Plasma-Enhanced ALD for Opening the ALD Temperature Window

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and Erwin Kessels

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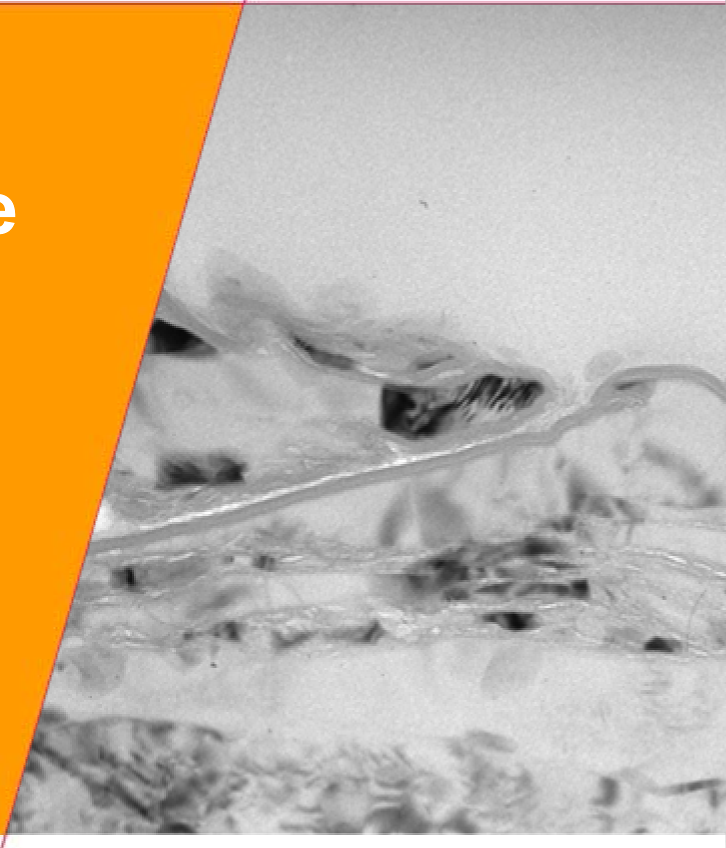
16th September 2010



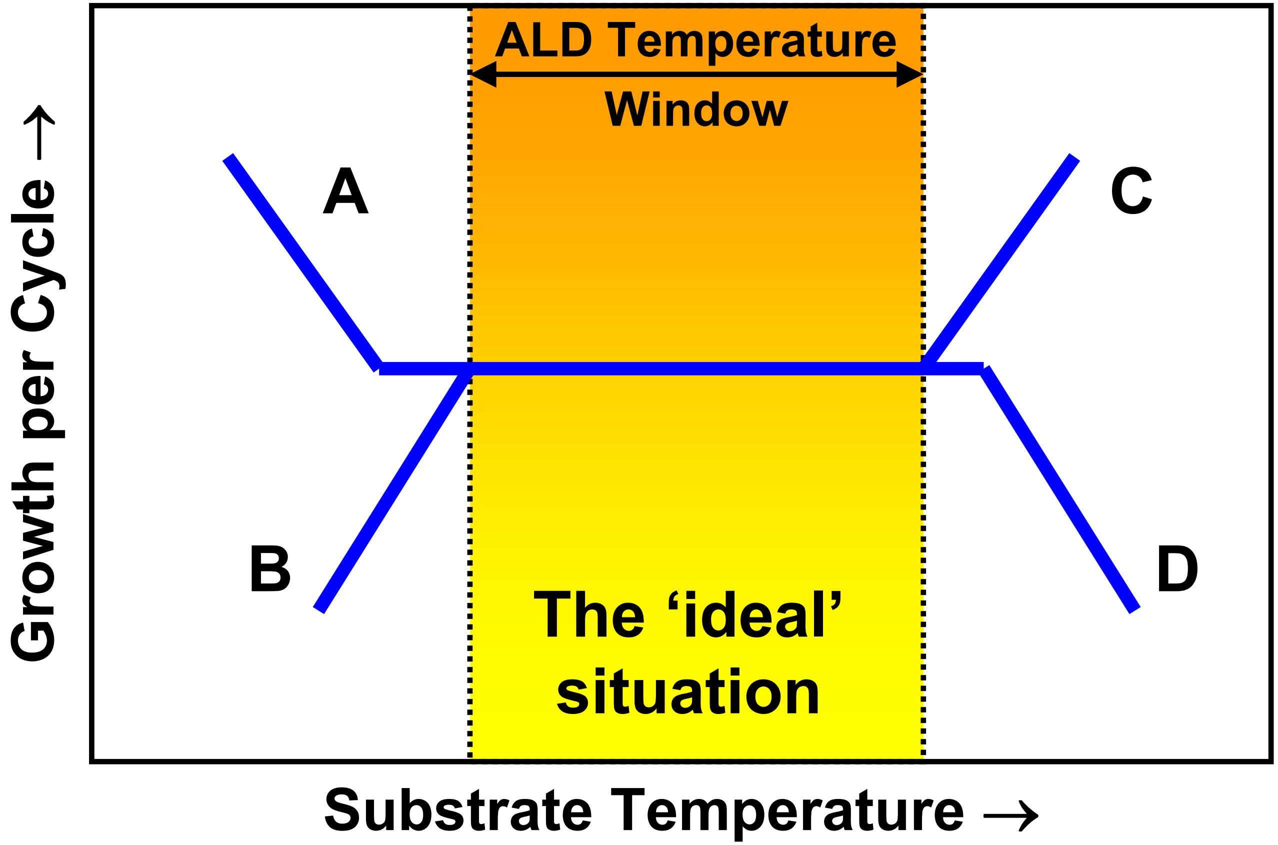
Technische Universiteit
Eindhoven
University of Technology

Where innovation starts

Outline

- **The ALD Temperature Window**
- **Plasma-Enhanced ALD**
  - What is plasma-enhanced ALD?
  - Merits
- **Experimental Details**
- **High(er) temperature ALD**
  - Motivation: Why high(er) temperature ALD?
  - Examples of ALD of TiO_2 to obtain the best electronic/optical properties
- **Low temperature ALD**
  - Motivation: Why low temperature ALD?
  - The plasma-enhanced and thermal ALD of Al_2O_3 as examples
    - Corrosion protection
    - Moisture permeation barrier for OLEDs
- **Conclusions**
- **Acknowledgements**

The ALD Temperature Window

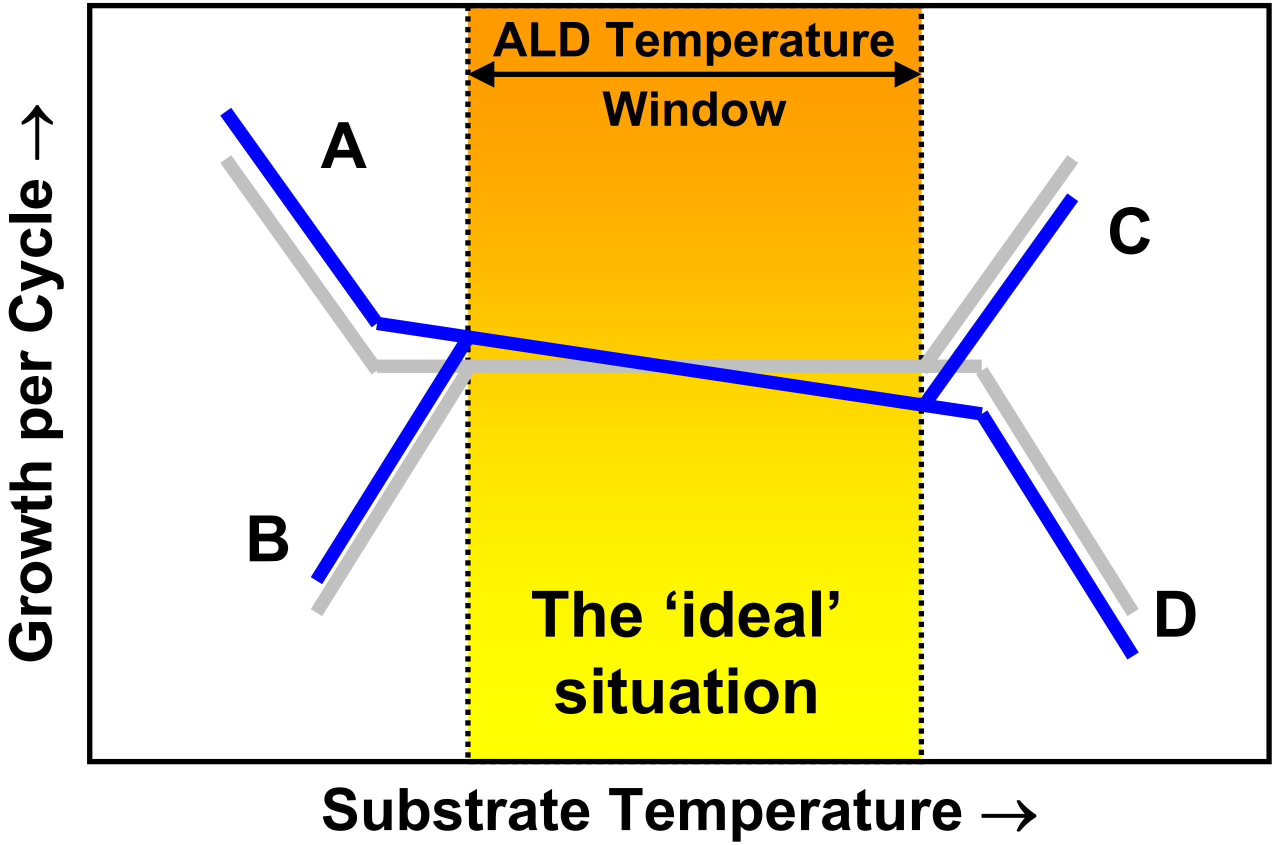


A. Condensation
B. Insufficient thermal energy
C. CVD
D. Evaporation

- Assumption: a sub-monolayer of material is deposited

T. Suntola, *Mater. Sci. Rep.*, **4**, 261 (1989).

The ALD Temperature Window



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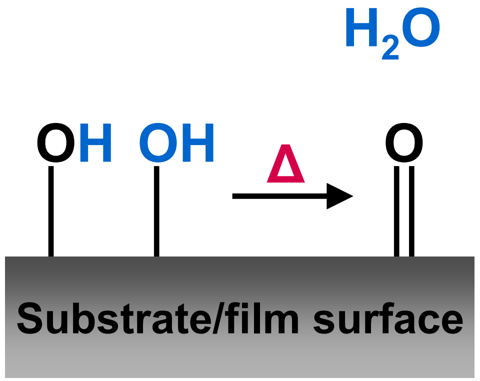


