Low Temperature Plasma-Enhanced ALD of Metal Oxide Thin Films

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PLASMA & MATERIALS PROCESSING

SEVENTH FRAMEWORK
PROGRAMME

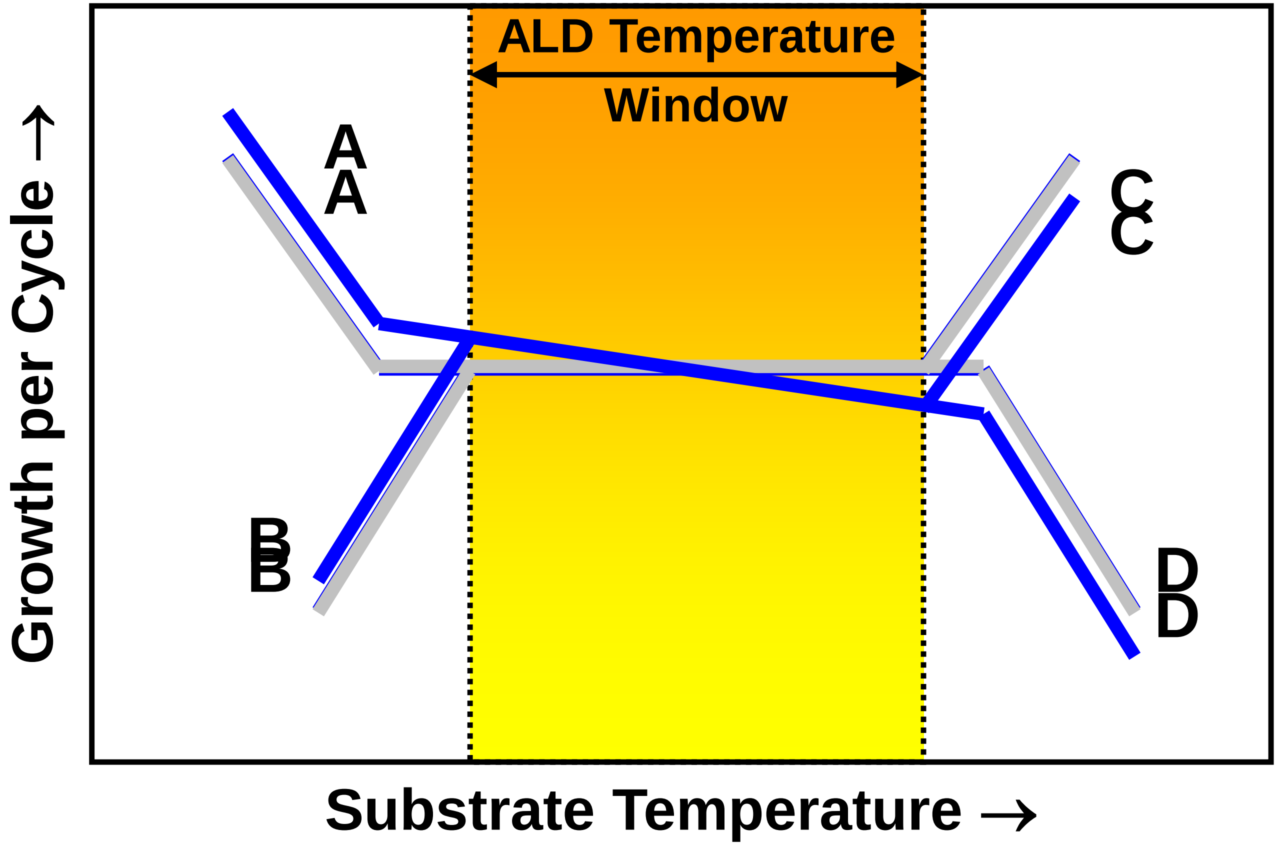
Technische Universiteit
Eindhoven
University of Technology

Where innovation starts

Outline

- The ALD temperature window
- Why low temperature ALD?
- Low temperature ALD in the literature
- Why plasma-enhanced ALD?
- Experimental details
- Overview of low temperature plasma-enhanced ALD of metal oxides: comparison with thermal routes
    - Al_2O_3
    - TiO_2
    - Ta_2O_5
- Conclusions

The ALD Temperature Window

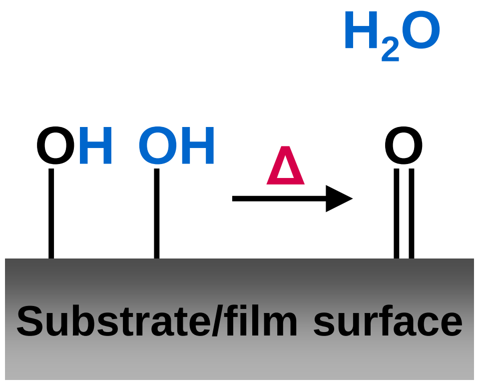


A. Condensation

B. Insufficient thermal energy

C. CVD

D. Evaporation



- Assumption: a sub-monolayer of material is deposited
- Loss of surface groups with increasing temperature

Why Low Temperature ALD?

