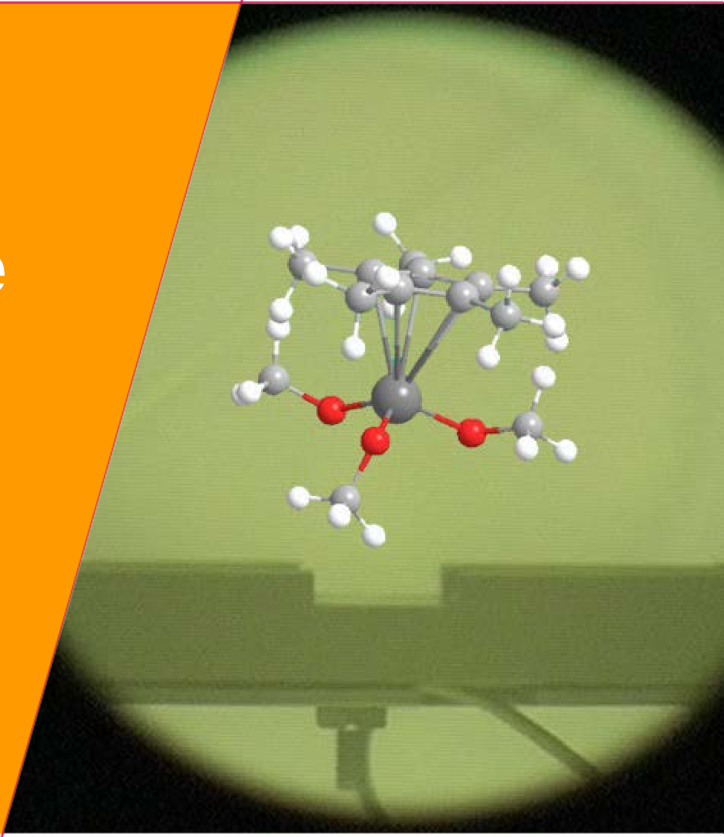
# Plasma-Enhanced ALD: Precursor Considerations for Opening the ALD Temperature Window

**Stephen E. Potts**
s.e.potts@tue.nl

1st ENHANCE Winter School, Bochum, Germany
25th-28th January 2011



TU/e Technische Universiteit Eindhoven University of Technology

The research leading to these results has received funding from the MaxCaps Research Project (Medea+).

Where innovation starts

# Outline



- **Merits of Plasma-Enhanced ALD (a reminder)**
- **Experimental**
  - ALD reactors & diagnostics (spectroscopic ellipsometry, RBS)
- **Low temperature ALD: $Al_2O_3$**
  - Depositions down to room temperature
  - Barriers against corrosion and atmospheric moisture
- **High(er) temperature ALD: $TiO_2$**
  - Ligand tailoring for increasing the maximum ALD temperature of a process.
- **Conclusions**



TU/e Technische Universiteit Eindhoven University of Technology

# Merits of Plasma-Enhanced ALD



1. **Improved material properties**
   - High reactivity of the plasma can reduce impurities
   - Higher film density
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
3. **Increased choice of precursors and materials**
   - Use of precursors with high thermal and chemical stability as plasmas can remove (combust) ligands which aren't easily hydrolysed
     - e.g. [Ti(Cp*)(OMe)$_3$], unreactive with water and low reactivity with ozone during ALD (see later)
   - Deposition of metals (a 'dark art')

**Plasma Atomic Layer Deposition**
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. Varying plasma
  - Composition: $TaN_x$ from $[Ta(NMe_2)_5]$ ($x$ = ~0-1.67)
  - Time: Pt or $PtO_2$ from $[Pt(Cp^{Me})Me_3]$

## 5. Increased growth rate

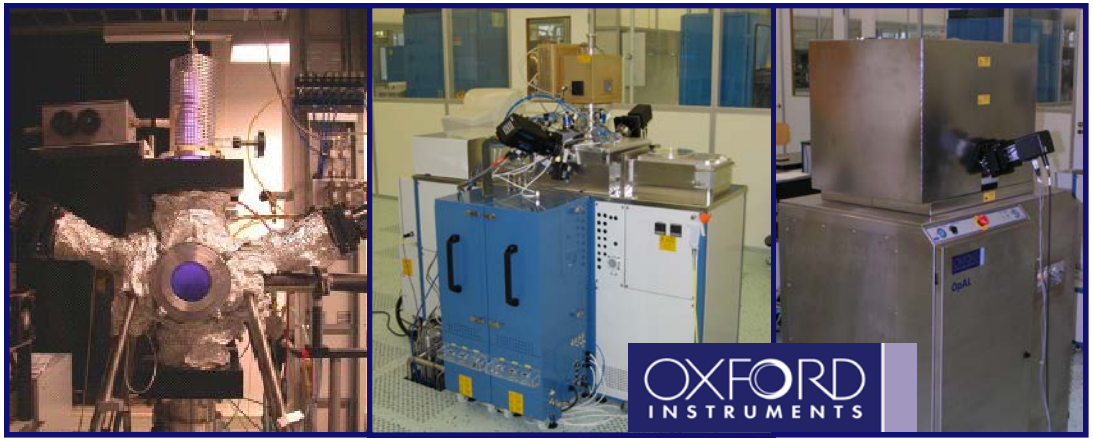
- Higher growth per cycle (increased number of nucleation sites)
- Shorter purges
- Shorter nucleation time

## 6. More processing versatility in general

- Possibility of *in situ* (pre-)treatment of the substrate/reactor
- Reactor cleaning (e.g. etching with $SF_6$ plasma) and wall conditioning

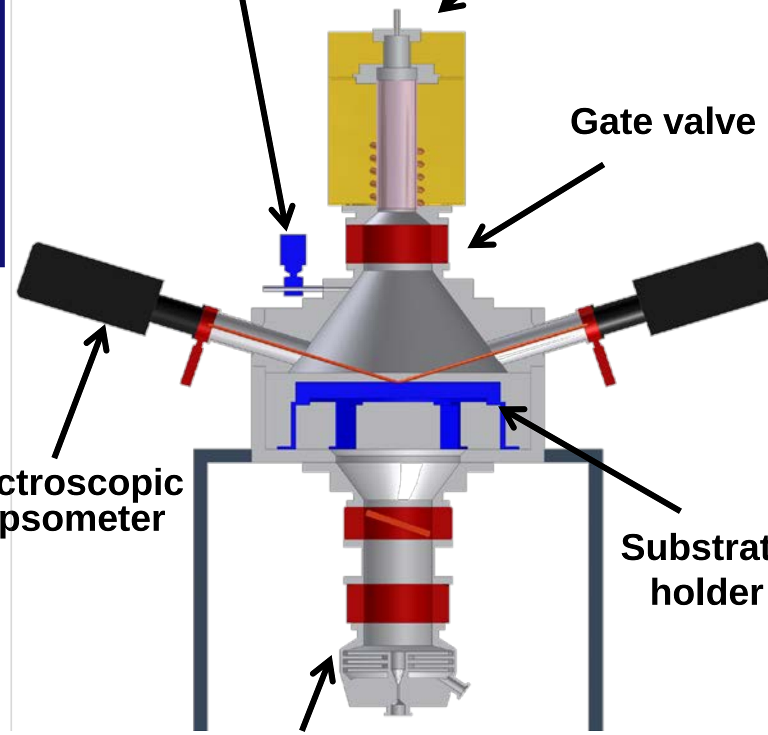
# Experimental Details (Plasma & Thermal ALD)

## 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)
- **Rutherford backscattering (RBS) and elastic recoil detection (ERD)**
  - Absolute areal density (atoms $cm^{-2}$)





