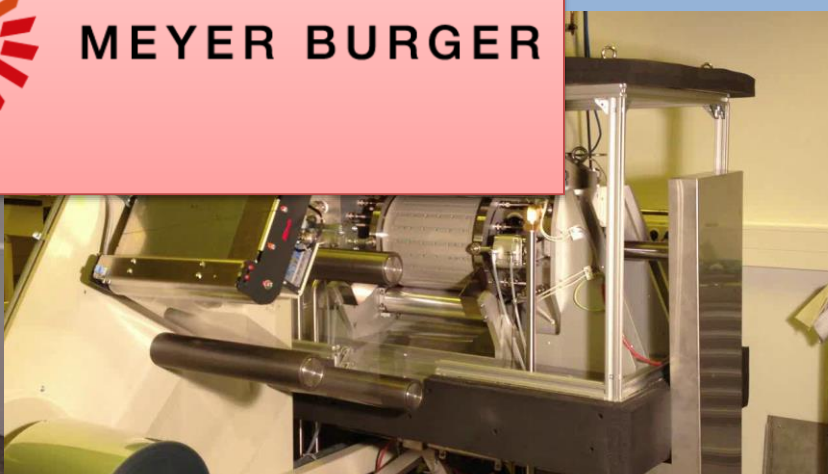


VDL-FLOW & Meyer Burger in the Netherlands
sell R2R S-ALD production systems

VDL FLOW

MEYER BURGER



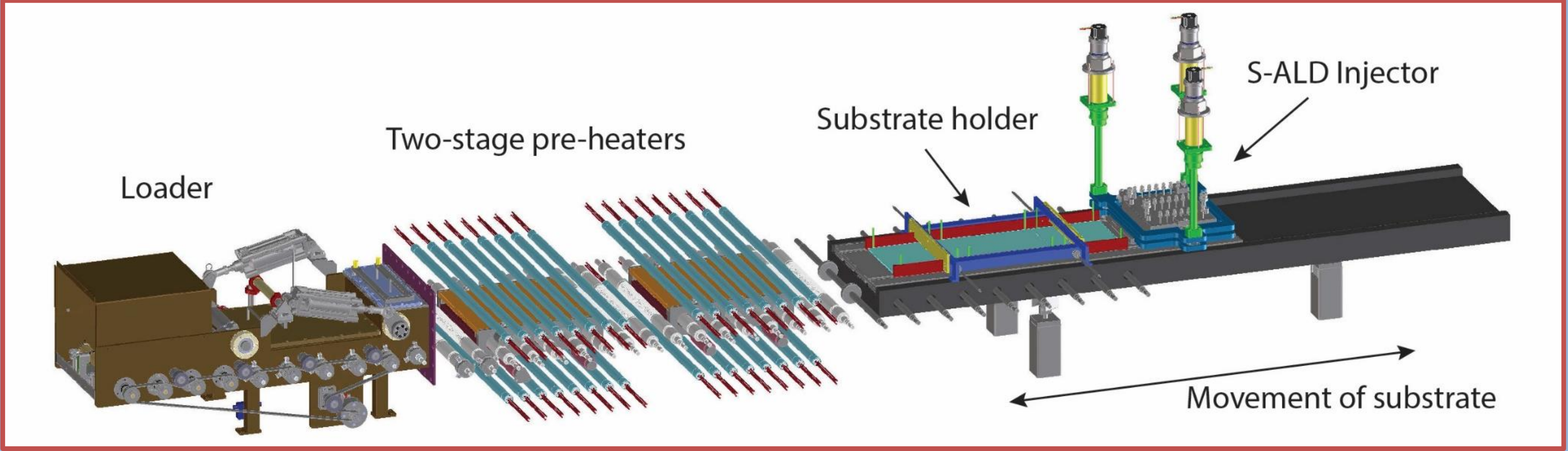


Up-scaling: R2R Spatial ALD

- **Large-scale tool available by Meyer Burger (the Netherlands)**

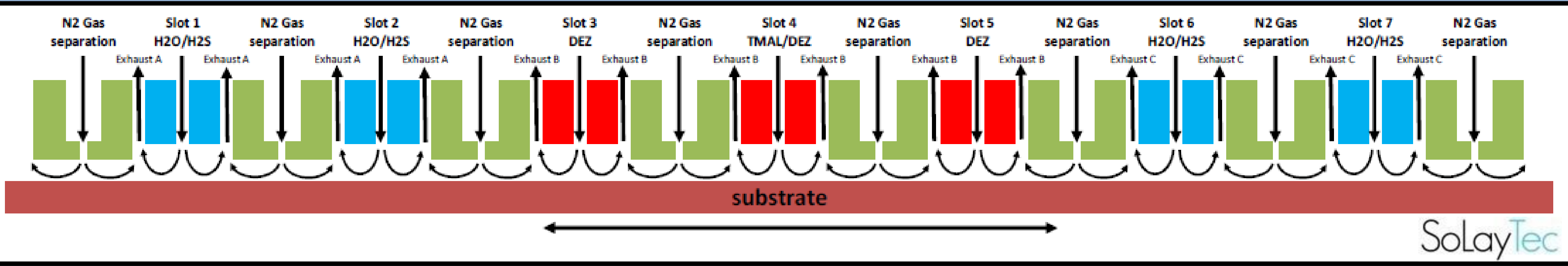
Large-area S2S Spatial ALD pilot line

- **Substrate: Maximum size 325 x 400 mm (includes Gen1)**
- **T_{dep} up to 350°C**

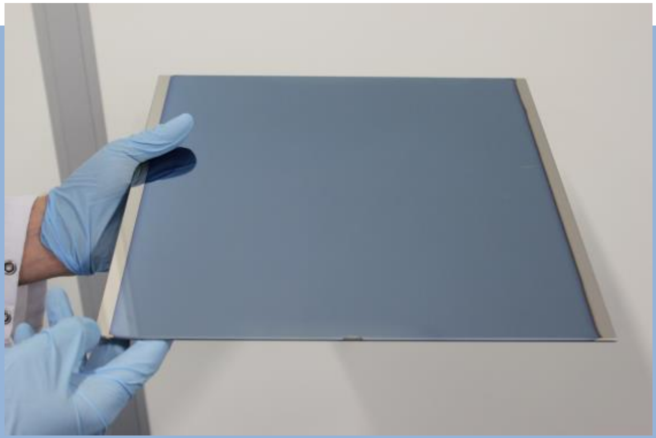


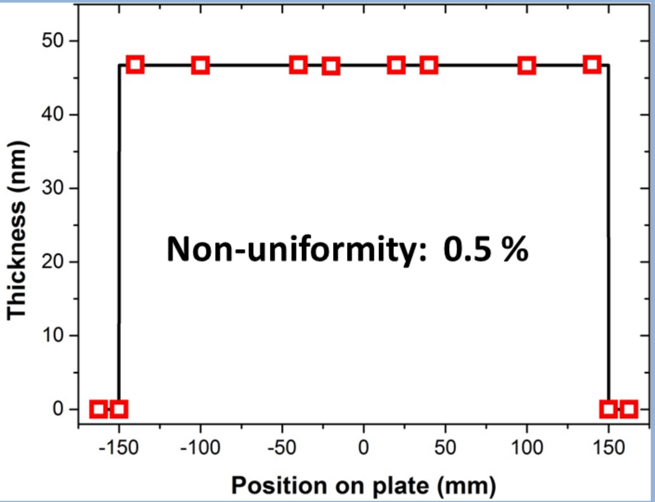
S2S SALD Pilot line

- **7 slot injector**
- **Precursors separated or premixed**
  - H_2O & H_2S
  - DEZ & TMA
- **Layers possible: ZnO, Al:ZnO, Al_2O_3, Zn(O,S), Al:Zn(O,S)**