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

- **Organic substrates**
  - Organic polymers or small organic molecules
  - Moisture permeation barriers in OLEDs
  - Thin film transistors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Flexible OLED display

- **Metals (or polymers) requiring a corrosion-resistant barrier layer**
  - Higher T_s can alter the metal's mechanical properties
  - Dense, defect-free films required
  - High resistance to wear and/or chemical attack
  - Al_2O_3, TiO_2, Ta_2O_5, combinations (stacks)


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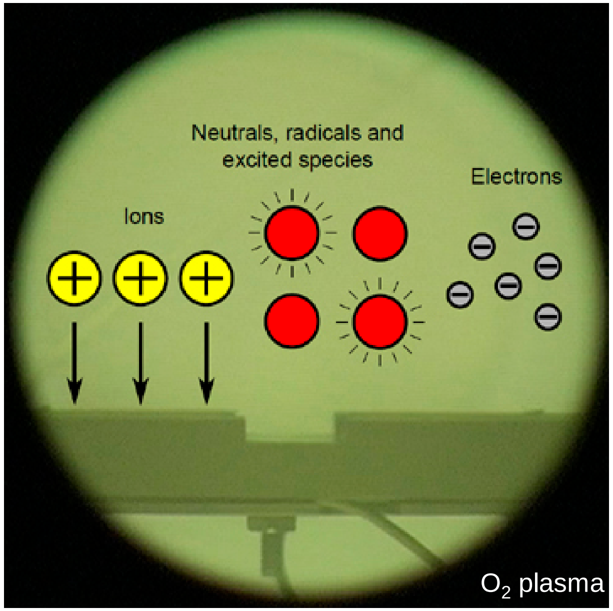
Corrosion on gears

Low Temperature 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	$TiCl_4$	H_2O	100	Aarik *et al.*
	$TiCl_4$	H_2O_2	100	King *et al.*
	$[Ti(O^iPr)_4]$	H_2O	150	Ritala *et al.*
	$[Ti(O^iPr)_4]$	H_2O_2	77	Liang *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	100	Heil *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.*

For full references, see S. E. Potts *et al.*, *ECS Trans.*, submitted (2009).

Why Plasma-Enhanced ALD?

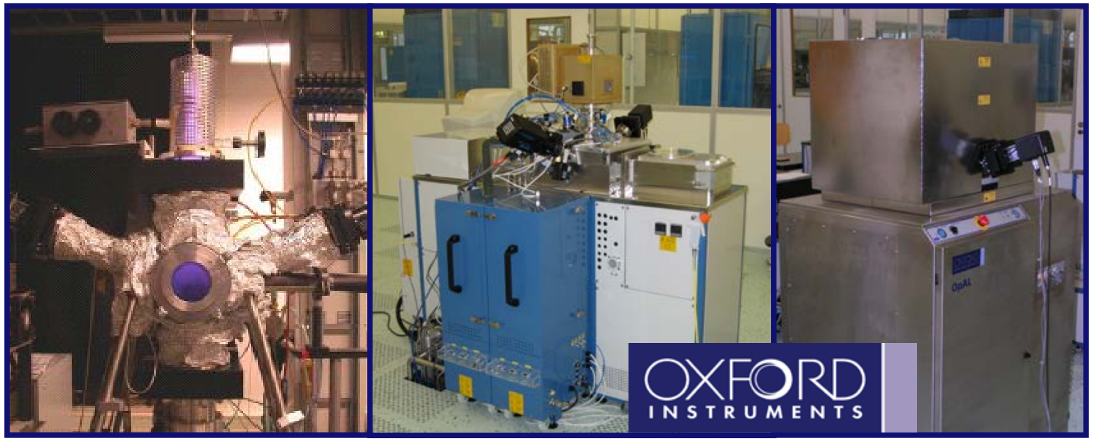


- **Gas ionised by electrical energy**
  - Ions
  - Electrons
  - Neutral species
  - Which (re)combine to form radicals
- **Radicals react with surface groups**
- **Ion energy and ion flux → surface ion bombardment**
  - Can lead to denser films
- **Increased reactivity**
- **Extension of temperature window down to room temperature?**

W. M. M. Kessels *et al.*, *ECS Trans.*, **3**, 183 (2007).

Experimental Details (Plasma & Thermal ALD)