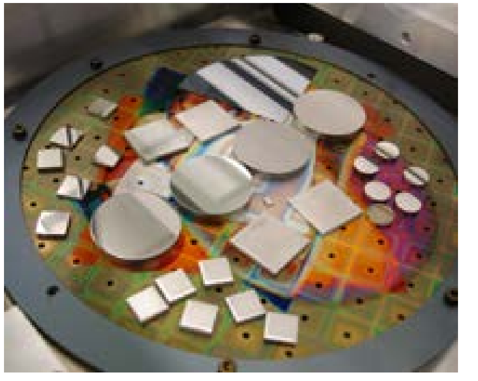

TU/e Technische Universiteit Eindhoven University of Technology

# Motivation: Low Temperature ALD

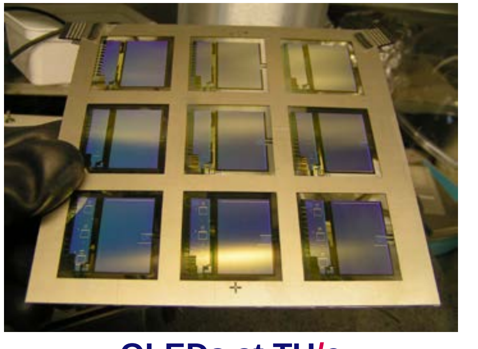


**Merits #1 & #2**

- **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**



TU/e Technische Universiteit Eindhoven University of Technology

# Low Temperature Oxide ALD in the Literature



| Material | Metal Precursor | Co-Reactant | Lowest $T_s$ (ºC) | 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.* |

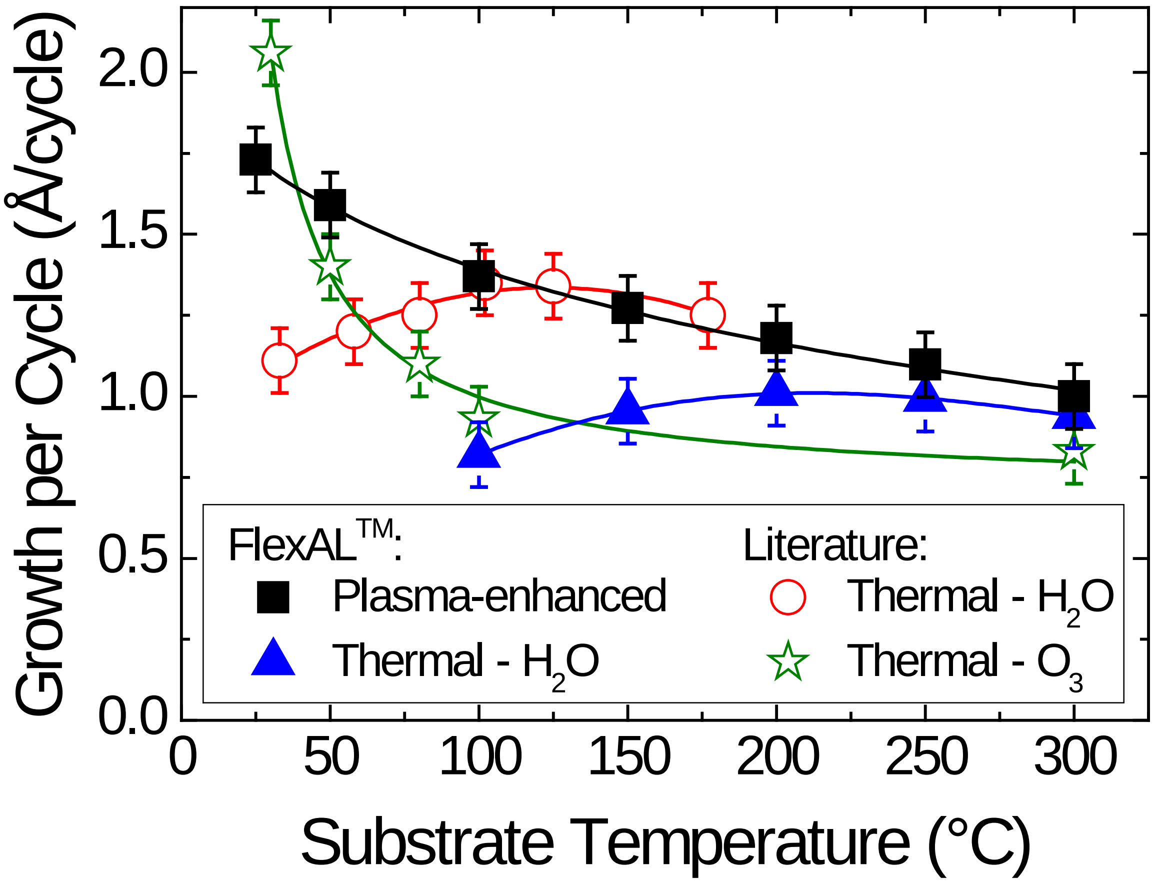
S. E. Potts *et al.*, *J. Electrochem. Soc.*, **157**, P66 (2010).



Technische Universiteit Eindhoven University of Technology

# Plasma-Enhanced & Thermal ALD of $Al_2O_3$






- Water processes: lower growths per cycle at low temperatures
- Ozone process: many extra surface groups at $T_s$ < 100 °C → very low density.
- Reduction in growth per cycle with increasing $T_s$ → dehydroxylation.

**Plasma-enhanced ALD gives high growths per cycle at low deposition temperatures.**

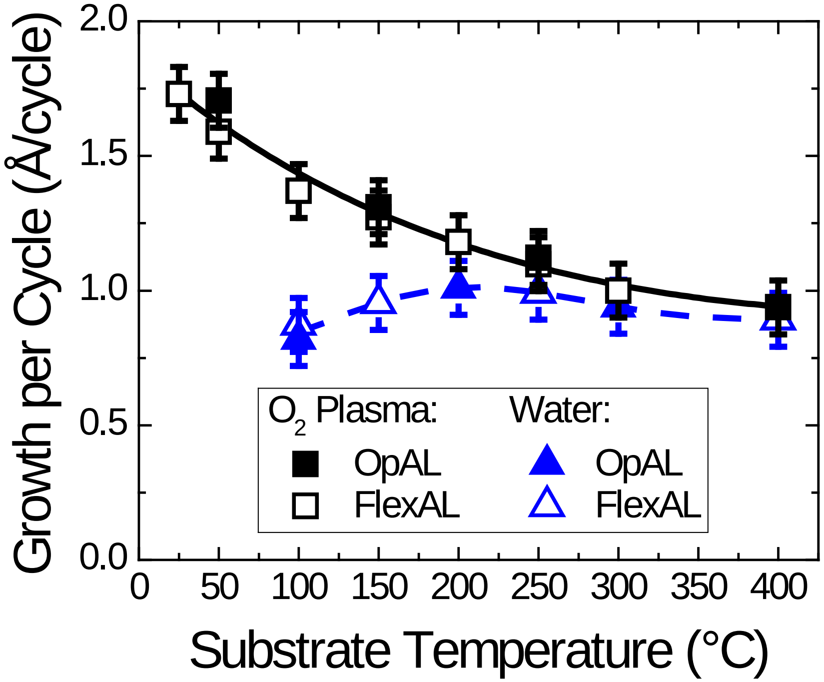
[■], [▲] J. L. van Hemmen *et al.*, *J. Electrochem. Soc.* **154**, G165 (2007).
[O] M. D. Groner *et al.*, *Chem. Mater.*, **16**, 639 (2004).
[☆] S. K. Kim *et al.*, *J. Electrochem. Soc.*, **153**, F69 (2006).