- Assumption: a sub-monolayer of material is deposited
- Loss of surface groups with increasing temperature
- Also affected by film density

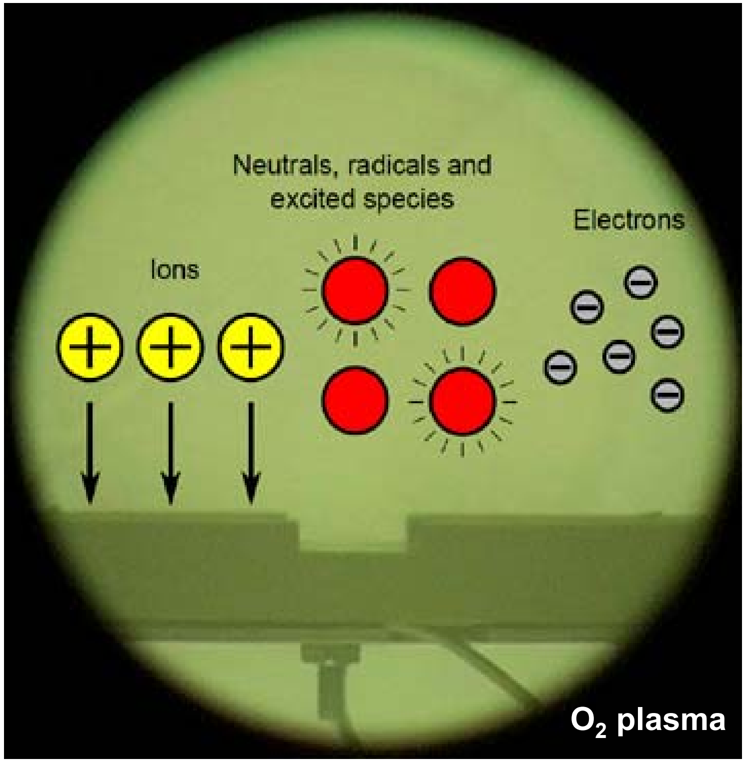
T. Suntola, *Mater. Sci. Rep.*, **4**, 261 (1989).

Plasma-Enhanced ALD

Plasma

- Collection of free charged particles and other gas-phase species:
  - Ions
  - Electrons

  } essential for plasma formation
  - Neutral species (called "plasma radicals")
- Electrically neutral, on average
- Plasma radicals are the main reacting species with surface groups
- Degree of ionisation is typically very low, ≤0.02%

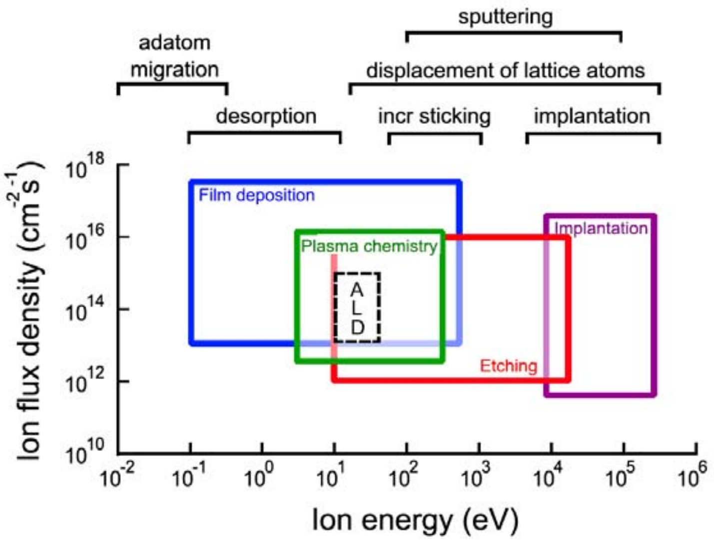


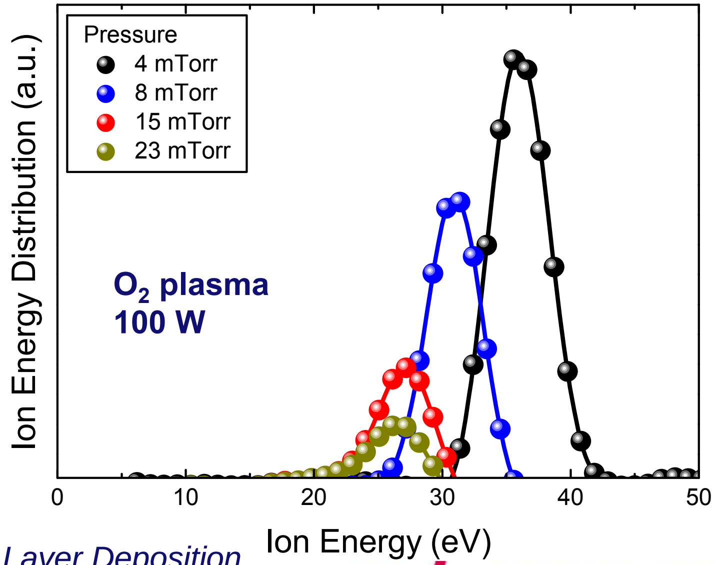
W. M. M. Kessels, H. B. Profijt, S. E. Potts and M. C. M. van de Sanden, *Atomic Layer Deposition of Nanostructured Materials*, editors: M. Knez and N. Pinna, Wiley-VCH (2011), **in press**.

Plasma-Enhanced ALD

Ion bombardment?

- Ions are accelerated through a plasma sheath
  - $v_e > v_{ion}$ (thermal velocity)
  - Net current to substrate = 0 → electrical field formed
  - Thin positive space-charge region
- **Ion bombardment more likely at lower reactor pressures**
  - E_{ion} depends on mean free path
  - Affected principally by pressure





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Merits of Plasma-Enhanced ALD

1. **Improved material properties**
    - High reactivity of the plasma can reduce impurities
2. **Deposition at reduced substrate temperatures**
    - Reactive plasma radicals and ions accelerated within the plasma sheath provide more reactivity than is possible with thermal energy alone
    - E.g. room temperature depositions of Al_2O_3, TiO_2, Ta_2O_5, ZnO…
    - Shorter co-reactant purges can be used
3. **Increased choice of precursors and materials**
    - Plasmas can remove ligands which aren't easily hydrolysed
    - Some Cp-based precursors have low reactivity with water during ALD e.g. $[Ti(Cp^*)(OMe)_3]$
    - Also limited reactivity with ozone at lower deposition temperatures

W. M. M. Kessels, H. B. Profijt, S. E. Potts and M. C. M. van de Sanden, *Atomic Layer Deposition of Nanostructured Materials*, editors: M. Knez and N. Pinna, Wiley-VCH (2011), **in press**.

Merits of Plasma-Enhanced ALD

4. Good control of stoichiometry and film composition

- Tuning physical variables to tune stoichiometry
- E.g. [$Ta(NMe_2)_5$] as a precursor to TaN_x

Plasma	Material
H_2-N_2 or NH_3	Insulating Ta_3N_5
H_2	Conducting TaN
H_2 (longer)	$TaN_{x<1}$ (almost Ta metal)

5. Increased growth per cycle

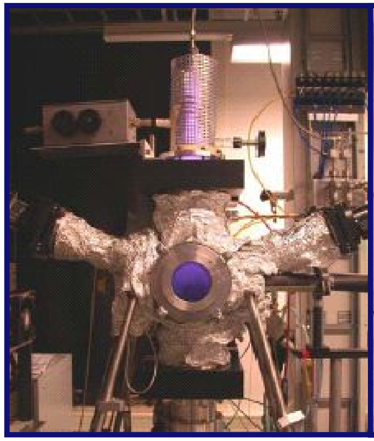
- Plasma species create a higher density of reactive surface sites
- E.g. [$Ti(O^iPr)_4$] at 200 °C: O_2 plasma: ~0.5 Å/cycle
  H_2O: ~0.15 Å/cycle

6. More processing versatility in general

- Possibility of *in situ* treatment of the substrate/reactor
- E.g. plasma cleaning - SF_6 plasma can etch TiN

Experimental Details (Plasma & Thermal ALD)