Remote Plasma ALD Reactors

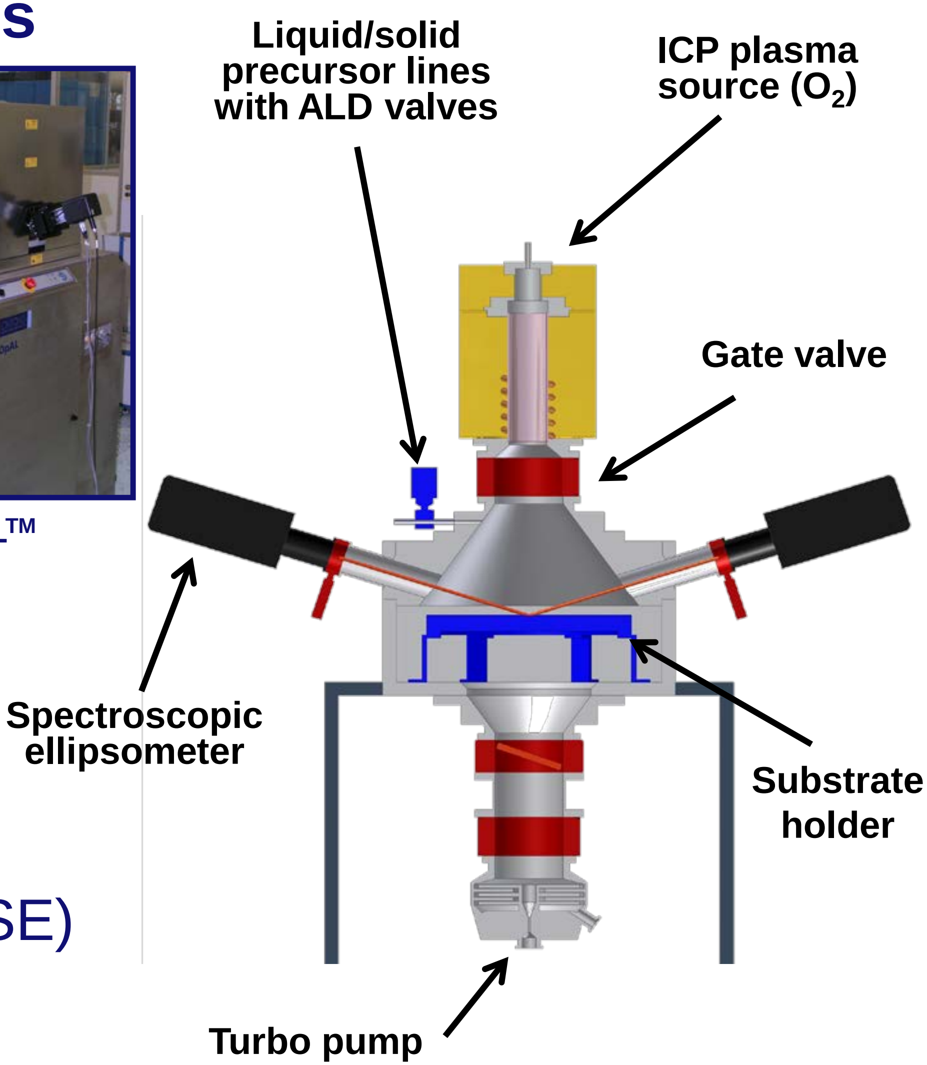


ALD-I (home-built)

FlexAL^{TM}

OpAL^{TM}

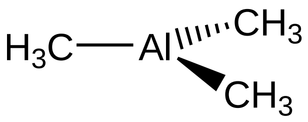
- **p-type Si{100} substrates**
- **Diagnostics**
  - Film thickness:
    - Spectroscopic ellipsometry (SE)
  - Film composition
    - RBS and ERD (H)



Plasma-Enhanced ALD of Metal Oxides

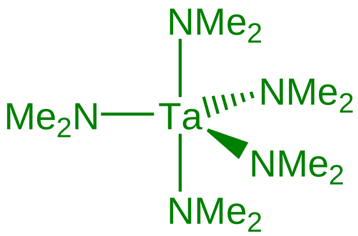
1\.

TMA

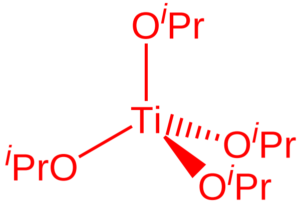


2\.

PDMAT

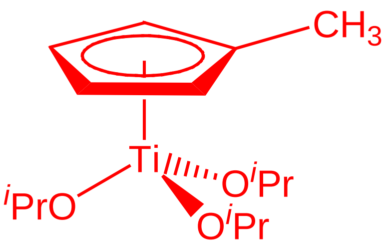


3\.