S2S SALD Pilot line

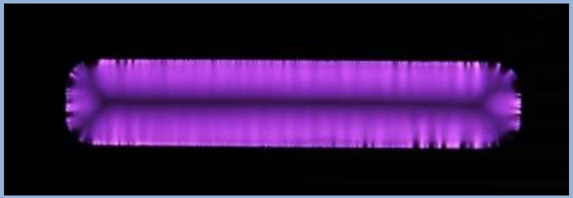




Atmospheric Plasma activated S-ALD

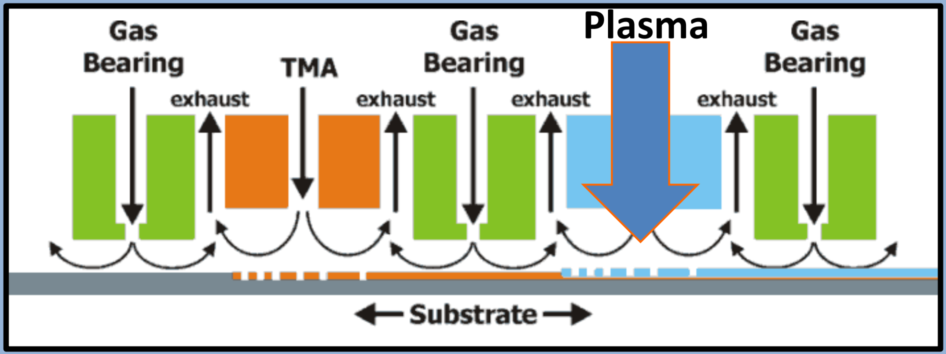
- **Surface Dielectric barrier Discharge plasma with N_2 or O_2 plasma**
- **Ag, SiO_2, ZnO, Al_2O_3, TiO_2**

Hans Pulker Award ICCG11



SDBD blanket

SDBD linear jet



Creygton et al, Proc. ICCG 11 Braunschweig, 2016, Developments in Plasma Enhanced Spatial ALD for High Throughput Applications

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  - **Flexible electronics**
  - **Glass based products**
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Prospects for Solar cell manufacturing

Solar cell type	Application	Thickness (nm)	ALD materials				
AlGaAs/GaAs	Multijunction Absorber	30–400	GaAs	AlGaAs	AlAs		
a-Si:H	Transparent conductive oxide	400	ZnO:B				
c-Si	Surface passivation layer	5–30	Al_2O_3				
CIGS	Buffer layer	10–70	ZnSe	(Zn,Mg)O	Zn(O,S)	In_2S_3	GaS
	Diffusion barrier layer	100–300	Al_2O_3				
	Encapsulation layer	10–55	Al_2O_3				
CdTe	Window layer/n-type layer	~100	Zn(O,S)				
Organic	Encapsulation layer	15–200	Al_2O_3	Al_2O_3 / HfO_2			
	Electron selective layer	1–35	Al_2O_3	ZnO	TiO_2		
	Transparent conductive oxide	150	ZnO:Al				
Dye-sensitized	Barrier layer	0.1–25	Al_2O_3	TiO_2	HfO_2	ZrO_2	
	Photoanode	5–90	TiO_2	ZnO:Al	SnO_2	ZnO	TiO_2:Ta
	Blocking layer	7–20	SnO_2	TiO_2			
	Compact layer		HfO_2				
	Transparent conductive oxide	7	In_2O_3:Sn				
	Sensitizer	5	In_2S_3				
Heterojunction nanostructured	Absorber		Cu_xS				

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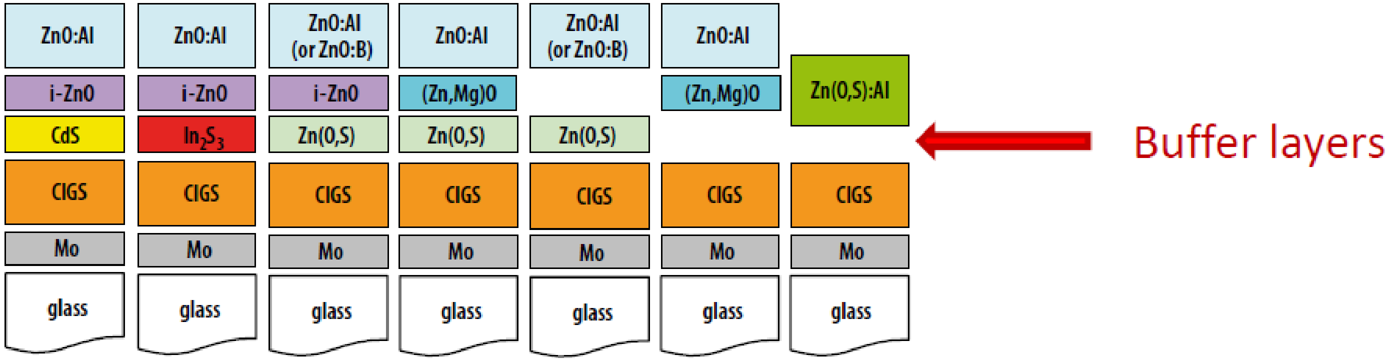
Production equipment by:
Solaytec
Levitech

van Delft et al, Semicond. Sci. Techn. 27 (2012) 074002

Zn(O,S) buffer layers in CIGS solar cells

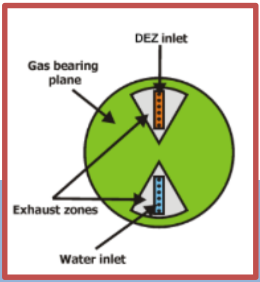
- **CdS buffers deposited by Chemical Bath Deposition (CBD)**
  - Cd unwanted compound & CBD of CdS is strongly polluting
- **Several groups studied alternatives using ALD**