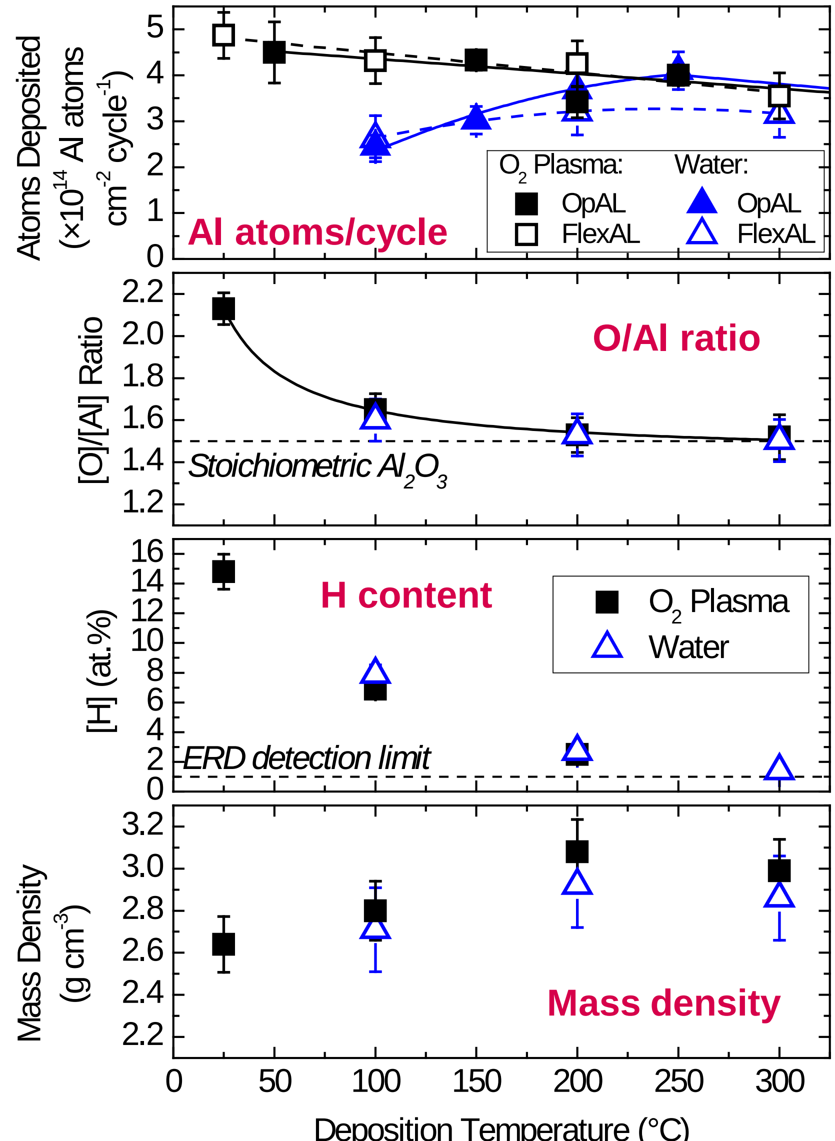
# Plasma-Enhanced & Thermal ALD of $Al_2O_3$



**On Si (100)**

- 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).

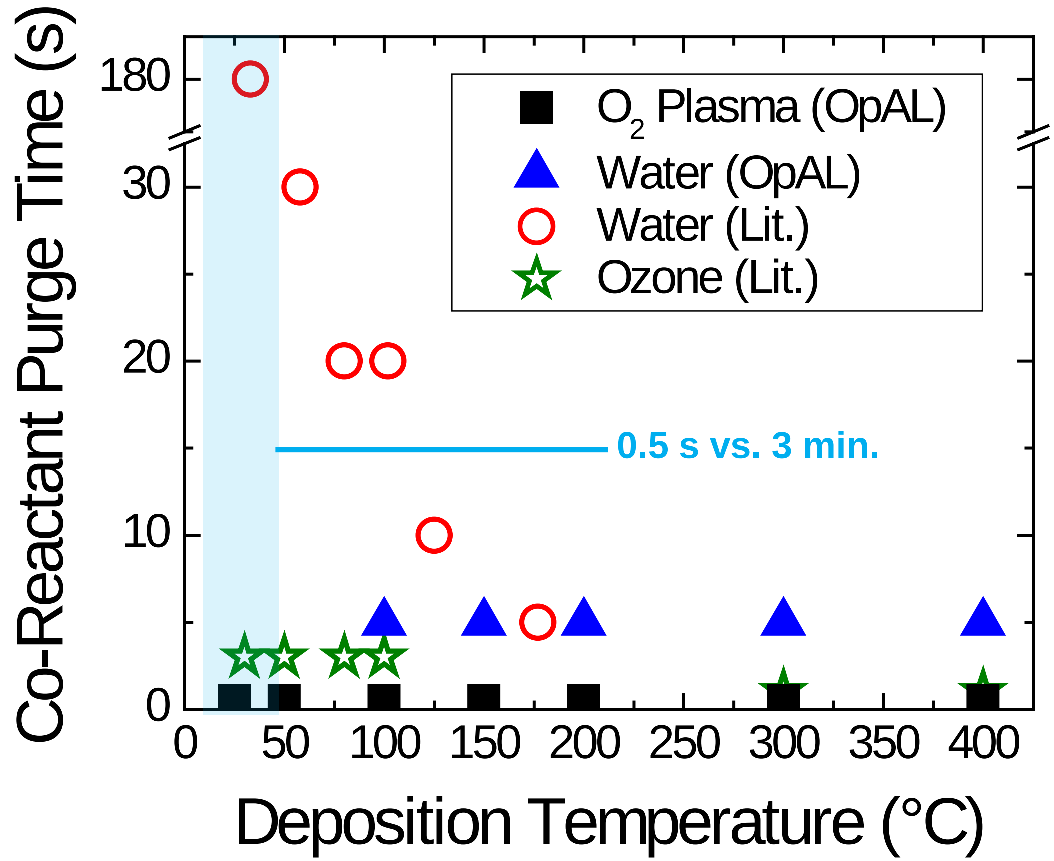


Technische Universiteit Eindhoven University of Technology

# $Al_2O_3$: Co-Reactant Purge Times



- Water build-up leads to a CVD-like effect
- Water requires substantial purging at low temperatures due to its ‘sticky’ nature
- Plasma(s) and ozone are more easily purged away
- If the plasma is long enough then purging may not be necessary