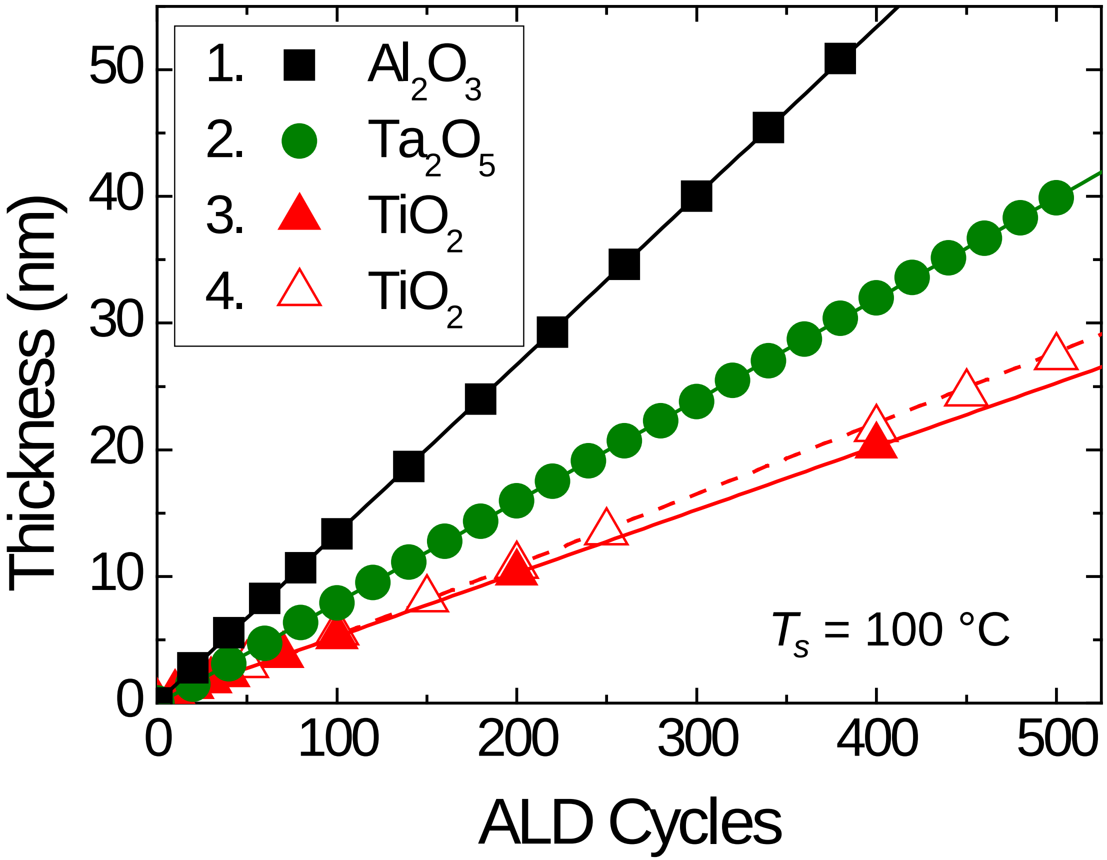


Titanium isopropoxide

4\.

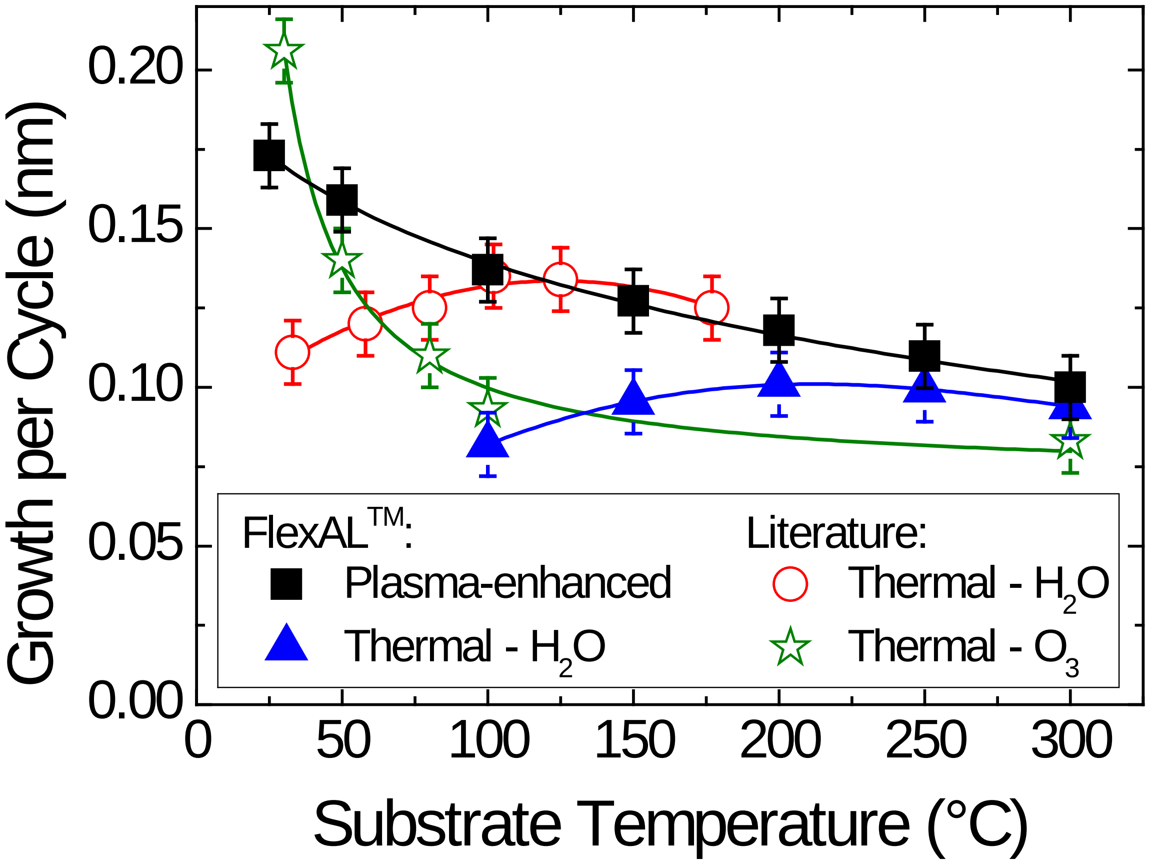


Methylcyclopentadienyl-tris(isopropoxy)titanium



- **Measured using *in situ* SE**
- **No nucleation delay**
- **Slope gives growth per cycle for the process**