Remote Plasma ALD Reactors

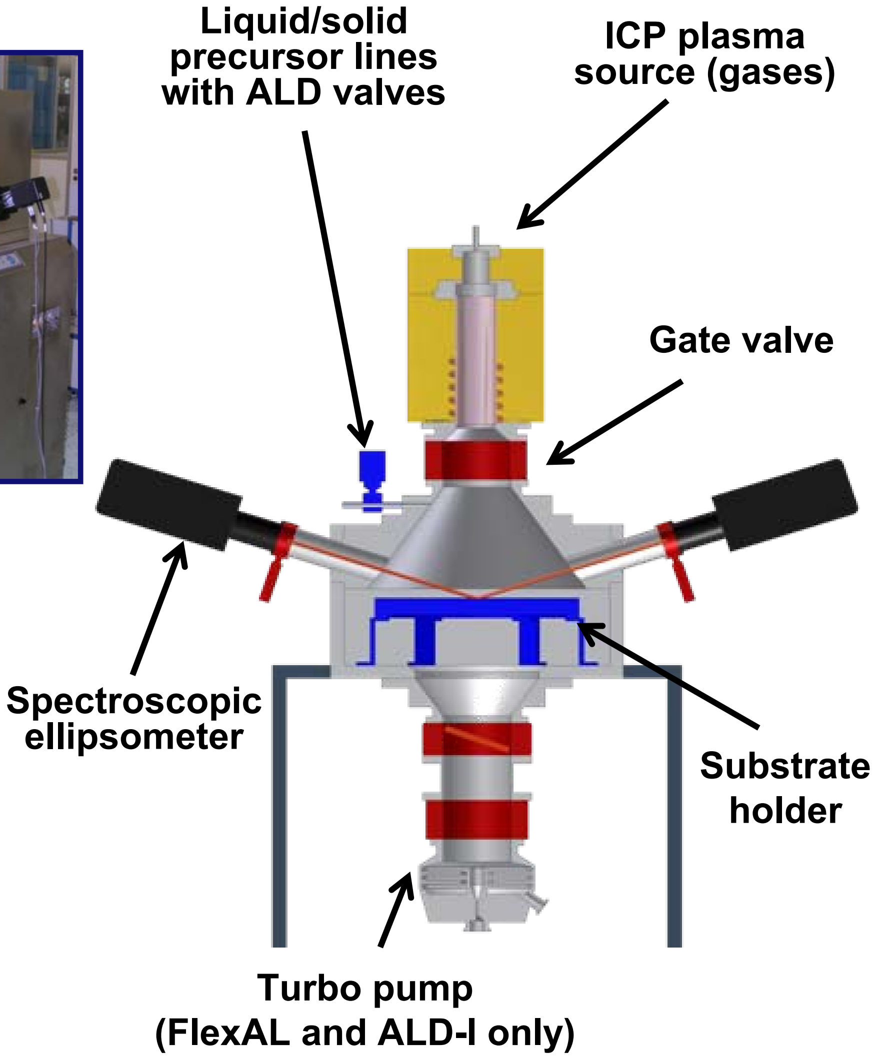


ALD-I
(home-built)

FlexAL™

OpAL™

- **100 mm n-type Si{100} substrates**
- ***In situ* spectroscopic ellipsometry (SE)**
  - Film thickness & growth per cycle (GPC)
- **RBS and ERD (H)**
  - Absolute areal density (atoms cm^{-2})



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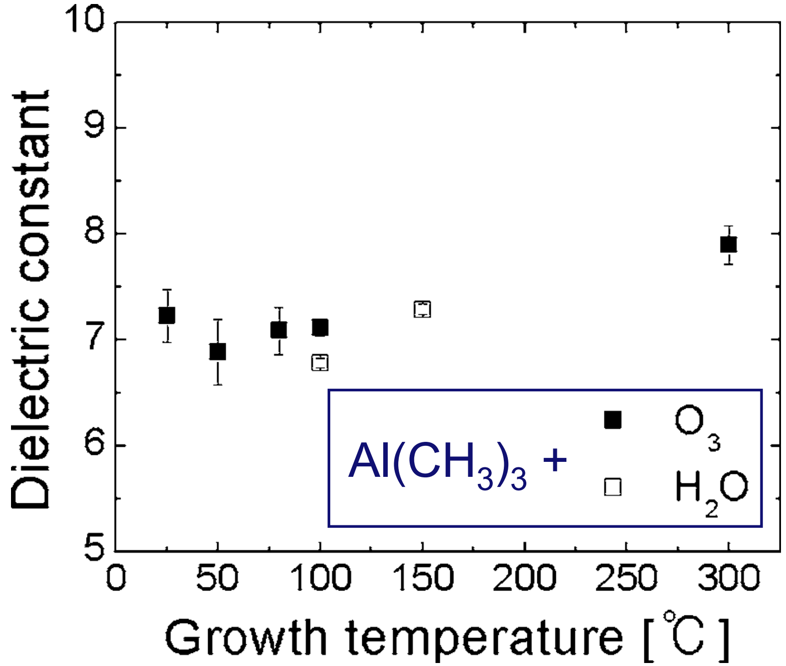
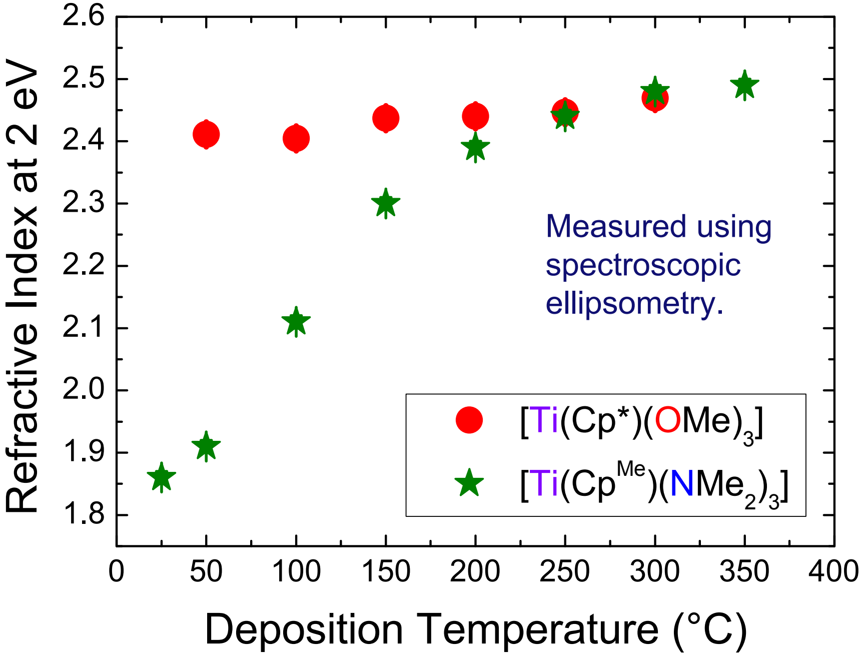
Why High(er) Temperature ALD?

Electrical and optical properties



S. K. Kim *et al.*, *J. Electrochem. Soc.*, **153**, F69 (2006).



S. E. Potts and A.Sarkar, TU/e

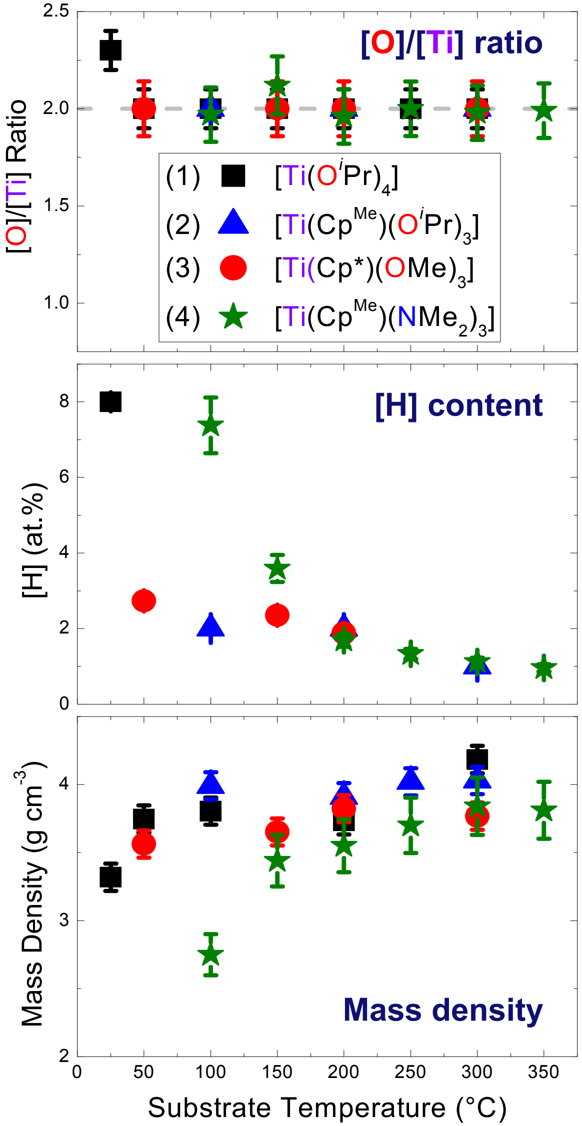
- **Dielectric constant increases at higher deposition temperatures**
- **Also depends on morphology, which can be controlled by a plasma**
- **Refractive index increases, linked to the density and composition of the film.**

Why High(er) Temperature ALD?