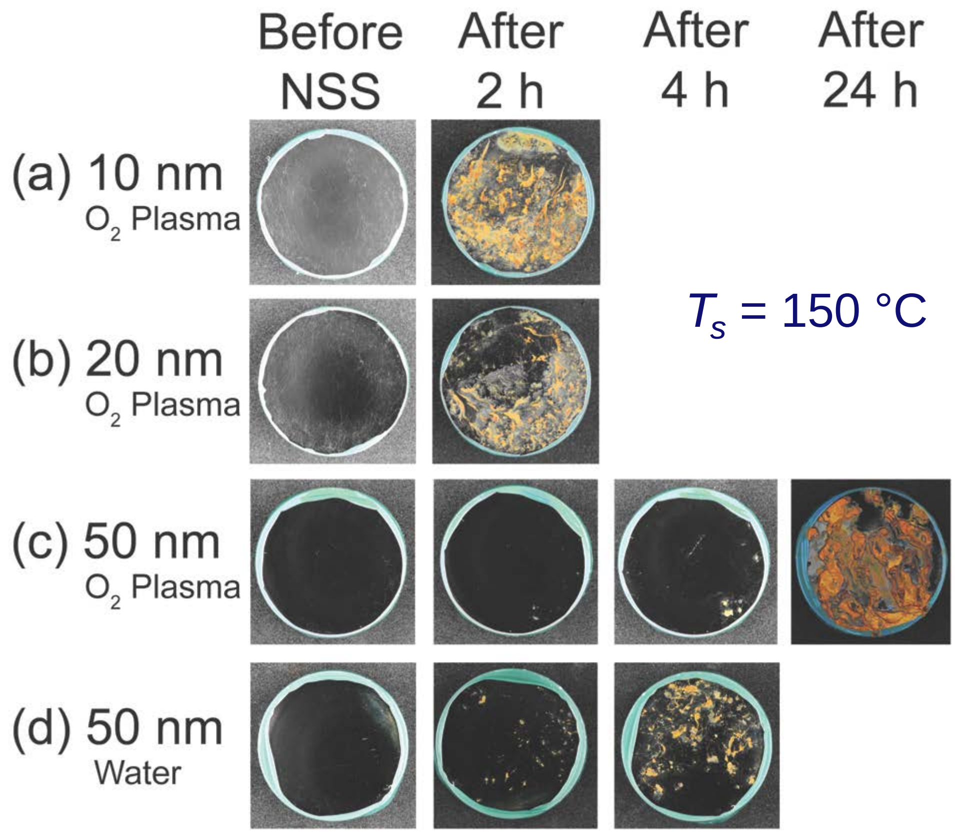

**Cycle times at low temperatures are reduced considerably.**


[■], [▲] J. L. van Hemmen *et al.*, *J. Electrochem. Soc.* **154**, G165 (2007).
[O] M. D. Groner *et al.*, *Chem. Mater.*, **16**, 639 (2004).
[☆] S. K. Kim *et al.*, *J. Electrochem. Soc.*, **153**, F69 (2006).

# $Al_2O_3$ as a Corrosion Barrier



- **Standard Industrial Alloys**
  - 100Cr6 mild steel
  - Aluminium Al2024-T3
- **Neutral salt-spray tests**
  - $Al_2O_3$ on 100Cr6 mild steel improves its resistance to corrosion.
  - Thicker films offer better protection
  - Plasma ALD films lasted longer than thermal ALD in the tests




This work has received funding from the European Community's FP7/2007-2013 project, grant agreement no. CP-FP213996-1 (CORRAL).

S. E. Potts *et al.*, *J. Electrochem. Soc.*, **in press** (2011).



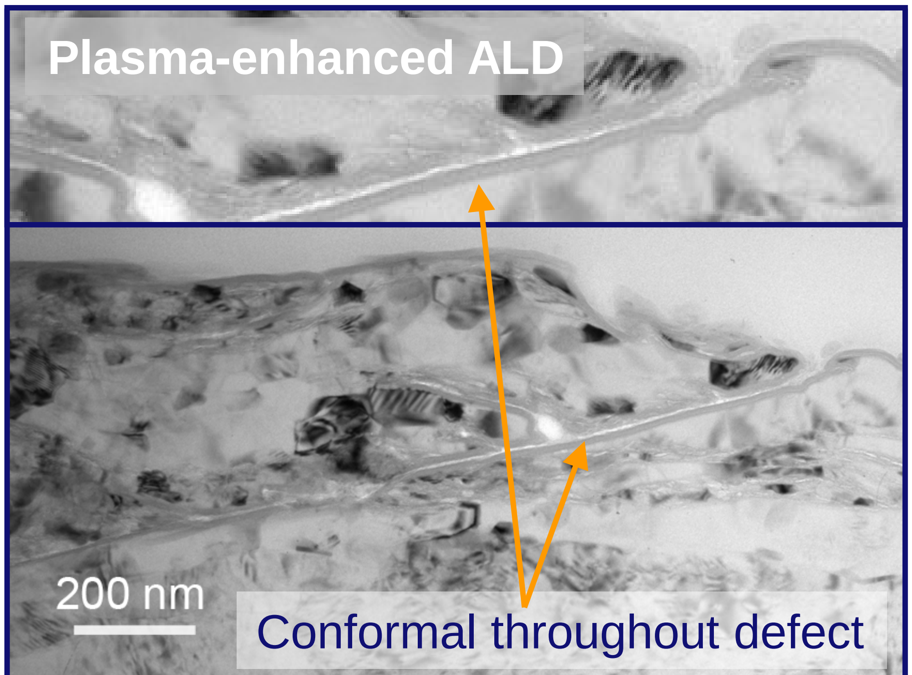
forschungsinstitut fem edelmetalle & metallchemie
TU/e Technische Universiteit Eindhoven University of Technology