Al_2O_3: Growth per Cycle

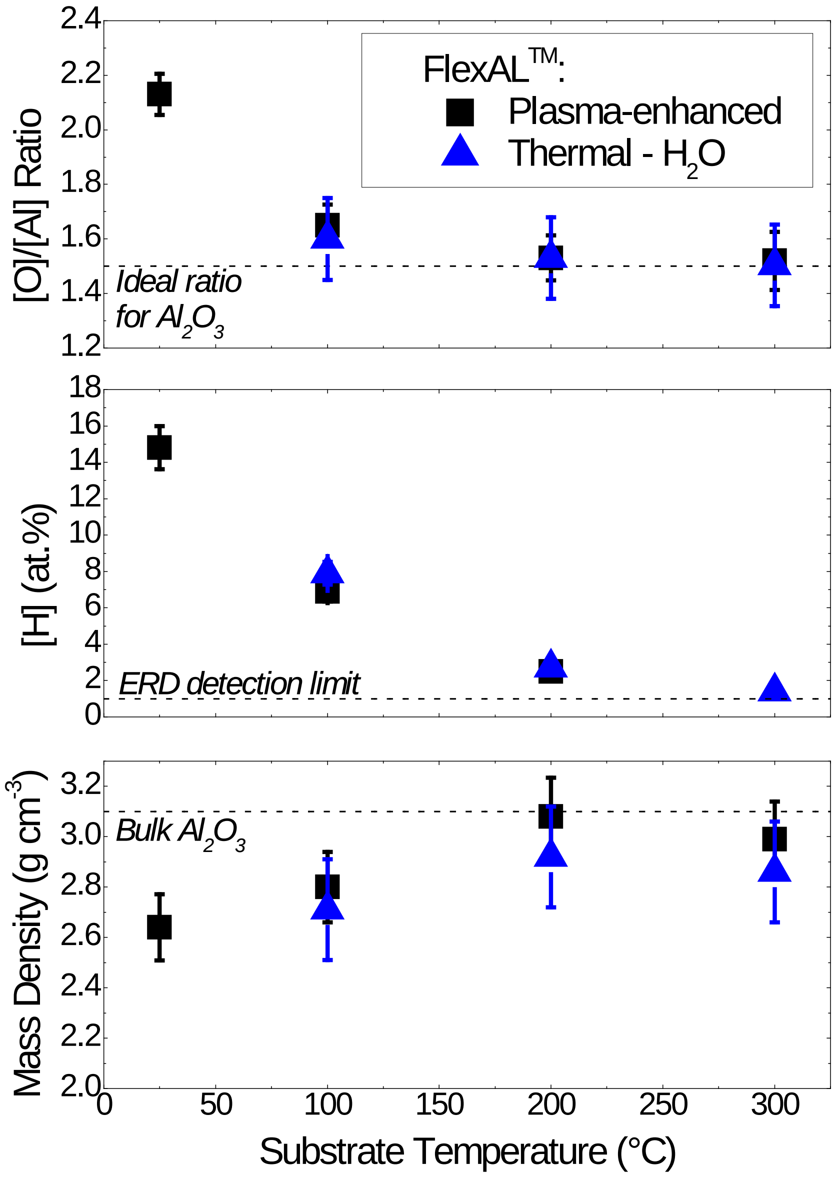


- **Water processes: lower growths per cycle at low temperatures**
- **Ozone process: many extra surface groups at T_s < 100 °C.**
- **Reduction in growth per cycle with increasing T_s → dehydroxylation.**

Plasma-enhanced ALD gives the higher growths per cycle at low deposition temperatures.