W. Witte *et al*, Vakuum in Forschung und Praxis, 26 (2014) 23.

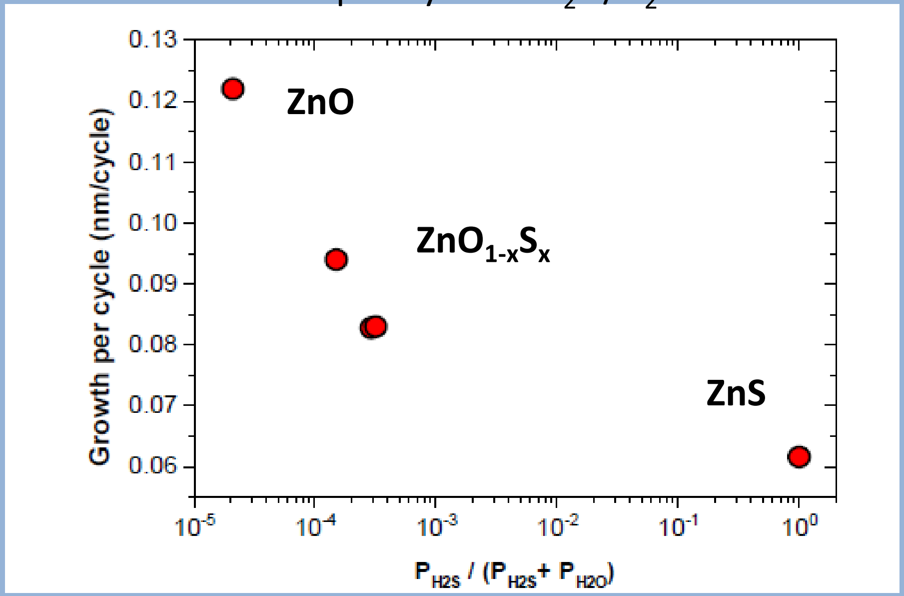
- **Zn(O,S) is promising candidate**
  - Increased efficiency (~+0.5%) & Comparable cost (~USD 0,02/Wp)

Zn(O,S)
in labscale S-ALD reactor

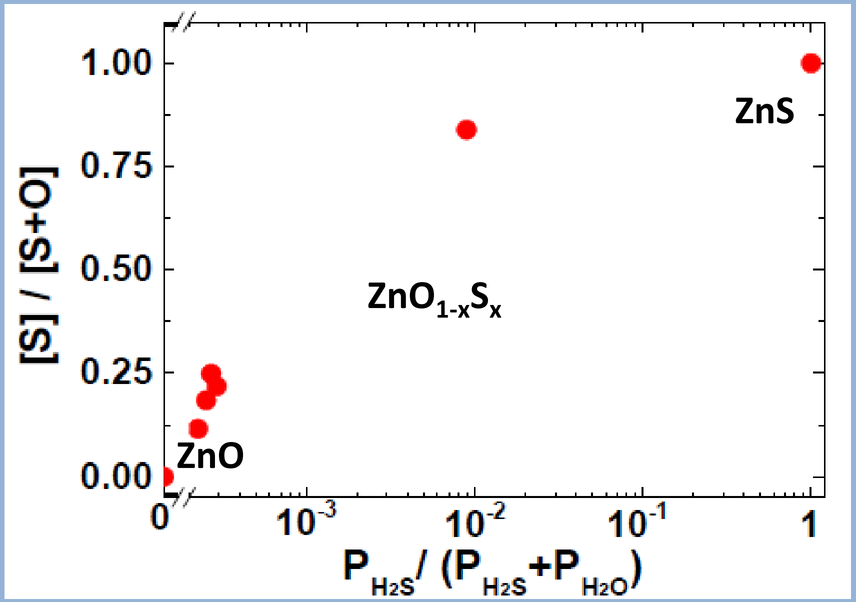


- Precursor DEZ + premix of H_2O/H_2S
- Film composition can be continuously controlled

Growth per Cycle vs H_2O/H_2S ratio



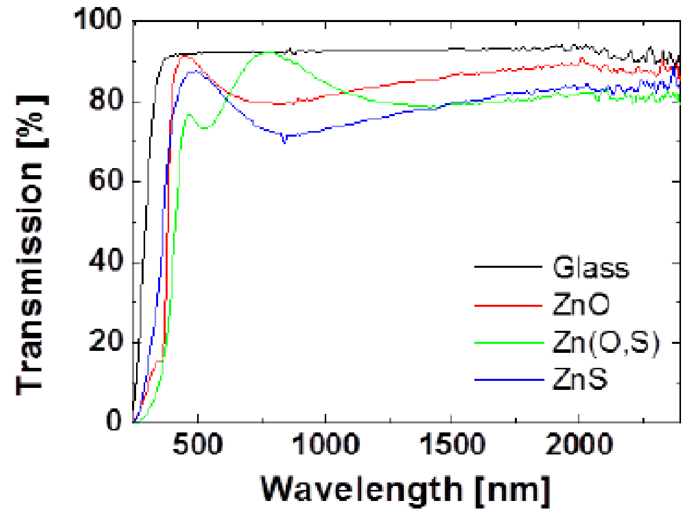
Film composition

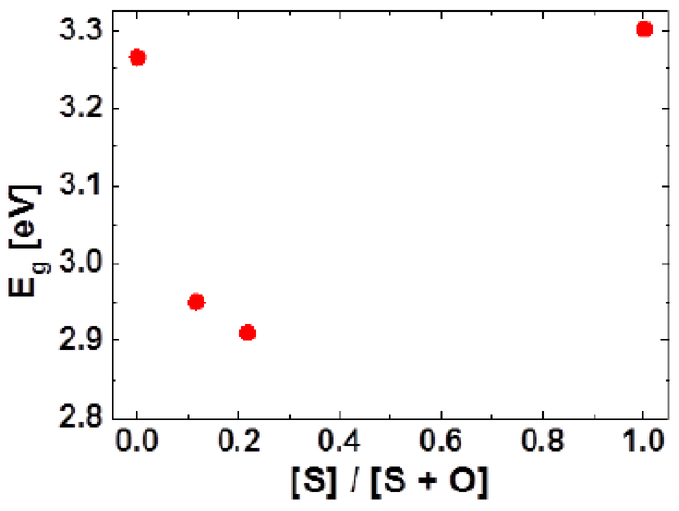


Zn(O,S) buffer layers

Results: Transparency

- Plotted below are $ZnO_{1-x}S_x$ with x=0 (ZnO), x=1 (ZnS) and x=0.22
- Characteristic "bowing " of the band gap observed, according to literature





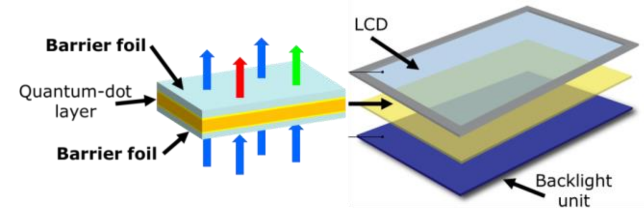
Flexible electronics

Application	ALD materials
Moisture barriers & Encapsulation	Al_2O_3 HfO_2 TiO_2
Transparent Oxide Semiconductors Thin film transistors	GIZO, ZnO
TCO's	AZO Graphene#
Buffer layers	ZnO
Light management Anti-reflection	TiO_2, SiO_2, ZrO_2

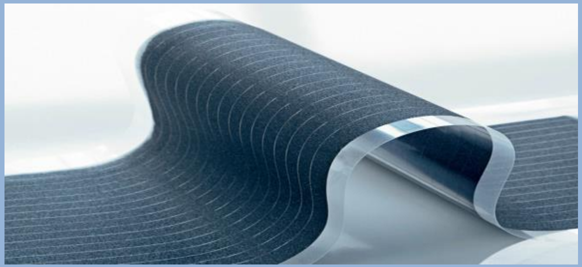
(# in development)

R2R Spatial ALD for barrier foils

- **Many applications require encapsulation**
  - Organic PV, CIGS, quantum-dot, Perovskites,