- **Generally, the best electronic and optical properties can be obtained at higher deposition temperatures.**

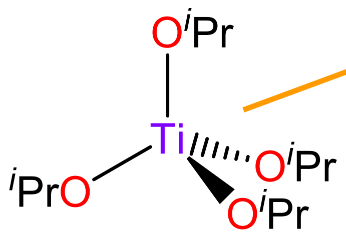
- **A result of:**
  - Fewer ‘impurities’ at higher temperatures
  - Impurities lead to films with lower densities

- **E.g. for TiO_2:**
  - Required for STOs and other ternary oxides
  - More H at lower temperatures (OH groups)
  - Highest densities obtained at ~150 °C and above



Ligand-Tailoring of TiO_2 Precursors

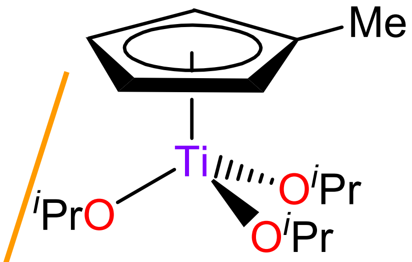
- **Tailoring ligands can allow for an increase in the maximum temperature**
  - Stronger M–L bonds
  - Incorporation of ligands less prone to decomposition



1

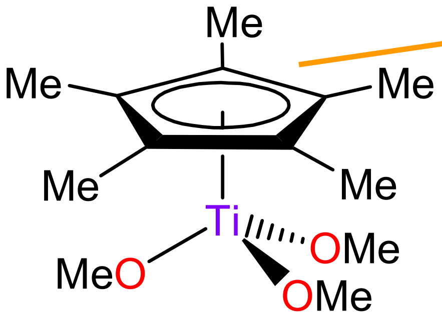
Homoleptic Ti compounds prone to oligomerisation

Isopropyl groups incorporating β-H: lowers decomposition temperature



2

Cp-based ligands: increased stability
Increased volatility



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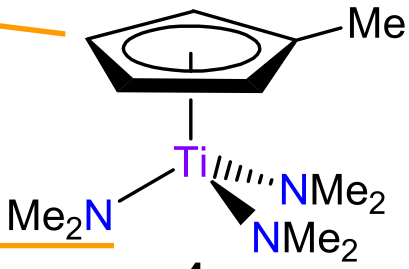
Amido ligands: increased reactivity (for oxides); more prone to decomposition



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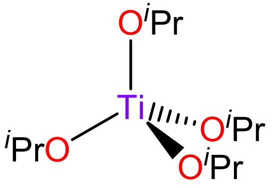
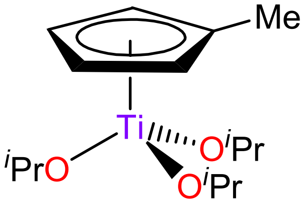
Higher Deposition Temperatures of TiO_2

Combination of OMe ligands and Cp result in the highest decomposition temperature.



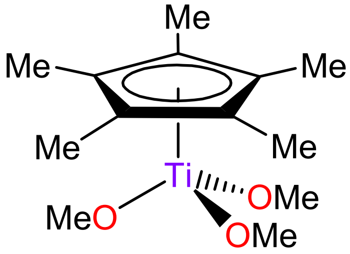
1

~300 °C



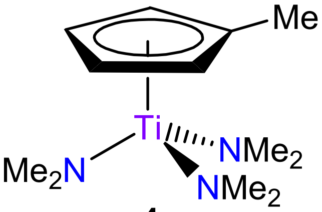
2

~350 °C



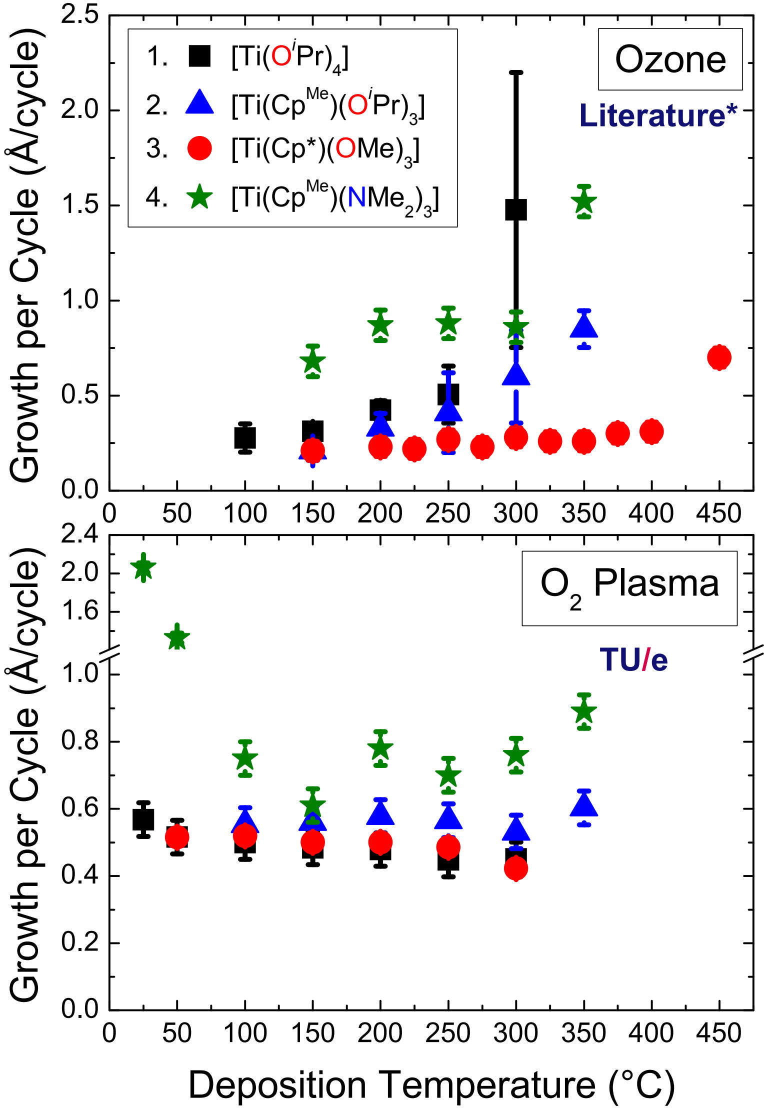
3

~450 °C



4

~350 °C



Upper limit of temperature window effectively increased

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* O_3 processes: 1, 2, 4: P. Williams at ALD 2008, Bruges, Belgium.
3: R. Katamreddy *et al.*, *ECS Trans.*, **25**, 217 (2009).

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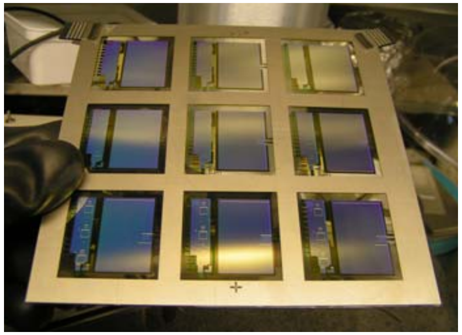
Why Low Temperature ALD?

- **Some applications require high film quality but the substrates required are temperature-sensitive.**

- **Alloys (or polymers) requiring a corrosion-resistant barrier layer**
  - Dense, defect-free films required.
  - Higher temperatures can alter the mechanical properties of industrial alloys.

- **Moisture permeation barriers for OLEDs**
  - Films need to be deposited on organic substrates

Coating metal substrates at TU/e



OLEDs at TU/e

Low Temperature Oxide ALD in the Literature

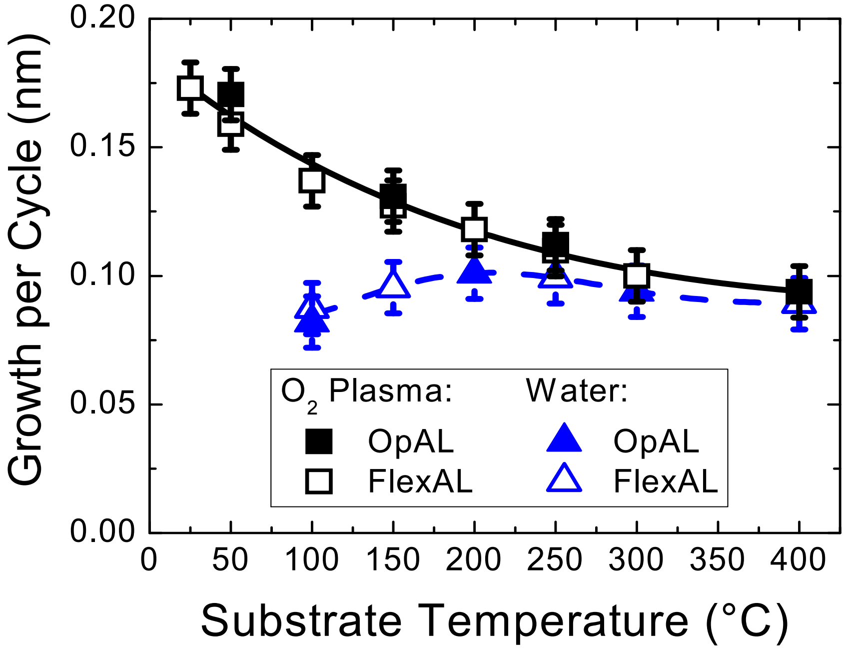
Material	Metal Precursor	Oxidant	Lowest T_s (°C)	Reference
Al_2O_3	$[Al(CH_3)_3]$	H_2O	33	Groner *et al.*
	$[Al(CH_3)_3]$	O_3	25	Kim *et al.*
	$[Al(CH_3)_3]$	O_2 plasma	25	van Hemmen *et al.*
TiO_2	$[Ti(O^iPr)_4]$	H_2O	150	Ritala *et al.*
	$[Ti(O^iPr)_4]$	H_2O_2	77	Liang *et al.*
	$[Ti(O^iPr)_4]$	O_2 plasma	25	Potts *et al.*
	$[Ti(Cp^{Me})(O^iPr)_3]$	O_2 plasma	50	Potts *et al.*
	$[Ti(Cp^*)(OMe)_3]$	O_2 plasma	50	Potts *et al.*
	$[Ti(Cp^{Me})(NMe_2)_3]$	O_2 plasma	25	Sarkar *et al.*
Ta_2O_5	$TaCl_5$	H_2O	80	Kukli *et al.*
	$[Ta(NMe_2)_5]$	H_2O	150	Maeng *et al.*
	$[Ta(NMe_2)_5]$	O_2 plasma	25	Potts *et al.*
PtO_x	$[Pt(acac)_2]$	O_3	120	Hämäläinen *et al.*
	$[Pt(Cp^{Me})Me_3]$	O_2 plasma	100	Knoops *et al.*
ZnO	$[Zn(CH_2CH_3)_2]$	H_2O	60	Guziewicz *et al.*
	$[Zn(CH_2CH_3)_2]$	H_2O_2	25	King *et al.*
	$[Zn(CH_2CH_3)_2]$	O_2 plasma	25	Rowlette *et al.*