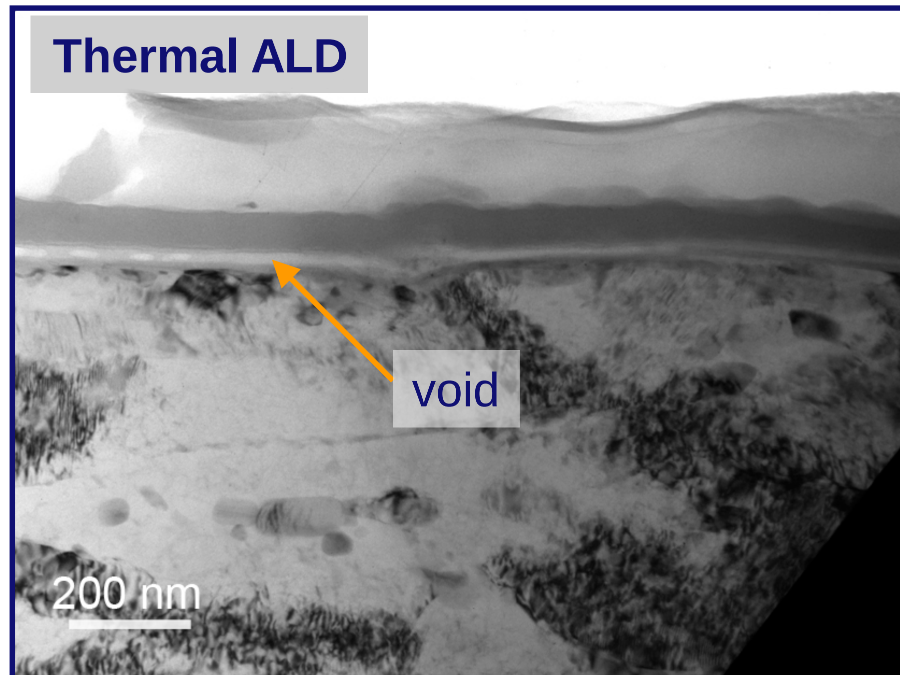
# $Al_2O_3$ as a Corrosion Barrier: TEM



## $Al_2O_3$ 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.




S. E. Potts *et al.*, *J. Electrochem. Soc.*, **in press** (2011).



Technische Universiteit Eindhoven University of Technology

# Moisture Permeation Barrier for OLEDs

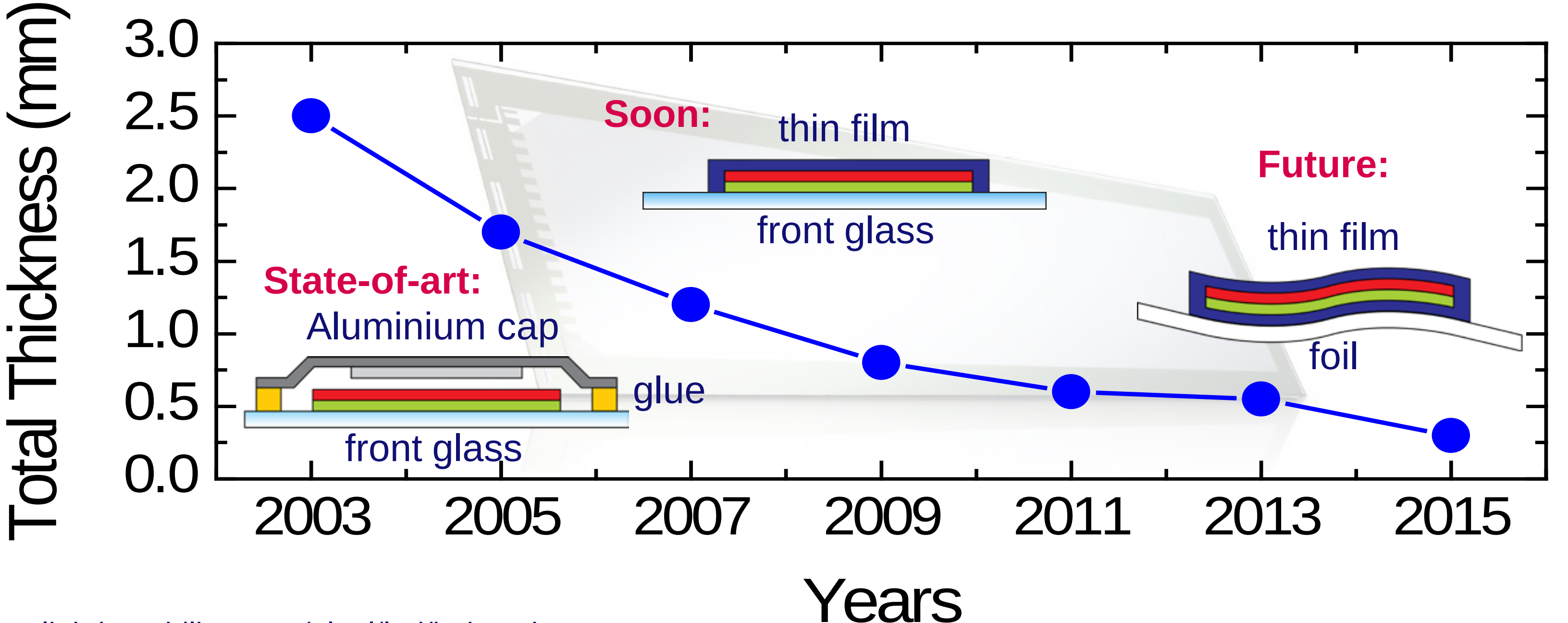


## Organic LEDs (OLEDs)

- 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$^{-1}$

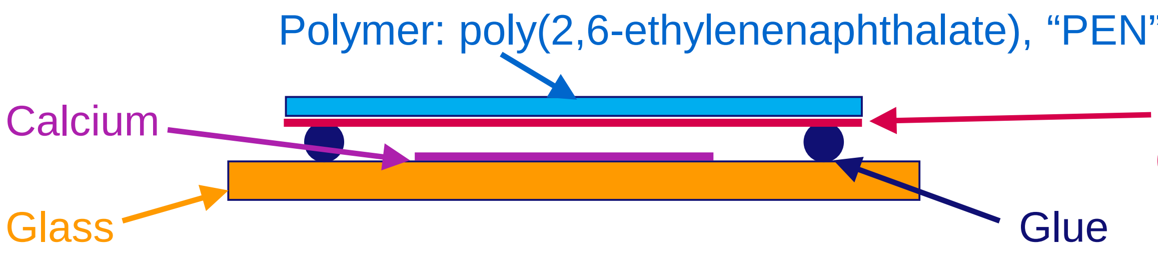


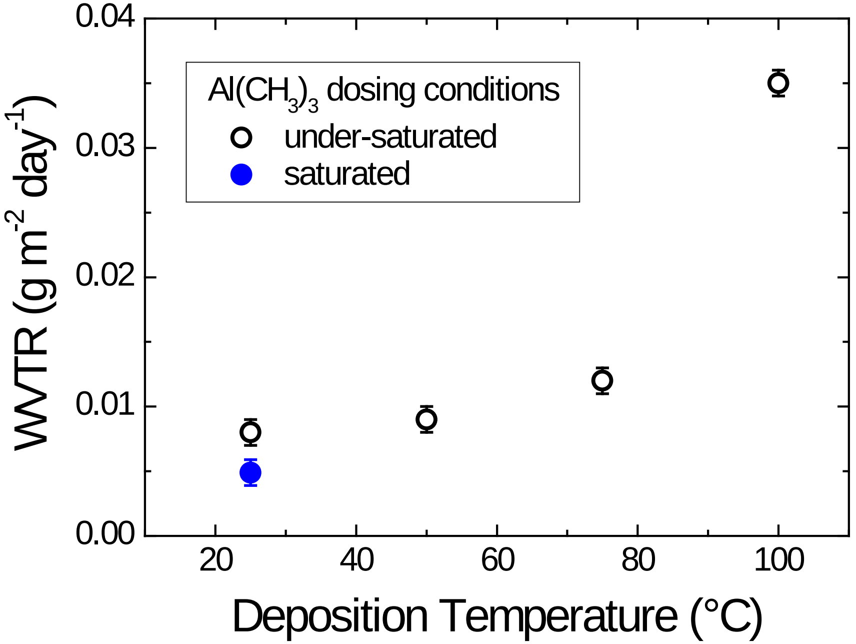

http://www.lighting.philips.com/nl_nl/led/index.php
http://www.lighting.philips.com/nl_nl/led/information/oled_lumiblade.php

# Plasma-Enhanced ALD for OLEDs

## 20-40 nm $Al_2O_3$ by plasma-enhanced ALD

- Calcium tests: films deposited at 25 °C gave lowest water vapour transmission rates

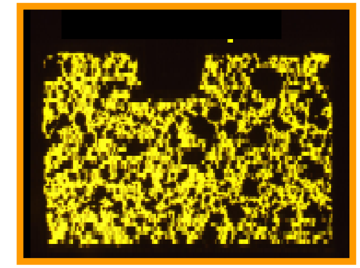


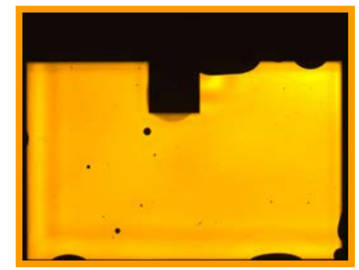

E. Langereis *et al.*, *Appl. Phys. Lett.*, **89**, 081915 (2006).

- Substantially thinner PE-ALD film offers better protection than an industry standard

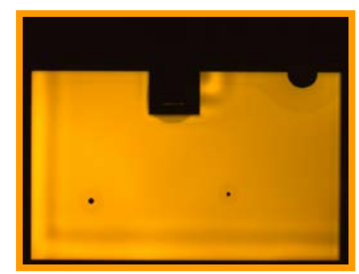
W. Keuning *et al.*, AVS 2009.



**Poly-LED**
*No encapsulation*



**PE-CVD**
*300 nm a-$SiN_x$:H*



**PE-ALD**
*40 nm $Al_2O_3$*



PHILIPS sense and simplicity
TU/e Technische Universiteit Eindhoven University of Technology

# Summary: Low Temperature ALD



- **Using plasma-enhanced ALD**
  - Deposit good to fair material down to room temperature
  - Significantly reduced co-reactant purging times for lower temperature (compare with water)

- **Corrosion barriers**
  - Protect industrial metal alloys
  - Plasma-enhanced ALD films offer improved protection (density)

- **Moisture permeation barriers**
  - Deposited at room temperature gave the best barrier properties



Technische Universiteit Eindhoven University of Technology

# Motivation: High(er) Temperature ALD



- **Many applications require $TiO_2$**
- **Mixed (Ternary) Oxides**
  - $SrTiO_3$ (STO) and $BaSrTiO_3$ (BST)
  - Ultra-high-*k* dielectric for DRAM trench capacitors

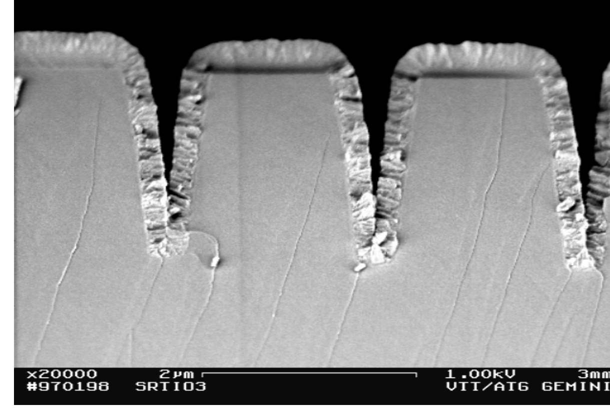
**14:45 Valentino Longo**

PA-ALD of Strontium Titanate using Cyclopentadienyl-Based Precursors

- **Requirements**
  - Ultra-thin films
  - Good conformality
  - Control of stoichiometry/atomic composition

**Merits #1 & #3**

$SrTiO_3$ on an Si trench structure.*




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

*From: M. Vehkamäki *et al.*, *Electochem. Solid-State Lett.*, **2**, 504 (1999).