- **Glass-based solutions are expensive, heavy and not flexible**



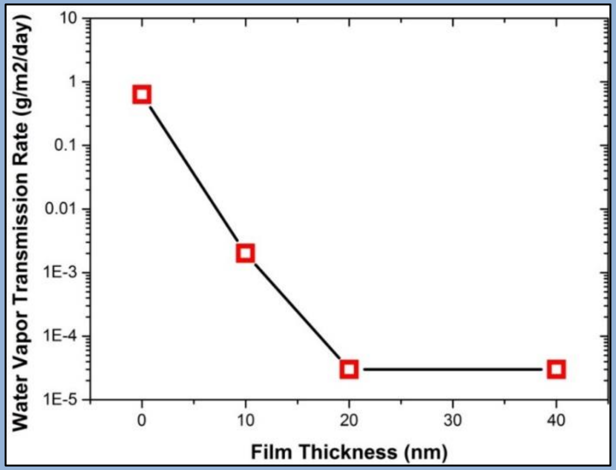
- **Barrier requirements:**
  - WVTR lower than 10^{-4} $g/m^2/day$
  - Highly transparent
  - For PV: 20+ years lifetime
  - High-throughput, low-cost

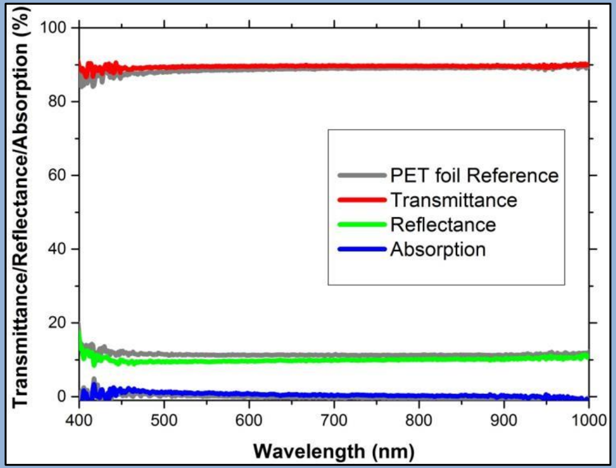
R2R Spatial ALD for barrier foils

- **Example: Al_2O_3 on PET foil**
- **No planarization, no pre-treatment, no cleaning**

- **WVTR measured by optical Calcium test**
- **Overall WVTR for 20 nm Al_2O_3:**
  - 2×10^{-5} g/m2/day at 20 ºC/50 %RH
  - 4×10^{-4} g/m2/day at 60 ºC/90 %RH

- **Excellent transparency**

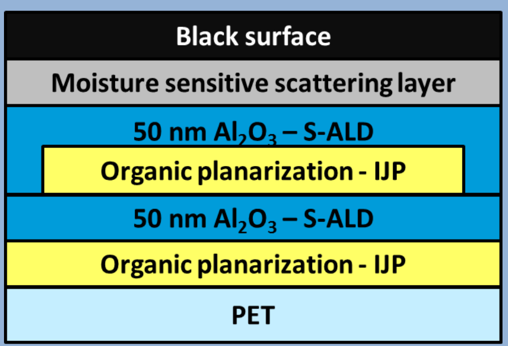


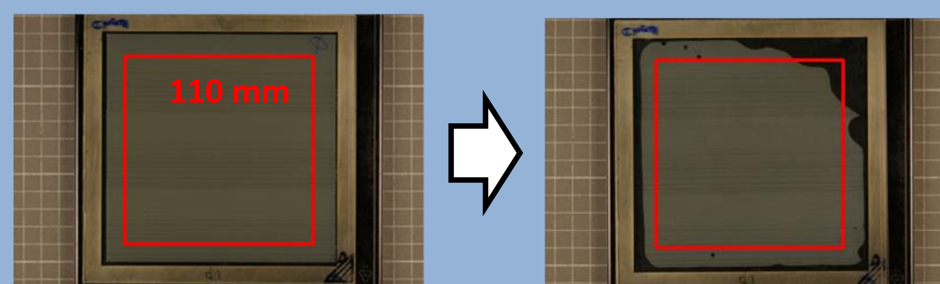


Spatial ALD of oxide semiconductors

- **Sheet-to-sheet Spatial ALD for *thin-film encapsulation***

- **Example: PET - Organic planarization – 50 nm Al2O3 – Organic – 50 nm Al_2O_3; 30 cm x 30 cm.**
  - Samples were not made in cleanroom: particles unavoidable





t = 0 hrs

t = 1100 hrs at 60ºC/90% RH

- **No visible defects after more than 1100 hrs at 60 ºC / 90 % RH**
- 1100 hrs at 60 ºC / 90 % RH is ~ 2.5 years at ambient conditions

InGaZnO for flexible low power consumption displays

Holst Centre
Open Innovation by IMEC and TNO

IGZO vs a-Si:H

- 20-50 times higher electron mobility
- twice the resolution
- 80-90% power saving

It's time !

Apple

Dell

Apple

Asus

2013

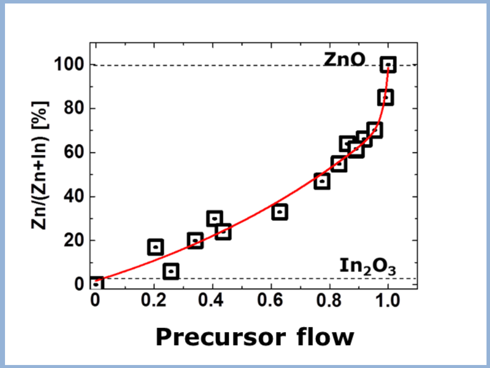
Commercial rigid displays using IGZO transistors

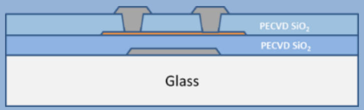
2004

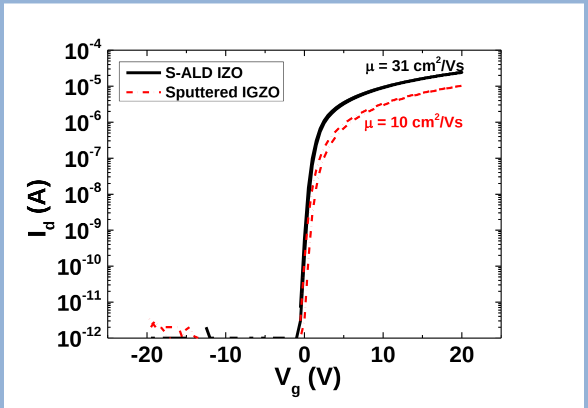
First flexible transparent transistor based on IGZO

Spatial ALD of oxide semiconductors

- **Sheet-to-sheet Spatial ALD for high mobility oxide semiconductors**
- **Example: InZnO (IZO) oxide semiconductor →higher mobilities than IGZO**
  - With our proprietary Spatial ALD process: full control of composition







- **Spatial ALD IZO Integrated ESL TFTs on 150 mm substrates**
  - 15 nm SALD IZO compared to baseline 15 nm sputtered stateof-the-art IGZO
  - Mobility >30 cm^2/Vs (10 cm^2/Vs for IGZO), Threshold / Onset ~ 0V. Down to 5 nm channels
  - Excellent bias stress stability