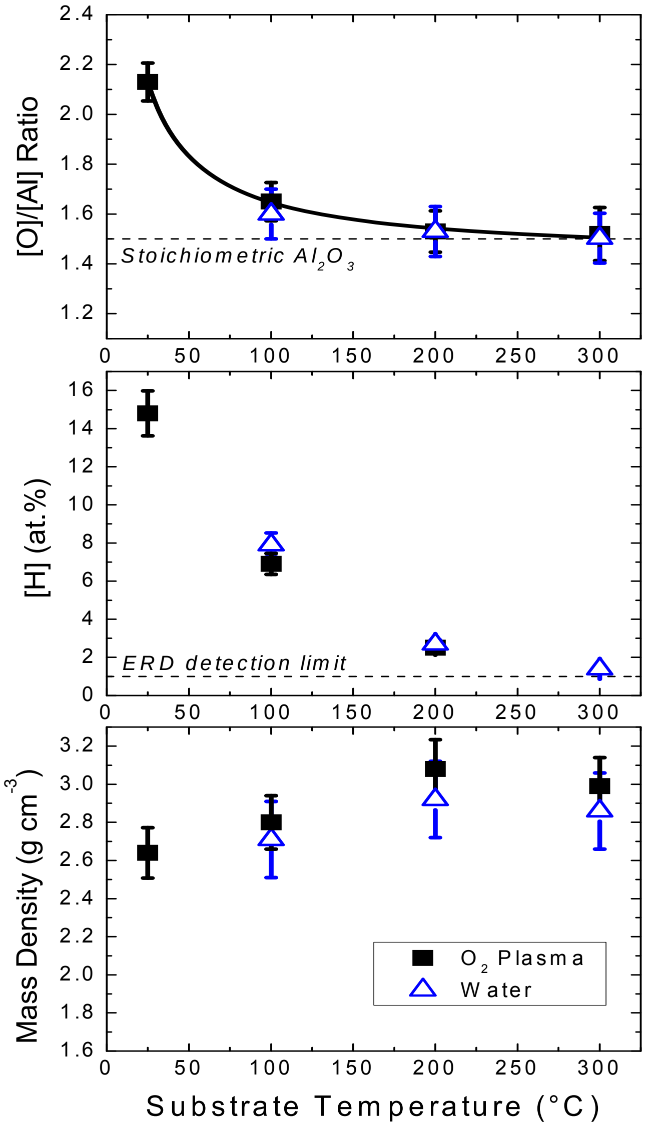
S. E. Potts *et al.*, *J. Electrochem. Soc.*, **157**, P66 (2010).

Plasma-Enhanced & Thermal ALD of Al_2O_3

On Si (100)

- Wide variation in growth due to changes in density (low T) and dehydroxylation (higher T)
- Densest films have lowest OH concentrations





J. L. van Hemmen *et al.*, *J. Electrochem. Soc.*, **154**, G165 (2007).
S. E. Potts *et al.*, *J. Electrochem. Soc.*, **157**, P66 (2010).

Corrosion Barriers: FP7 CORRAL Project

- **Corrosion protection with perfect atomic layers = CORRAL**
- **EC FP7 project**

SEVENTH FRAMEWORK PROGRAMME

Goal:

- **The complete sealing of industrial metal alloys for corrosion protection**
- **Test criteria:**
  - Films must be deposited at $T_s \leq 160$ °C
  - Films must have a density >90% of the bulk material
  - show complete coverage on polished surfaces: porosity <0.2%

Current state-of-the-art for corrosion protection:

- 3 μm thick films
- Aim for ≤50 nm

Corrosion Barriers: Substrates

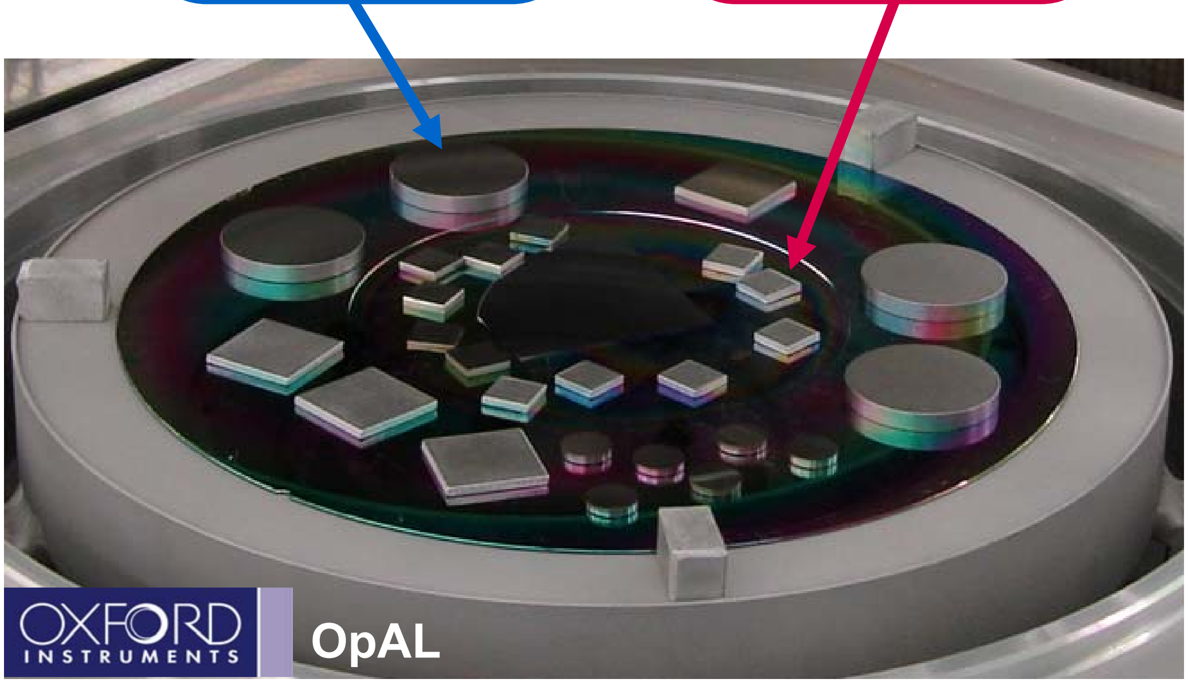
- **Same alloys as those used for industrial applications**
- **3 sizes for analysis**
- **2D substrates, two surface finishes:**
  - Lapped
  - (Fine) ground
- **N-type Si reference**

Steel 100Cr6

1.5% Cr
~1% C

Aluminium Al2024-T3

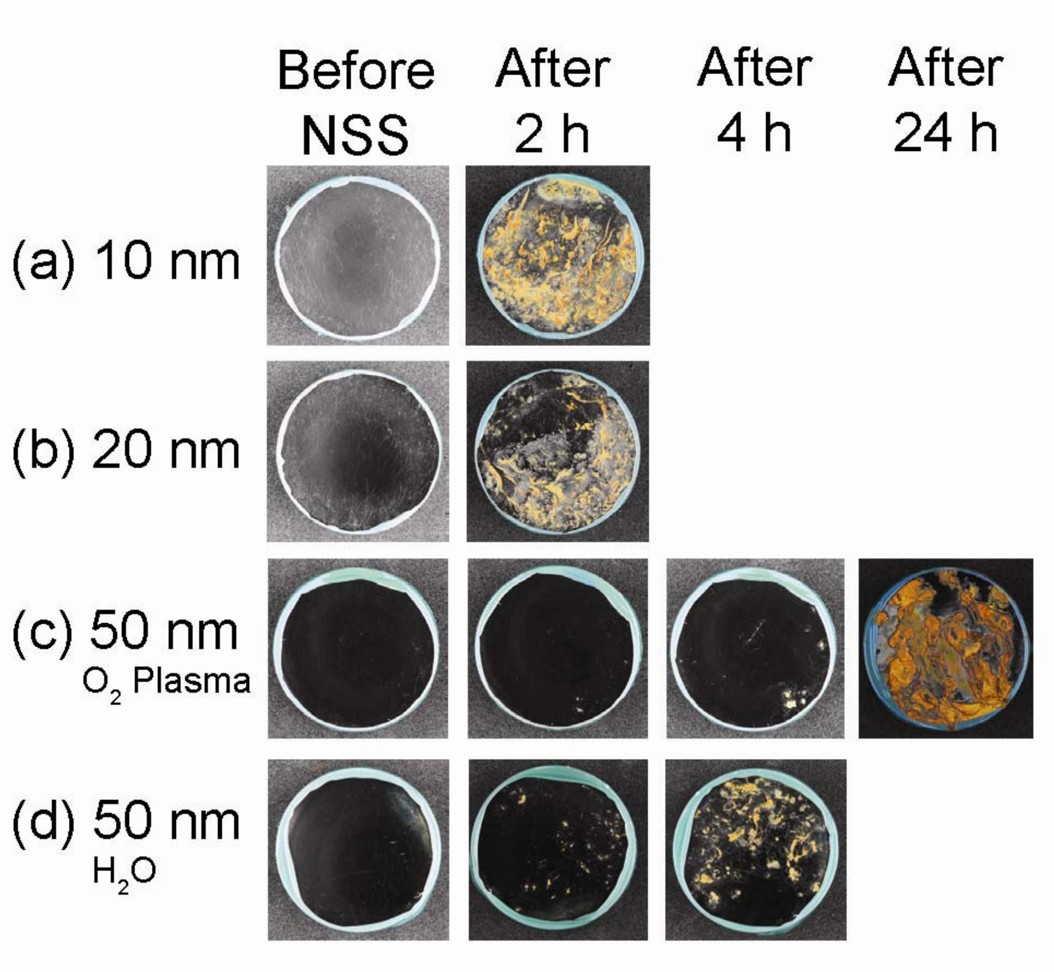
~4.2% Cu
~1.5% Mg



Corrosion Barriers: NSS Tests

Neutral salt-spray tests

- Addition of Al_2O_3 to 100Cr6 mild steel improves its resistance to corrosion.
- Thicker films offer better protection
- Plasma ALD films lasted longer than thermal ALD in the tests