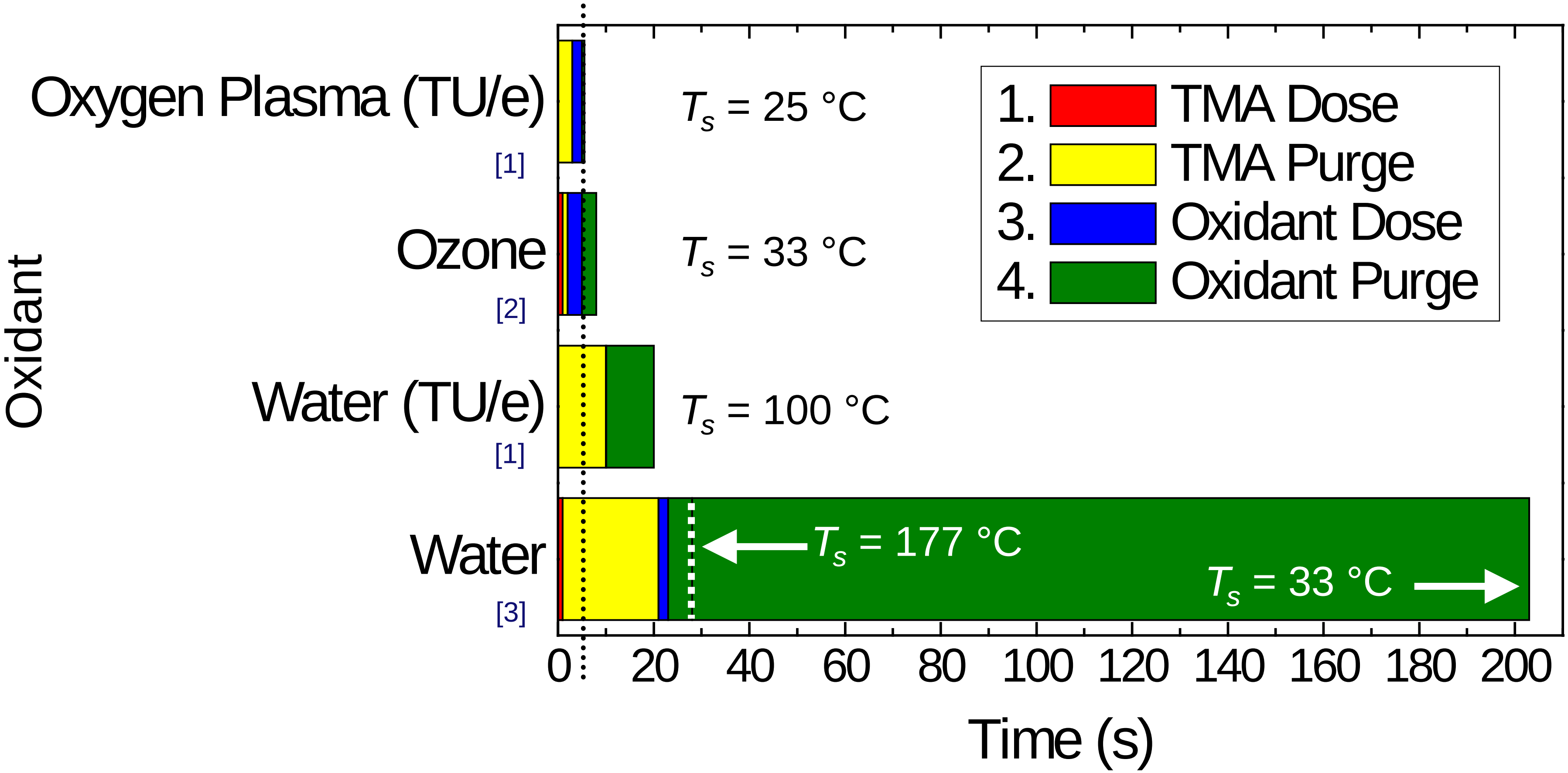
[■], [▲] J. L. van Hemmen *et al.*, *J. Electrochem. Soc.* **154**, G165 (2007).
[○] M. D. Groner *et al.*, *Chem. Mater.*, **16**, 639 (2004).
[☆] S. K. Kim *et al.*, *J. Electrochem. Soc.*, **153**, F69 (2006).

Al_2O_3: Film Composition



- **[C] < 1 at.% in each case.**
- **–OH is prominent at lower temperatures.**
- **Leads to increasing mass density of the films with deposition temperature.**
- **No significant composition difference between plasma and thermal ALD.**