Possibilities for Display, Architectural & Automotive glass

Application	ALD materials
Moisture barriers & Encapsulation	Al_2O_3 HfO_2 TiO_2
Transparent Oxide Semiconductors Thin film transistors	GIZO, ZnO
TCO's	AZO Graphene#
Buffer layers	ZnO
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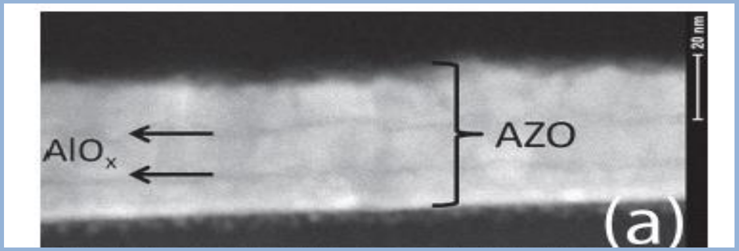
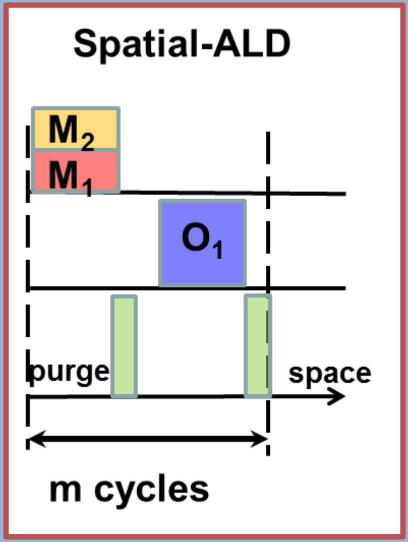
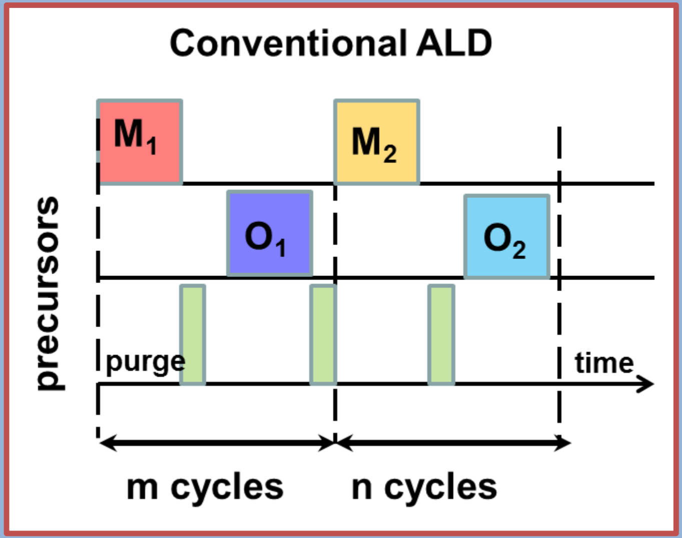
ALD of Al:ZnO