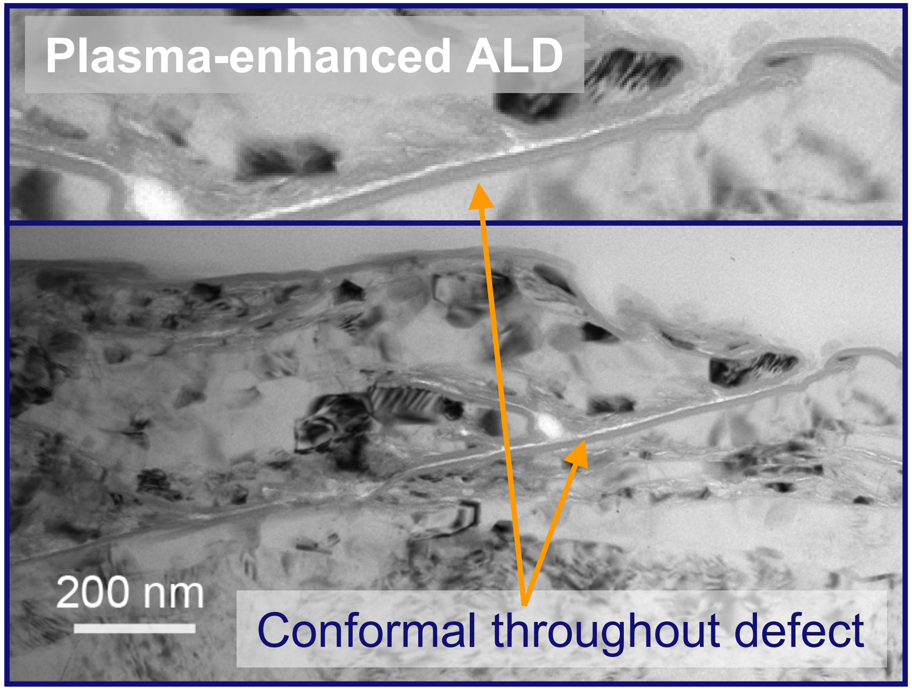


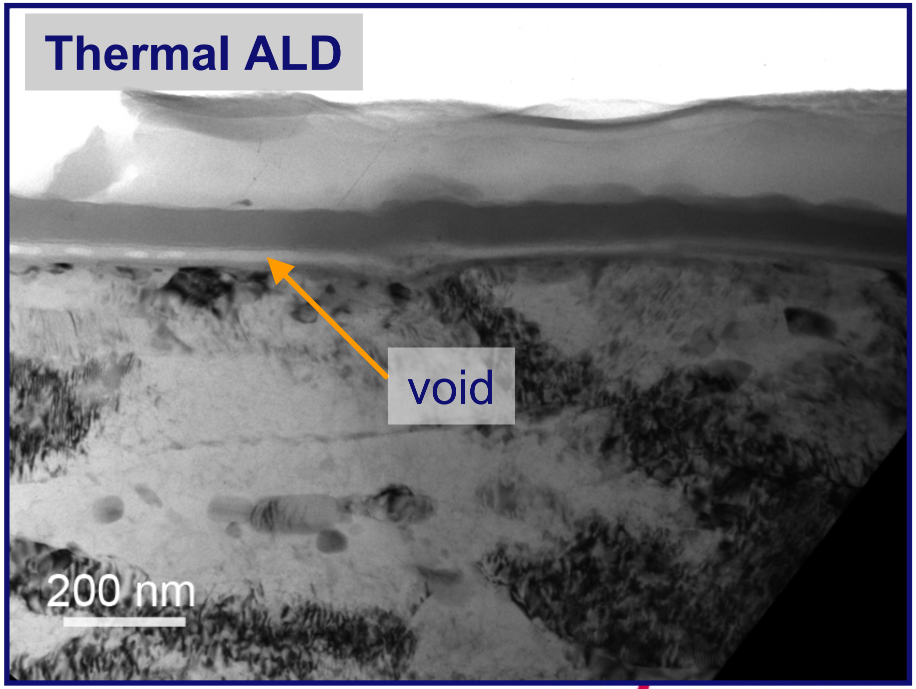
T_s = 150 °C

Corrosion Barriers: TEM

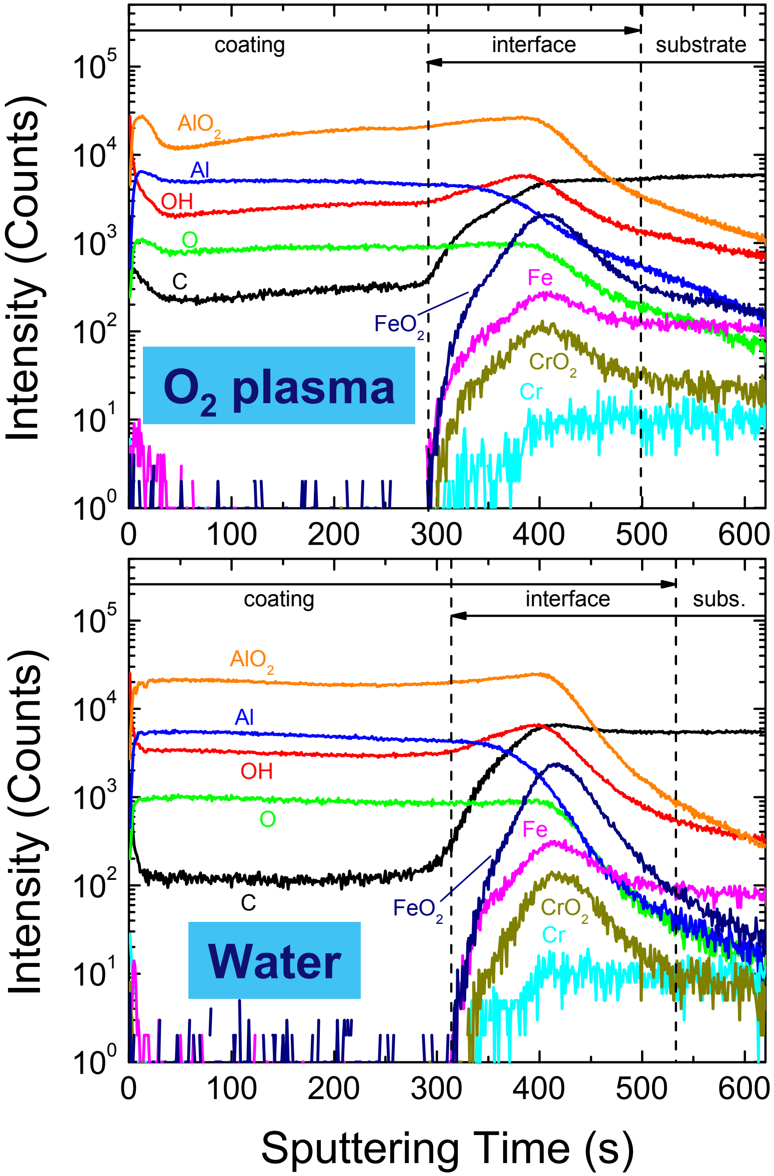
Al_2O_3 on Al2024-T3

- Films conformal on the substrates in both cases
- Gap between coating in the case of thermal ALD suggests poor adhesion
- Plasma-enhanced ALD affords better adhesion in this case.

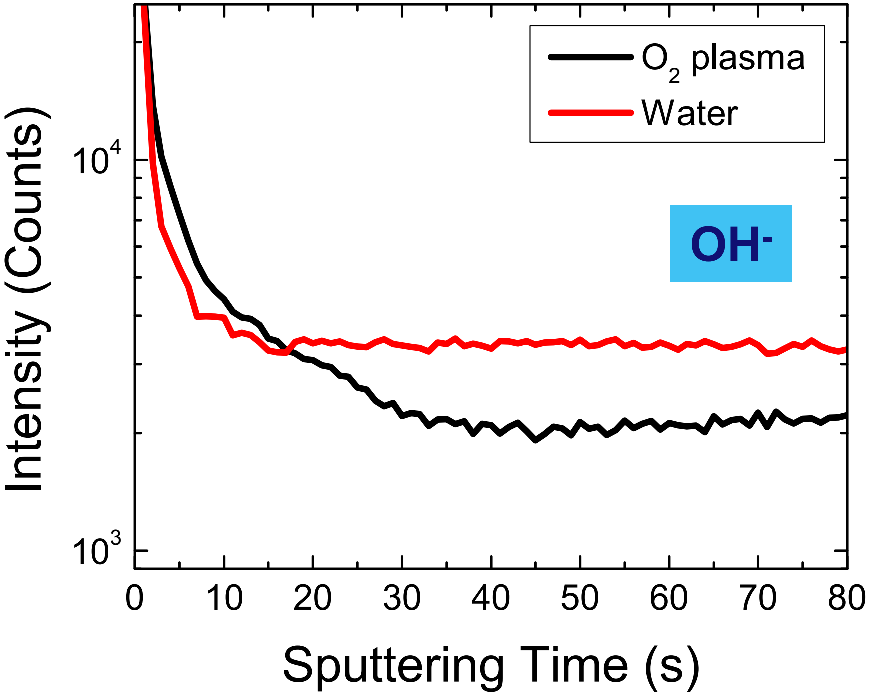




Corrosion Barriers: ToF-SIMS



- **50 nm Al_2O_3 on 100Cr6**
  - Show a slightly higher C and FeO_2 content at the interface for thermal ALD
  - Confirm lower OH levels in bulk of plasma ALD coating