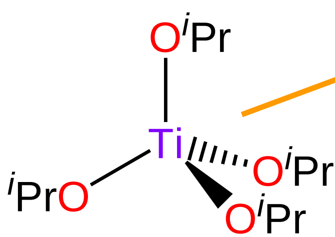


Technische Universiteit Eindhoven University of Technology

# Ligand-Tailoring of $TiO_2$ Precursors



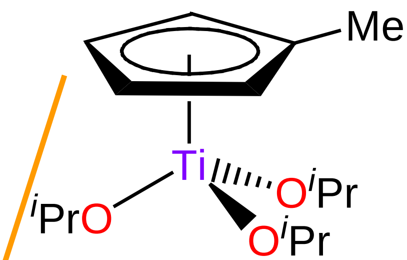
- **Tailoring ligands can allow for an increase in the maximum temperature**
  - Stronger M–L bonds
  - Incorporation of ligands less prone to decomposition



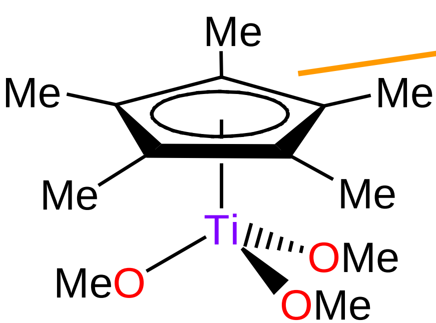

**1**

Homoleptic Ti compounds prone to oligomerisation

Isopropyl groups incorporating β-H: lowers decomposition temperature



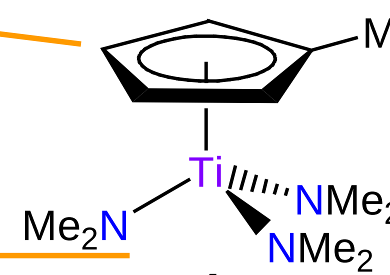

**2**




**3**

Cp-based ligands: increased stability
Increased volatility

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



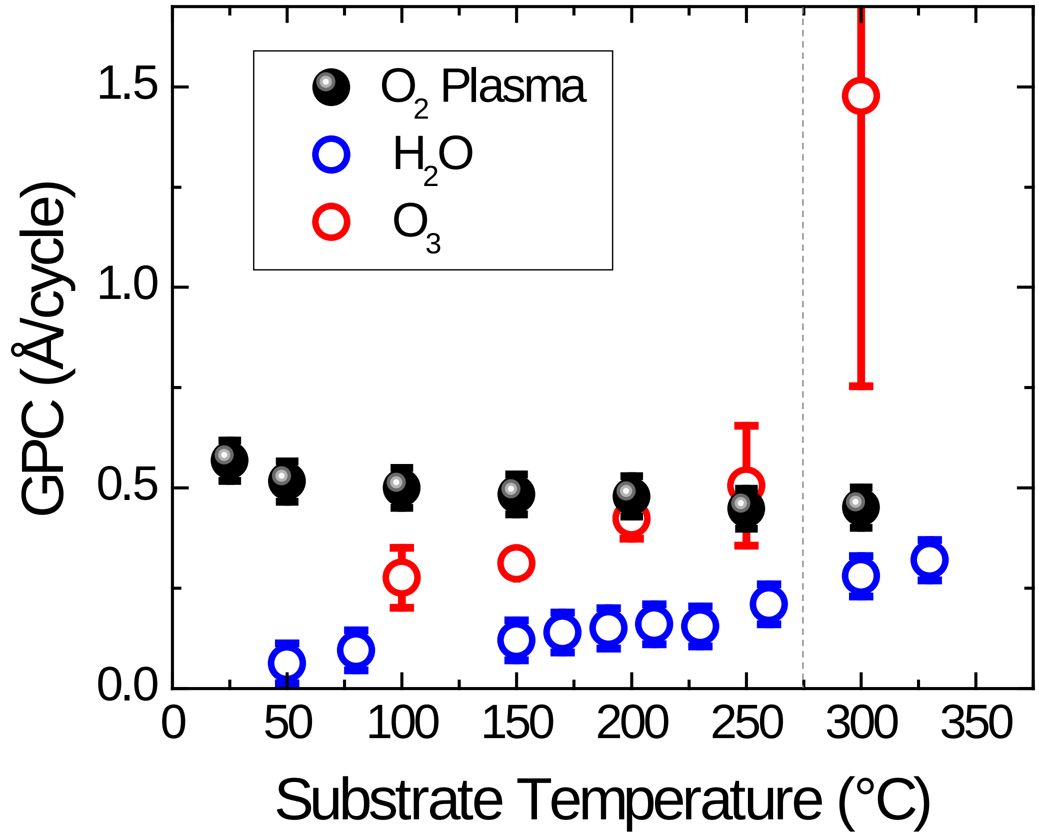

**4**



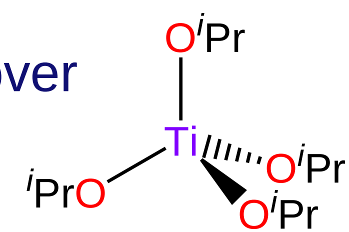
TU/e Technische Universiteit Eindhoven University of Technology

# Growth per Cycle (GPC) • Ti Precursor #1

- **[Ti(O$^i$Pr)$_4$]**
  - "TTIP"
  - A standard $TiO_2$ precursor
  - Homoleptic alkoxide
  - Tendency to dimerise
  - Decomposition at 300 °C
- **ALD with water and ozone**
  - Increase in GPC with increasing substrate temperature:
  - Thermally-driven process.
- **Plasma ALD**
  - Consistently high GPC over the temperature range.




Precursor decomposition at $T_s$ > dashed line.




$H_2O$ process: Q. Xie *et al.*, *J. Appl. Phys.*, **102**, 083521 (2007).