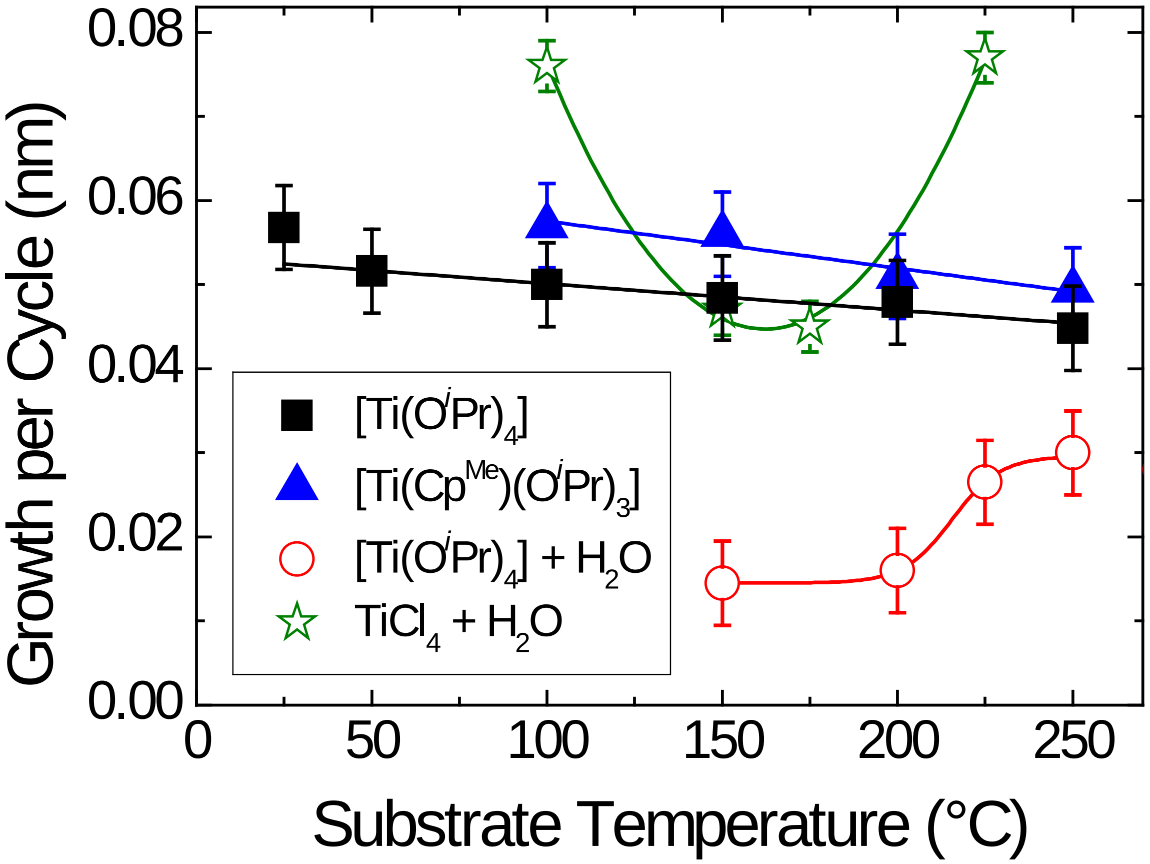
Al_2O_3: Cycle Time



Lower deposition temperatures require a longer oxidant purge.