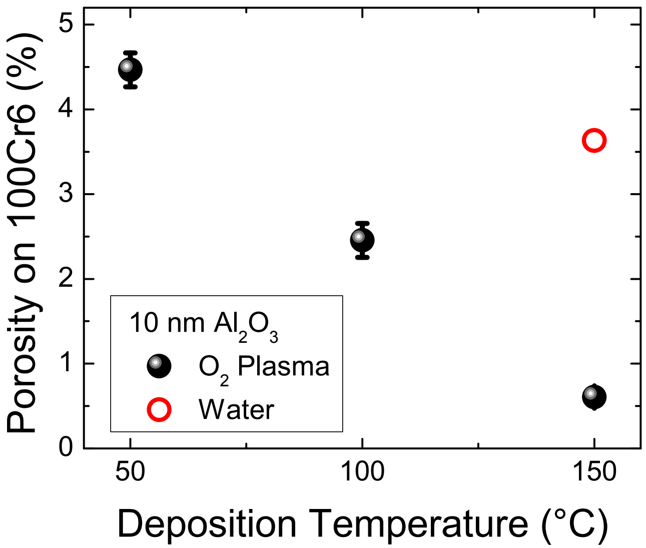


Corrosion Barriers: Porosity

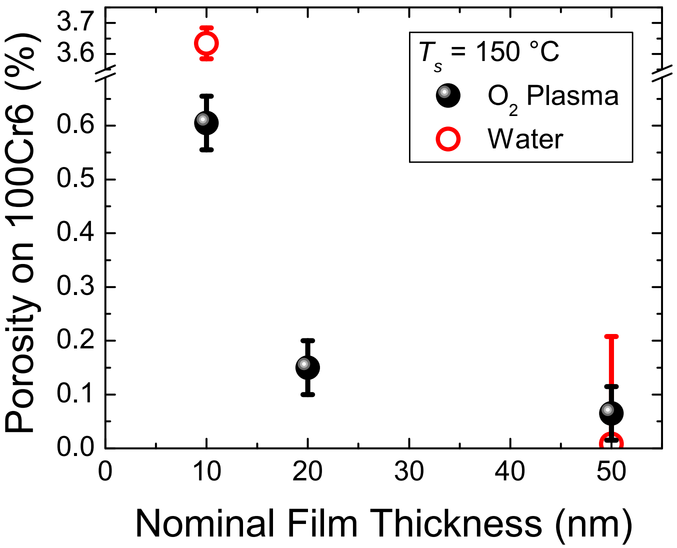
Film porosity = % bare substrate surface

- Obtained using capacitance-voltage measurements on 100Cr6 mild steel
- Inversely proportional to film thickness
- Lowest deposition temperatures give higher porosities
- Plasma-enhanced ALD gives lower porosity at lower thicknesses

Temperature Series



Thickness Series



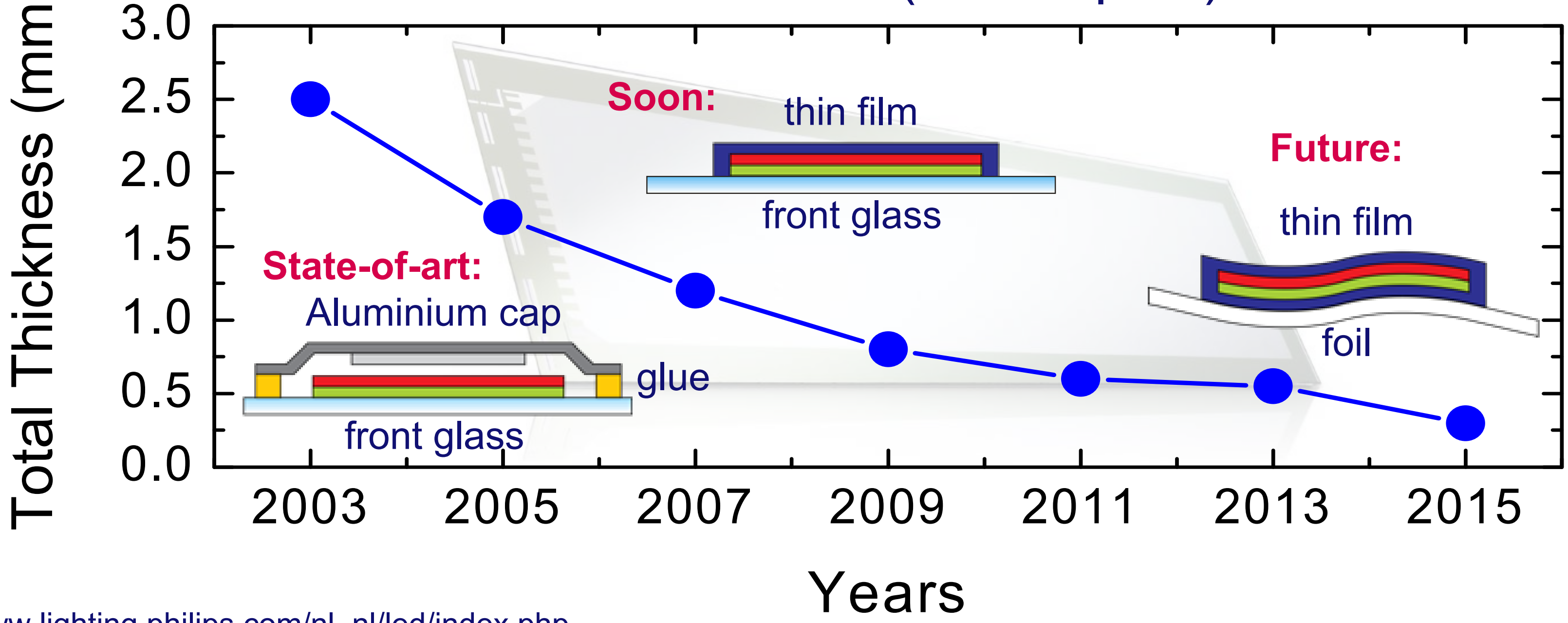
Moisture Permeation Barrier for OLEDs

Organic LEDs (OLEDs)

- Energy-efficient lighting
- Large luminous area
- Sensitive to H_2O, O_2 and temperature

Requirements:

- Deposition temperature <110 °C
- Water vapour transmission rate (WVTR) <10^{-6} g m^{-2} day^{-1}
- No visible defects after calcium tests (black spots)



http://www.lighting.philips.com/nl_nl/led/index.php
http://www.lighting.philips.com/nl_nl/led/information/oled_lumiblade.php

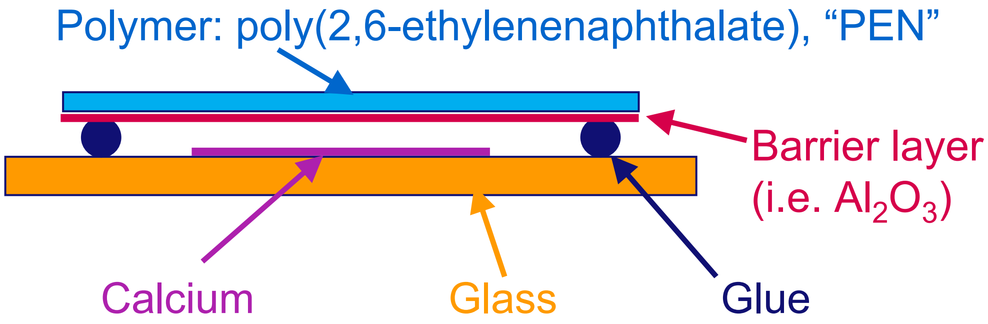
Testing the Water Vapour Transmission Rate

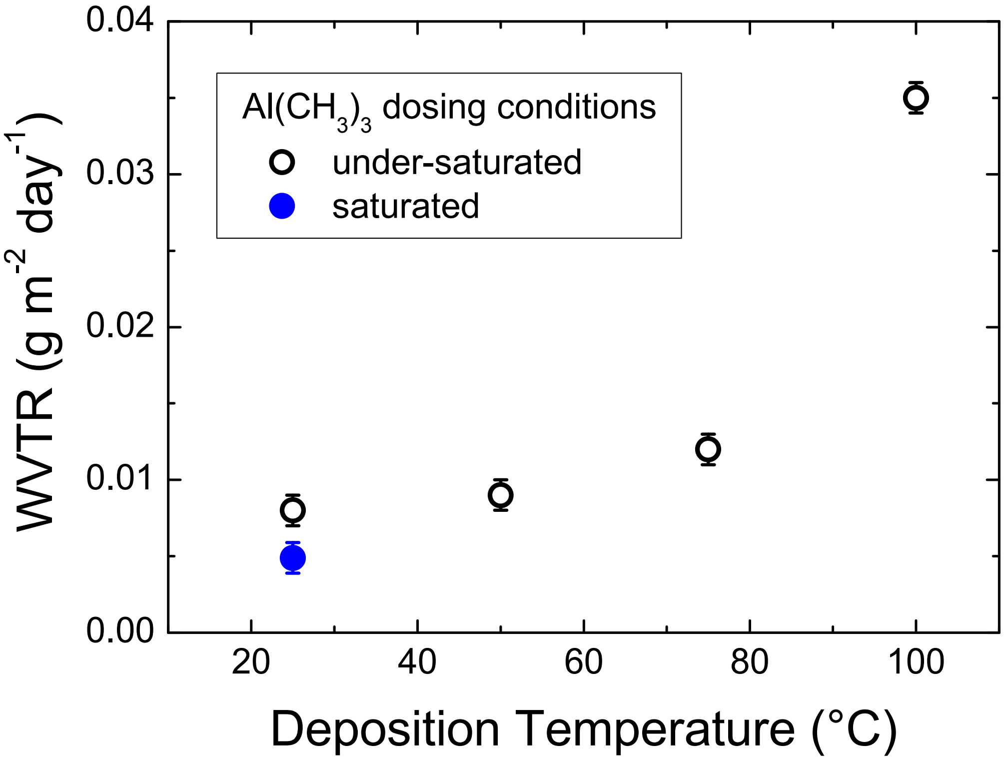
Calcium Tests

- Metallic calcium turns transparent on reaction with water (CaO)
- WVTR from Ca tests on PEN decreases with deposition temperature
- Lowest reported value ~10^{-6} g m^{-2} day^{-1}