- **Premix possible with S-ALD**



TEM cross section of Al:ZnO by conventional ALD

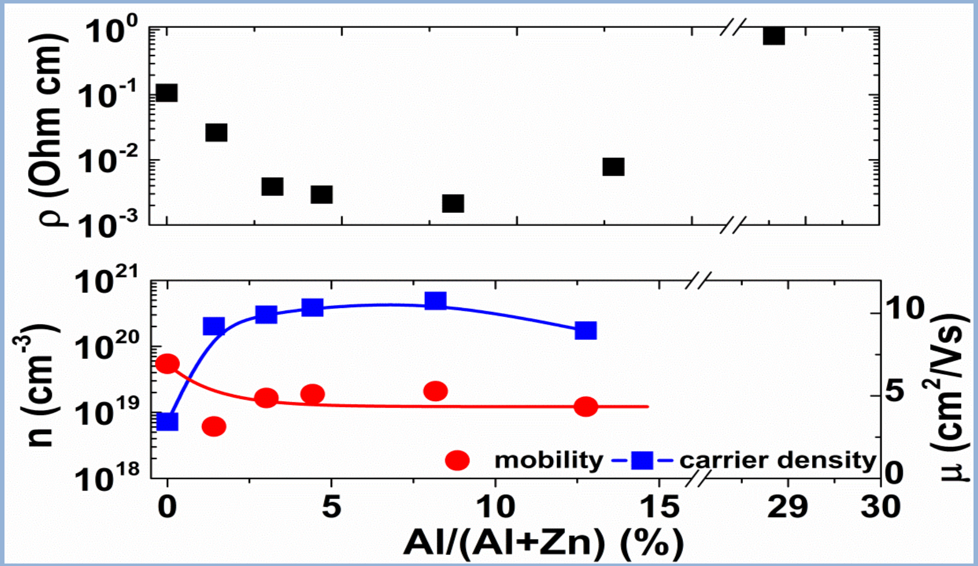


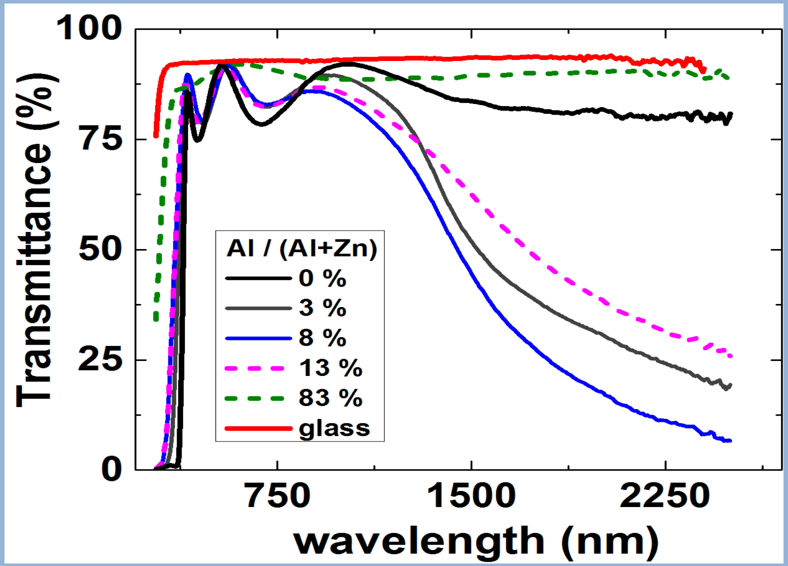


Y. Wu et al Journal of Applied Physics 114, 024308 (2013)

Spatial atomic layer deposition of Al:ZnO

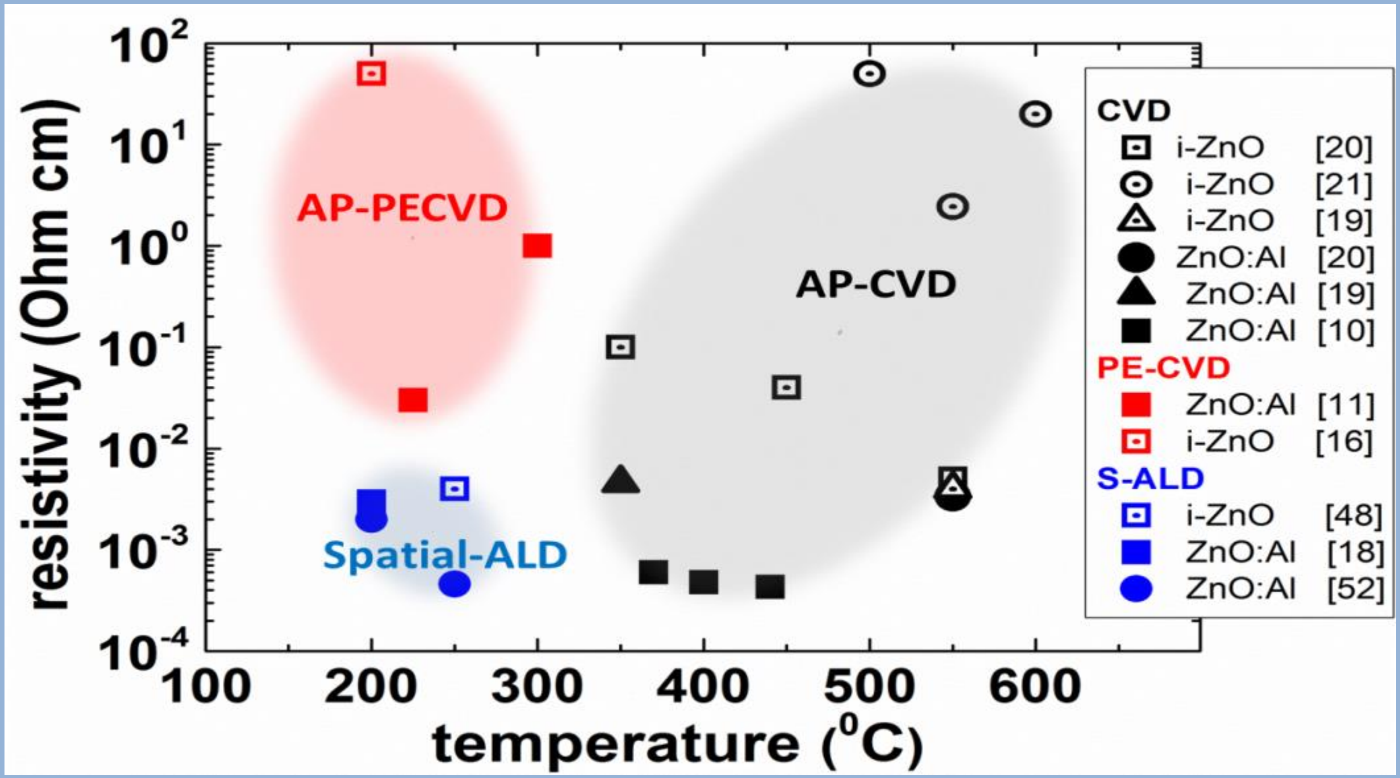
- Precursors DMZ, TMA and H_2O





A. Illiberi et al ACS Applied Materials and Interfaces 5, 13124 (2014)

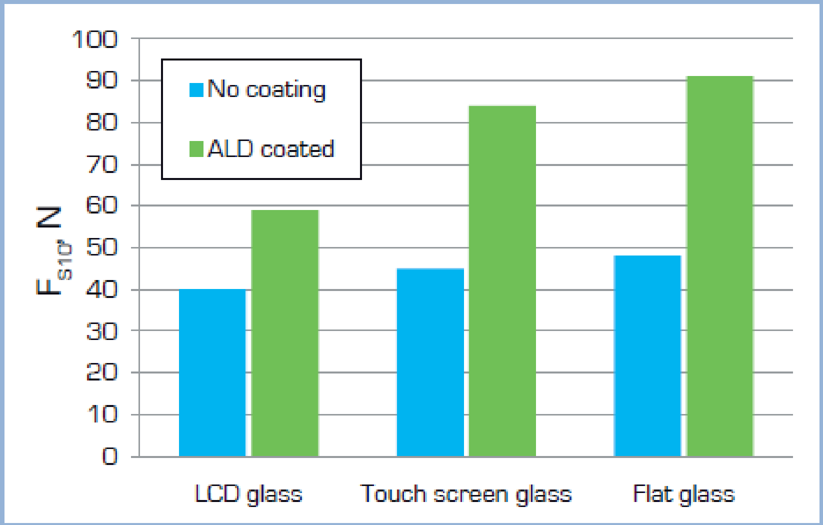
Spatial atomic layer deposition of Al:ZnO

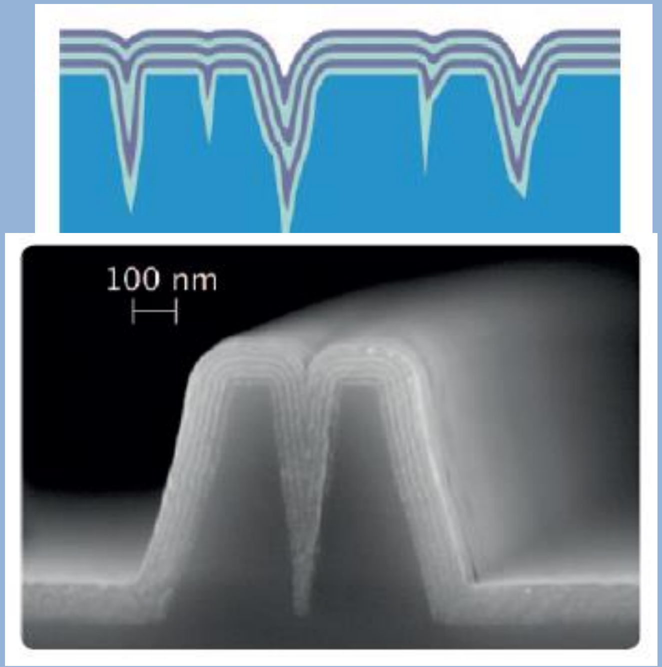


A. Illiberi et al. Solar Energy Materials and Solar Cells 95, 1955 (2011)

Strengthened Glass

- **Beneq multilayer ALD for better glass crack resistance**





Source: Beneq Strengthened Glass Brochure

Anti-reflection coatings
Optical coatings

- SiO_2, TiO_2, Al_2O_3 and other oxides have frequently been deposited by ALD
- Li et al deposited amorphous TiO_2/Al_2O_3 bilayer on BK7 @ 120°C using $TiCl_4$, TMA and H_2O