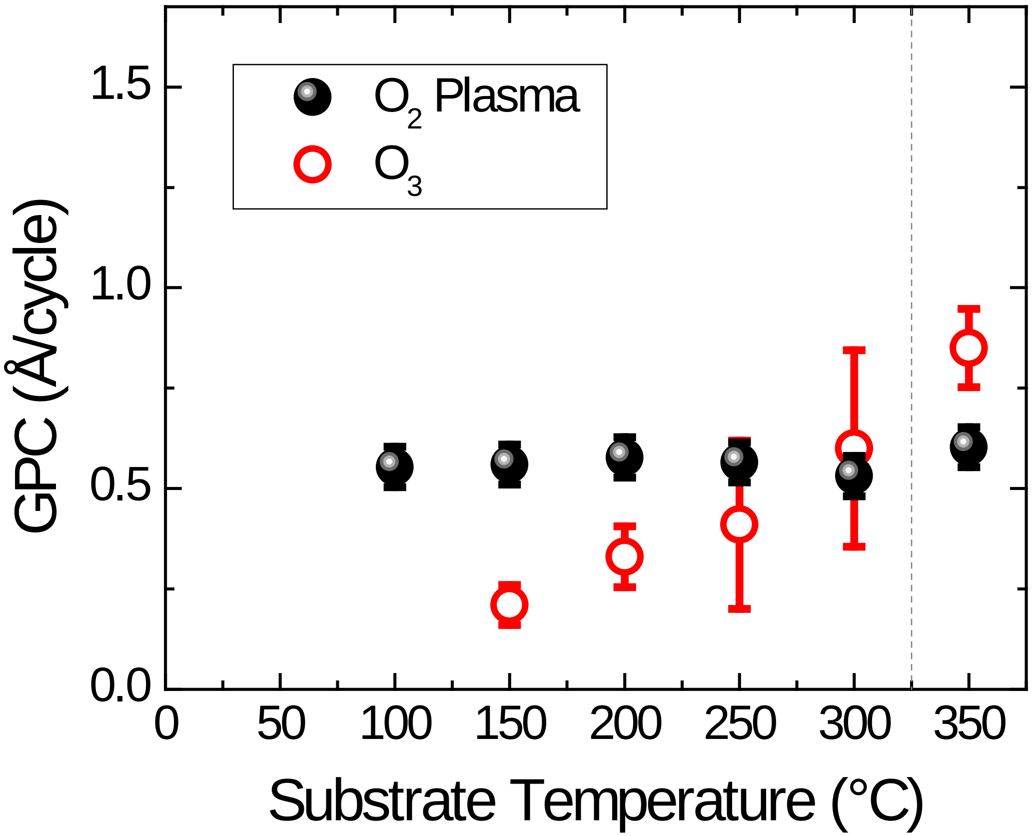
$O_3$ process: P. Williams at ALD 2008, Bruges, Belgium.



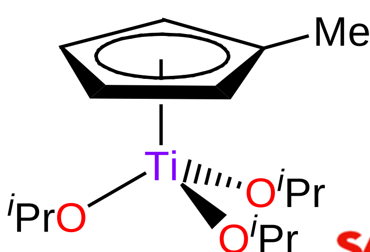
TU/e Technische Universiteit Eindhoven University of Technology

# Growth per Cycle (GPC) • Ti Precursor #2

- **[Ti(Cp$^{Me}$)(O$^i$Pr)$_3$]**
  - Cp$^{Me}$ for increased stability and volatility
  - No oligomerisation
  - Decomposition above 300 °C (β-H on $^i$Pr groups)
- **Not reactive with water in ALD process.**
- **Thermally-driven mechanism for ozone.**
- **Flat GPC profile for plasma process.**
- **Comparable GPC to #1.**




Precursor decomposition at $T_s$ > dashed line.




O$_3$ process: P. Williams at ALD 2008, Bruges, Belgium.



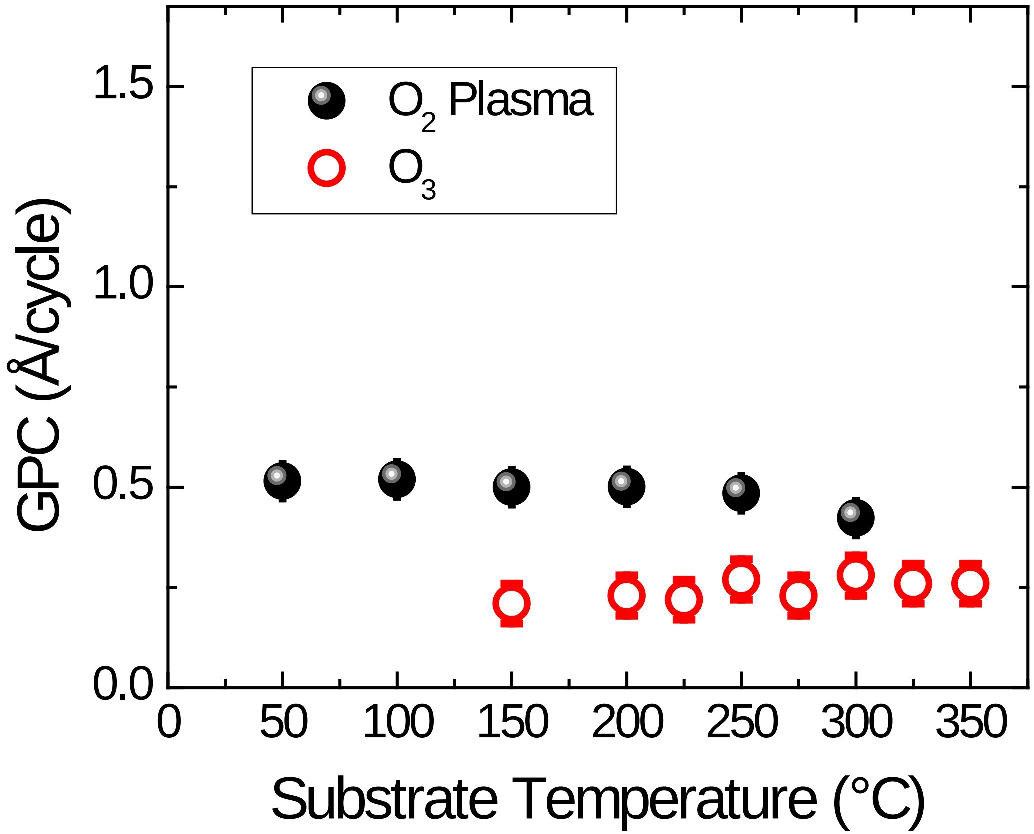
SAFC Hitech™ Enabling Technology

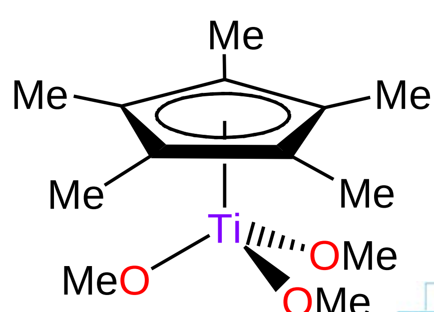
TU/e Technische Universiteit Eindhoven University of Technology

# Growth per Cycle (GPC) • Ti Precursor #3



- **[Ti(Cp*)(OMe)$_3$]**
  - “Ti-Star” or “StarTi”
  - No obvious decomposition
  - OMe groups have no β-H
- **Similar GPC to #1 and #2.**
- **Increase in GPC with temperature for ozone less prominent.**
- **Preliminary DFT calculations**
  - Full chemical bonding does not take place with OH surface groups.*
  - H-bonding *via* OMe groups.
  - Cp$^x$ left on surface.