Al_2O_3 at TU/e

- Best barrier film obtained at room temperature (25 ºC)
- Opposite trend to Al_2O_3 deposited by thermal ALD



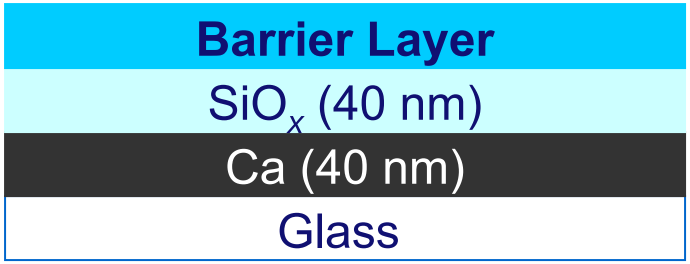


E. Langereis *et al.*, *Appl. Phys. Lett.*, **89**, 081915 (2006).

Testing the Water Vapour Transmission Rate

Comparison with standard to find the intrinsic WVTR of Al_2O_3

- Standard: 300 nm a-SiN_x:H
- Allows bleeding from pinholes to be discounted

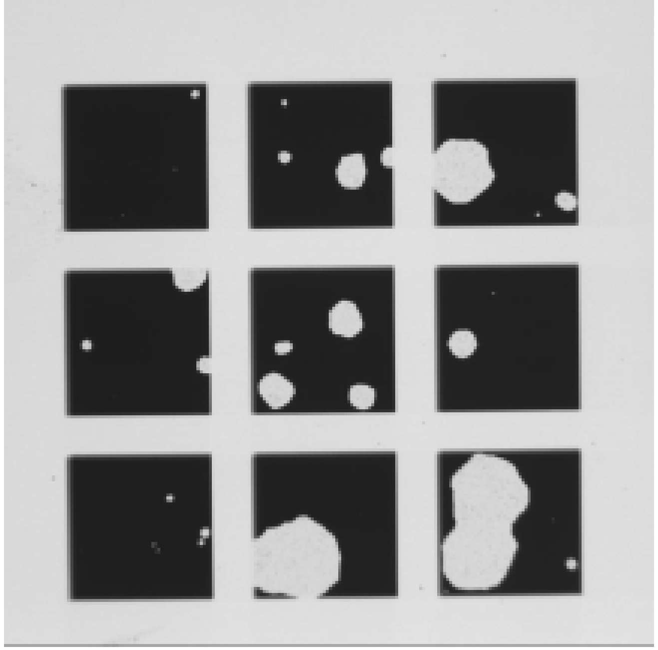


Barrier Layer

SiO_x (40 nm)

Ca (40 nm)

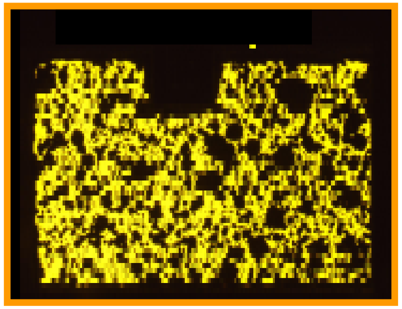
Glass



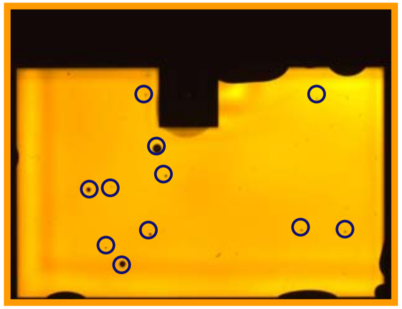
System	Plasma Deposition	Material	Thickness (nm)	WVTR (10^{-6} g m^{-2} day^{-1})
Plasmalab 100	CVD	a-SiN_x:H	300	<1
FlexAL	ALD	Al_2O_3	40	2

P. van de Weijer *et al.*, *Proceedings of the OSC* (2008).

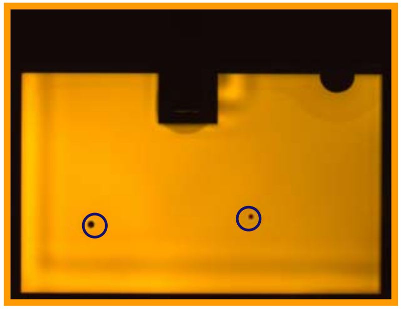
OLED Encapsulation: Defect Density



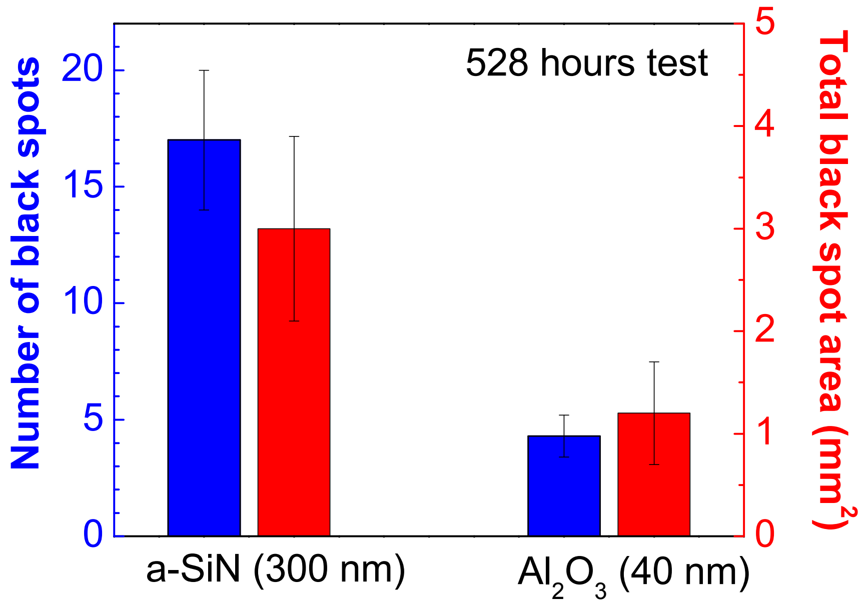
Poly-LED
No encapsulation



PE-CVD
300 nm a-SiN_x:H



PE-ALD
40 nm Al_2O_3



- **Lower black spot density on poly-LED/Al_2O_3: enhanced conformal growth in the case of ALD**
- **Temperature window for Al_2O_3 is effectively extended down to room temperature**

Conclusions/Summary

- **Plasma-Enhanced ALD at high(er) deposition temperatures**
  - Better electronic and optical properties
  - Able to use stable precursors (stronger M–L bonds)

- **Plasma-Enhanced ALD at low deposition temperatures**
  - Higher OH content, lower density
  - Al_2O_3 as barrier layers
    - Protects 100Cr6 and Al2024-T3 alloys from corrosion
    - Gives a lower film porosity at lower temperatures
    - Lowest water vapour transmission rates at room temperature

- **The temperature window is subjective and dependent on the process requirements**

- **Plasmas allow for ALD at higher and lower temperatures than those possible with thermal ALD**

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Al_2O_3 Depositions

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TiO_2 Depositions

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Philips Lighting (OLED barriers)

PHILIPS
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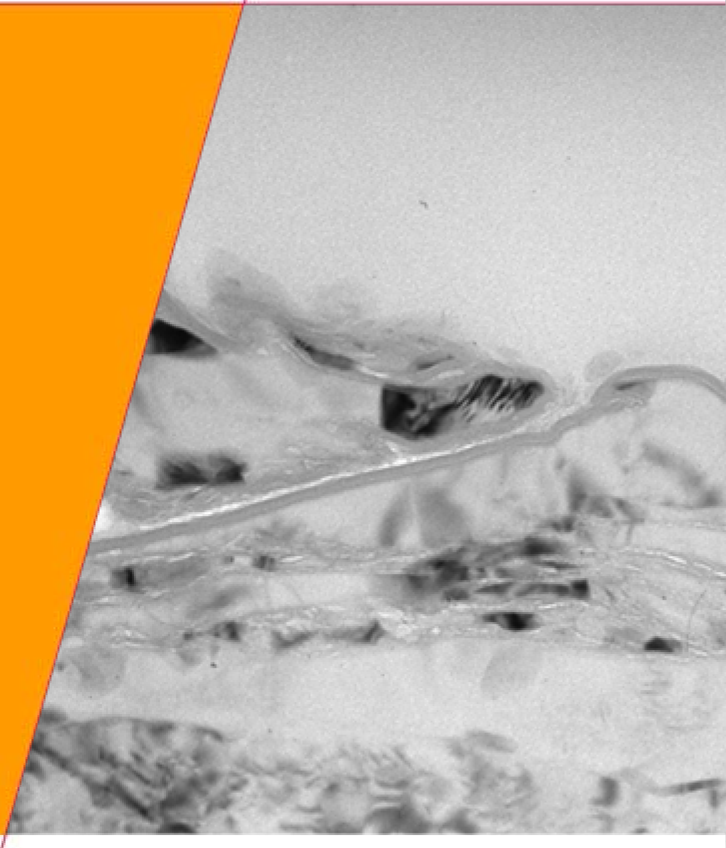
SEVENTH FRAMEWORK PROGRAMME

TU/e Technische Universiteit Eindhoven University of Technology

Thank you for your attention!



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