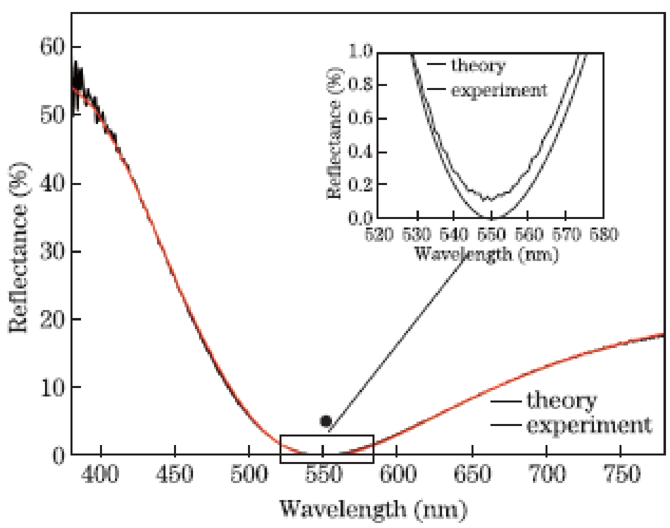
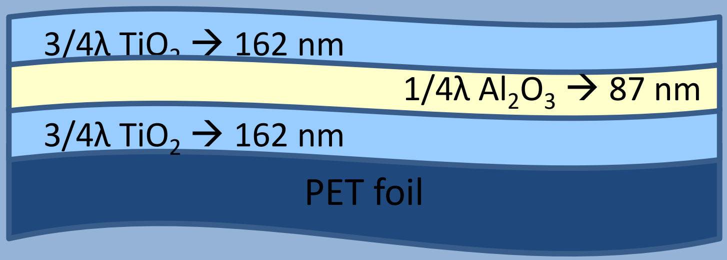


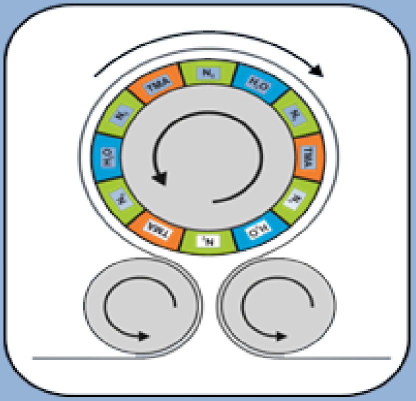
Fig. 5. (Color online) Reflectance of AR coating at 550 nm; at the top right corner, the reflectance is demonstrated in detail, and the reflectance is no more than 0.2% at 550 nm.

Li et all, Chinese Opt. Lett., COL 11 (Suppl.) S10205(2013)

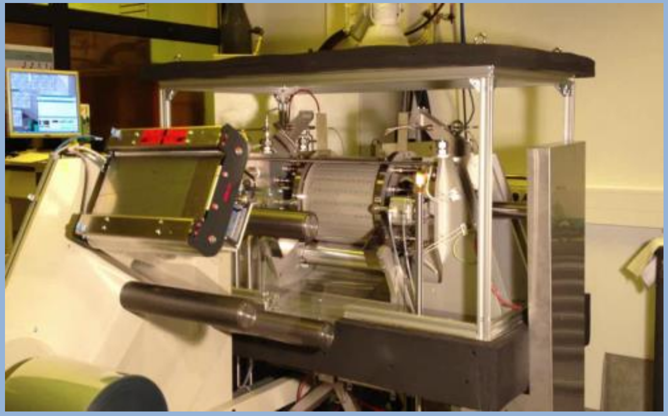
R2R S-ALD of an optical stack

- **Substrate PET**
- **$TiCl_4$ + H_2O and TMA + H_2O**
- **Deposition temperature: 100 °C**



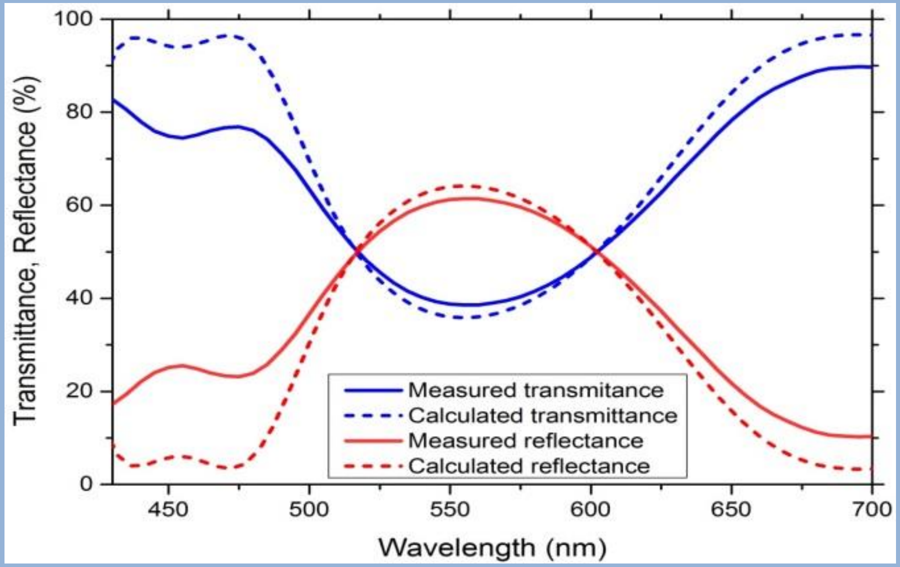


- **An optical stack of Al_2O_3 and TiO_2 was calculated to achieve a reflectance maximum at 525 nm on PET foil**



R2R S-ALD of an optical stack

- **Uniform reflective coating with excellent optical properties**
- **Transmittance and Reflectance fit excellently with an offset of only λ~28 nm**



Self-cleaning TiO_2

- **Both Anatase & Rutile TiO_2 using ALD reported in literature**

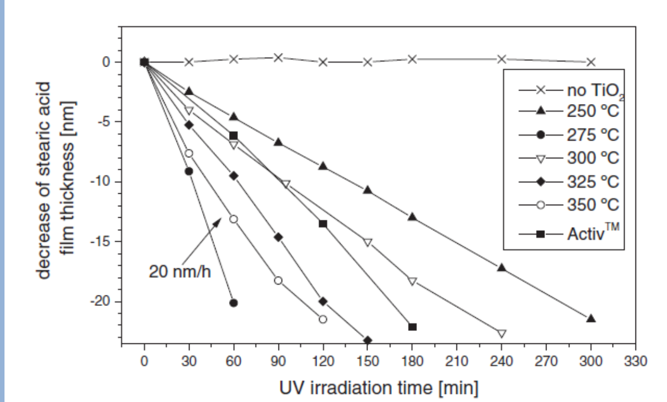


Fig. 5. Time dependence of the stearic acid layer thickness decrease, measured by FTIR, for TiO_2 films deposited at various temperatures. Pilkington Activ self-cleaning glass is included for comparison.

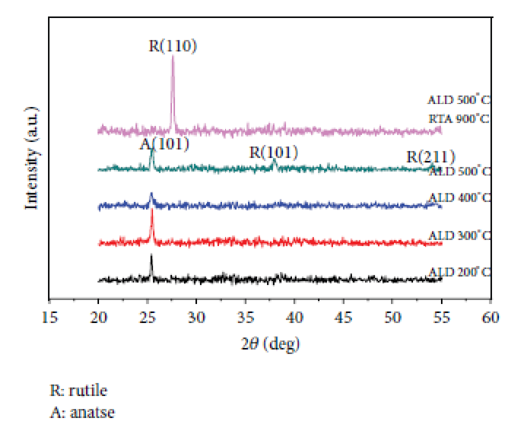


FIGURE 4: XRD patterns of TiO_2 thin films deposited at 200°C, 300°C, 400°C, 500°C, and RTA 900°C.