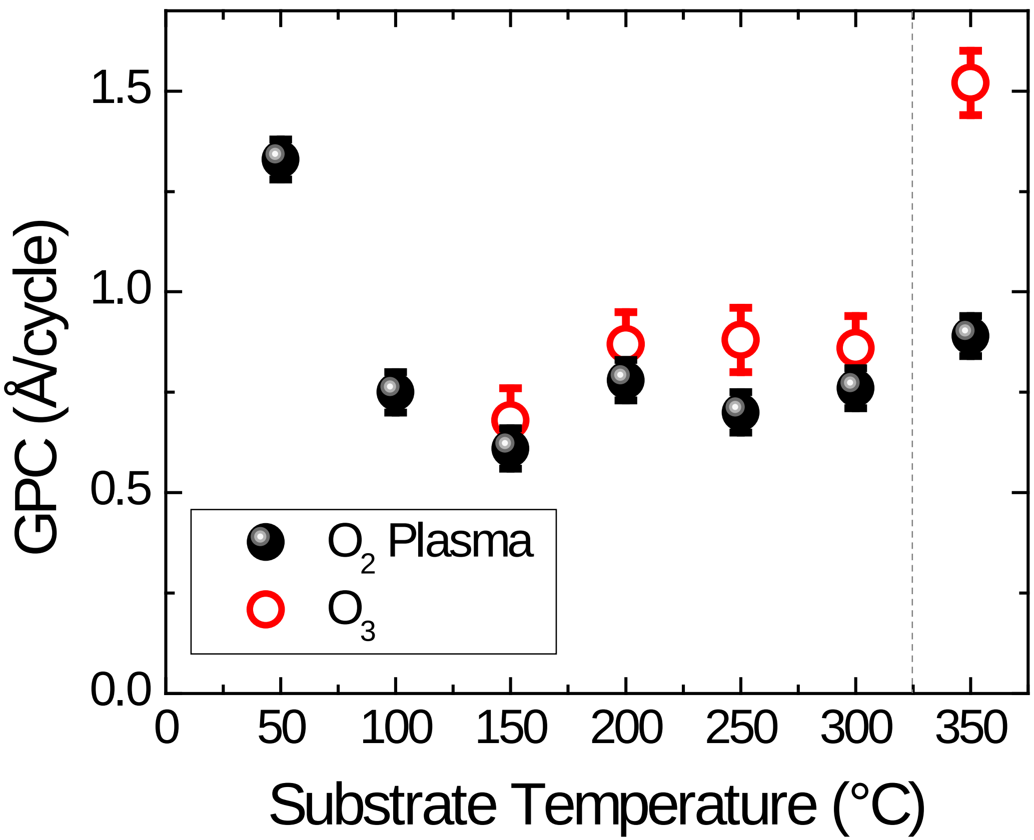

$O_3$ process: R. Katamreddy *et al.*, *ECS Trans.*, **25**, 217 (2009).
*S. D. Elliott *et al.* at ALD 2010, 22nd June.

AIR LIQUIDE
TU/e Technische Universiteit Eindhoven University of Technology

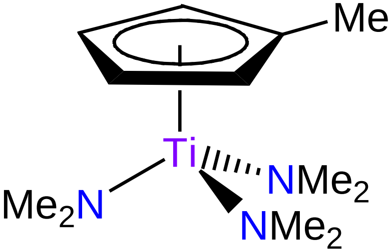
# Growth per Cycle (GPC) • Ti Precursor #4



- [Ti(Cp$^{Me}$)(NMe$_2$)$_3$]
  - Possibility of oxides and nitrides.
  - NMe$_2$ more reactive towards oxidants.
- **GPC of plasma and ozone processes follow similar trend.**
- **Higher GPC than #1-3.**
- **Reactivity of NMe$_2$ ligands higher than OR.**
- **This reactivity reduces at $T_s$ < 200 °C.**




Precursor decomposition at $T_s$ > dashed line.



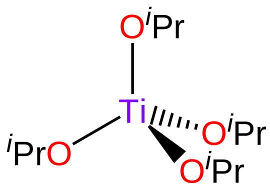

$O_3$ process: P. Williams at ALD 2008, Bruges, Belgium.
See also: A. Sarkar at the 218th ECS meeting, Las Vegas, Oct. 2010.

SAFC Hitech™ Enabling Technology

# Higher Deposition Temperatures of $TiO_2$

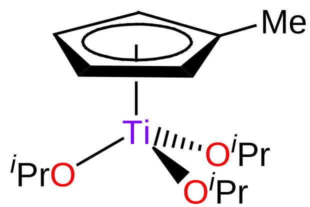


**Combination of OMe ligands and Cp result in the highest decomposition temperature.**



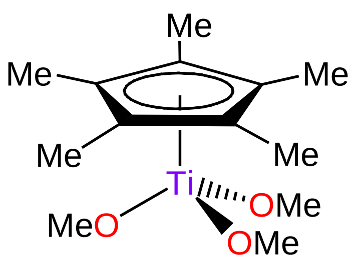

**1**

~300 °C



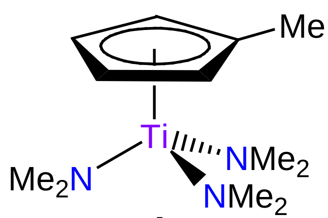

**2**

~350 °C



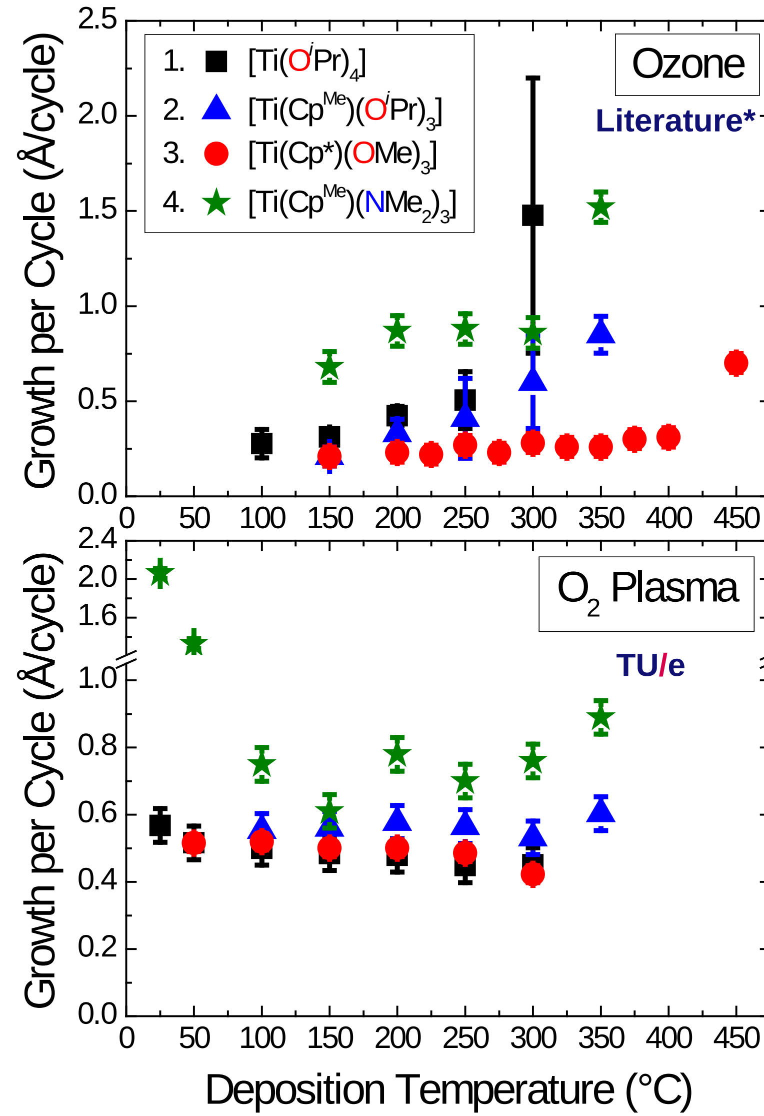

**3**

~450 °C




**4**

~350 °C




**Upper limit of temperature window effectively increased**

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

# Summary: High(er) Temperature ALD



- **$H_2O$, $O_3$ and an $O_2$ plasma give very different results for the same ligands.**

- **For plasma ALD, the precursor reactivity with the substrate surface (1) is, in practice, the only limiting step.**

- **Reactivity of ligands in Ti compounds towards surface groups at low temperature:**

$$Cp^x \ll OR < NR_2$$

- **Ability to H-bond with surface groups is key to the reaction mechanism.**

- **Plasmas allow Cp-based precursors to be used for microelectronics applications:**
  - Give good ALD behaviour
  - $Cp^x$ ligands provide stability to the precursors

# Conclusions



- **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

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

- **Plasmas allow for ALD over a wider temperature range than possible with thermal ALD**



Technische Universiteit Eindhoven University of Technology