Anatase: $Ti(OMe)_4$ + H_2O ALD 250-500°C

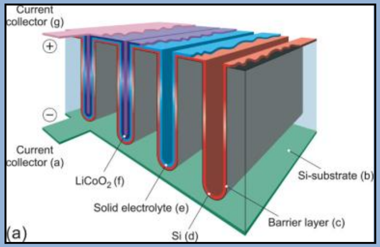
Pore et al, Chem. Vap. Dep. 2004, 10, No.3 p.143

Rutile: $TiCl_4$ + H_2O ALD 500°C + RTA 900°C

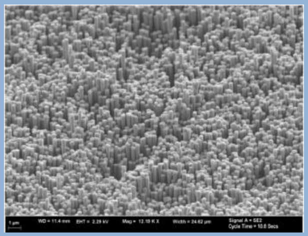
Yu et al, Int. J. Photoenergy, Vol 2013, ID 431614

Introduction: ALD in porous substrates

- **ALD is famous for its ability to conformally coat high aspect ratio structures and porous substrates**
- **New applications are emerging for ALD in porous materials**
  - 3D batteries, smart textiles, catalysis, membranes……

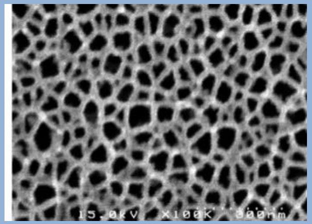


Philips/ Eindhoven University
P. Notten et al, Adv. Mater. 19 (2007) 4564



D. DeMeo et al, Nanotechnology and Nanomaterials » "Nanowires - Implementations and Applications“ Chapter 7 (2011)

Tyndall (M.Pemble)
https://www.youtube.com/watch?v=DG-tNR0mXH0

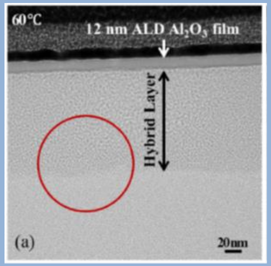


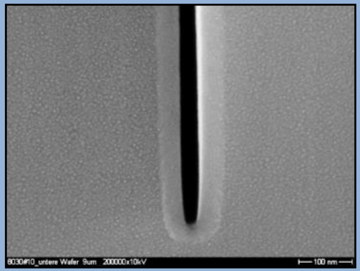
Integrated On-Chip Energy Storage Using Porous-Silicon Electrochemical Capacitors, D.S. Gardner, C.W. Holzwarth, Y. Liu, S.B. Clendenning, W. Jin, B.K. Moon, C.L. Pint, Z. Chen, E. Hannah, R. Chen, C.P. Wang, C. Chen*, E. Mäkilä**, and J.L. Gustafson, Intel Corp., *Florida Int'l Univ., **University of Turku**)**

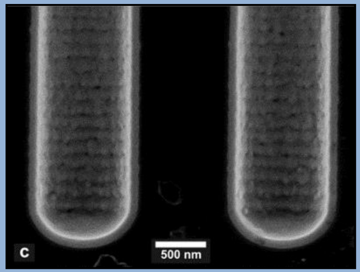
- **Often requires high throughput, large-area, roll-to-roll**
- ***Can we do this with Spatial ALD?***

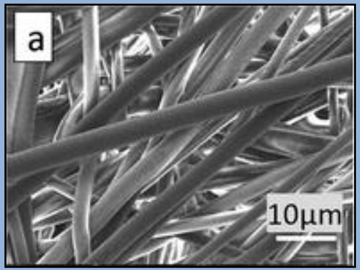
Spatial ALD in porous materials

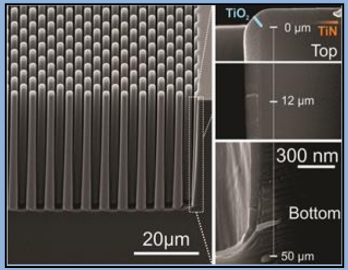
- We have demonstrated ***high speed***, high ***step coverage*** Spatial ALD at ***atmospheric pressure*** inside a variety of porous materials
- Many potential applications; Possible to use e.g. Roll-to-Roll Spatial ALD











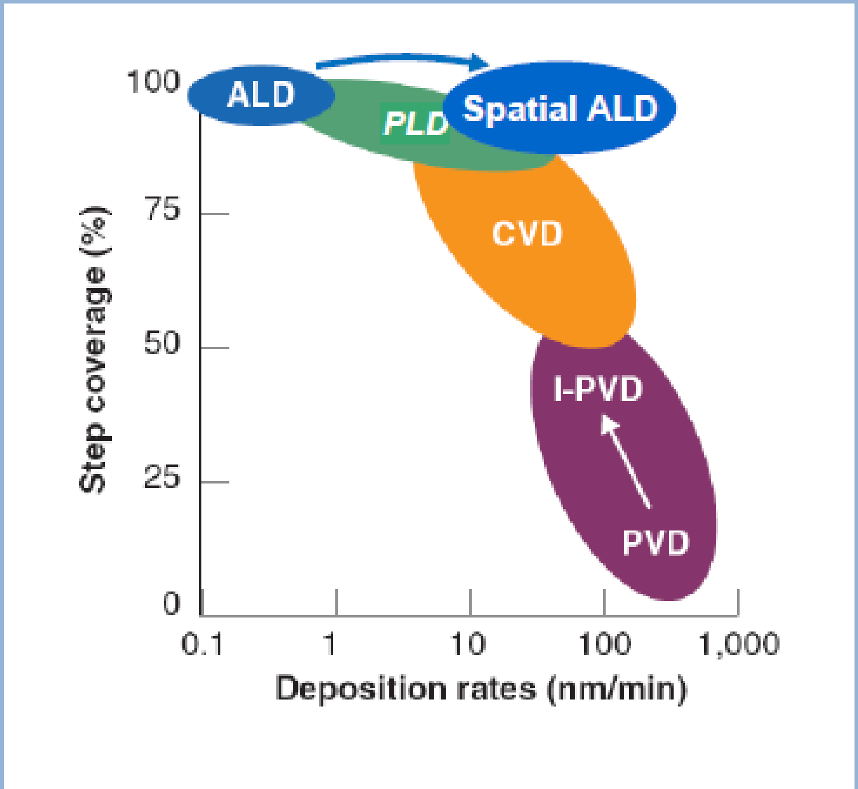
Polymer modification | Electronics | Catalysis | Textile functionalization | 3D batteries

Barriers, membranes and separators | Sensors | Photovoltaics

Nano-porous → Micro-porous

Conclusions

- **Speed enhancement up to 100x brings CoO considerably down → new application opportunities**



Conclusions

- **SALD serious competitor for PVD/CVD**
- **Many materials already deposited using S-ALD**
- **Already 4 companies who sell TNO based SALD equipment**
- **Several companies develop products using SALD**
- **Many glass and plastic foil applications possible**

Acknowledgements

- **ALD-team:**
  - Paul Poodt
  - Fieke van den Bruele
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  - Valerio Zardetto
  - Ellis Balder

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  - Ahmed Salem
  - Pradeep Panditha
  - Peter van der Weijer

- **TFT- team**
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  - Gerwin Gelinck

WWW.SOLLIANCE.EU

karel.spee@solliance.eu

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