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

TiO_2: Growth per Cycle

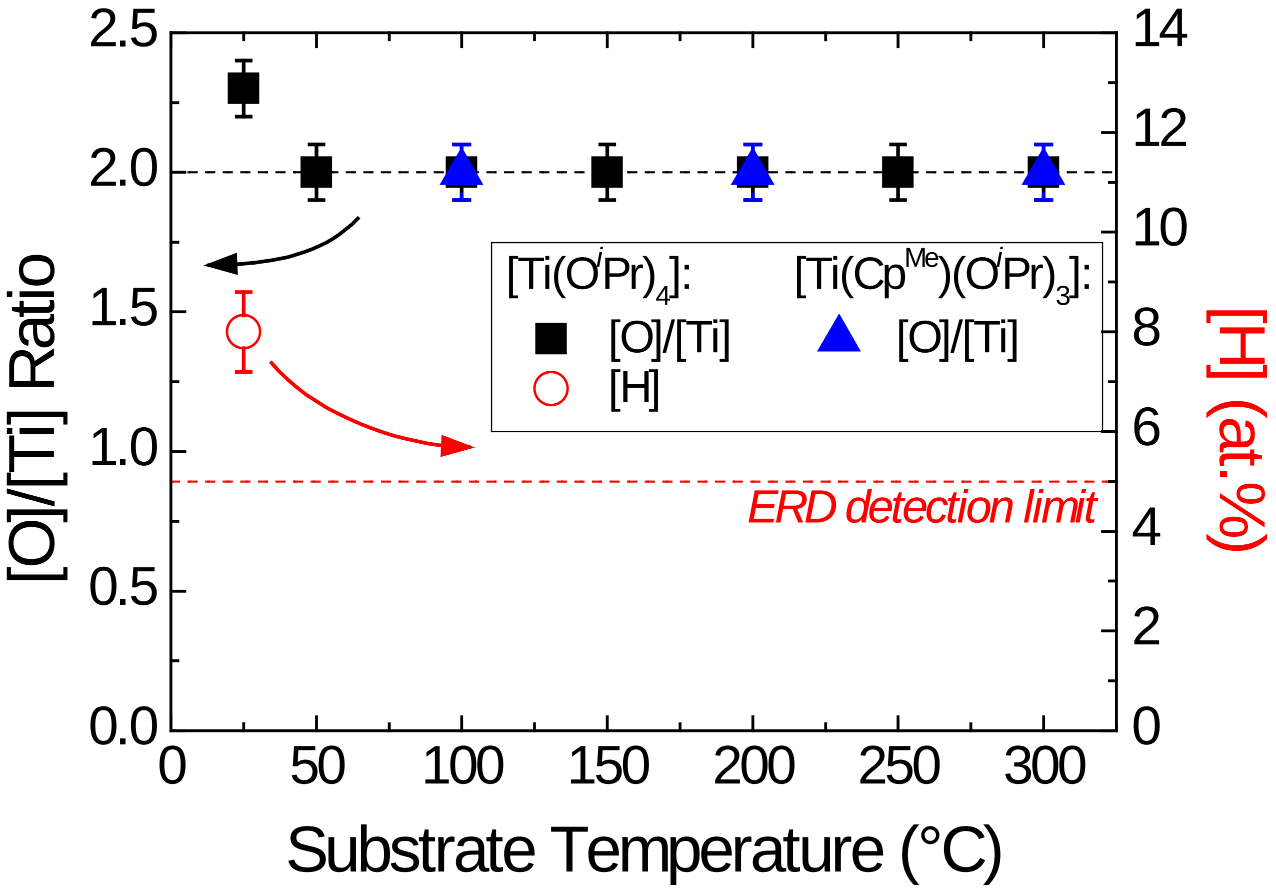


- **Dehydroxylation with increasing T_s.**
- **Use of alkoxy-based precursors → no chlorine in final film.**
- **[Ti(O^{i}Pr)$_4$] + water process: very low growth per cycle**
- **$TiCl_4$ process: etching at T_s = 150-175 °C.**

Plasma-enhanced ALD: higher growth per cycle

[■] W. Keuning *et al.*, work to be published.
[▲] E. Langereis *et al.*, work to be published.
[○] M. Ritala *et al.*, *Chem. Mater.*, **5**, 1174 (1993).
[☆] J. Aarik *et al.*, *J. Cryst. Growth*, **220**, 531 (2000).

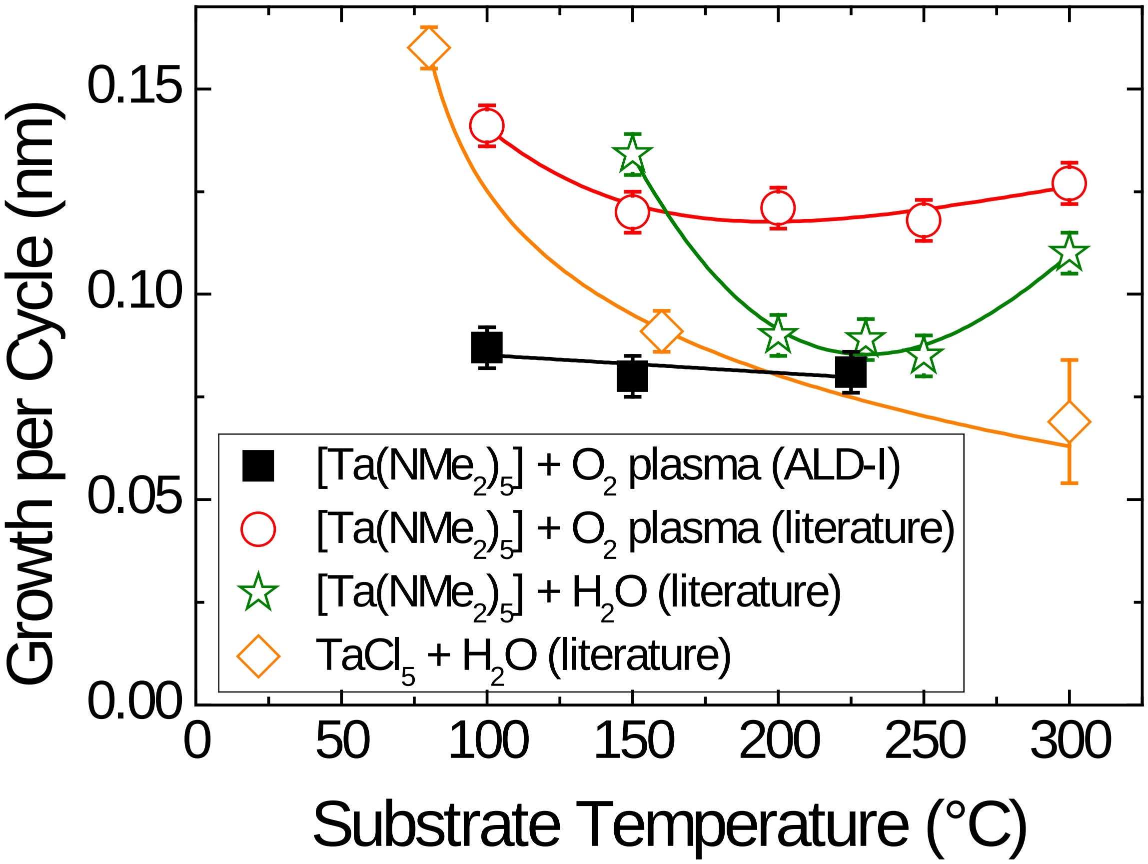
TiO_2: Film Composition



- **Both precursors: same film composition**
- **[C] < 1 at.%.**
- **[H] below detection limit at *T_s* ≥ 50 °C**
- **Thermal route [H] ~0.3 at.%**

Hydroxyl groups only seen at room temperature.

Ta_2O_5



- **[O]/[Ta] Ratio:**
- **Our films = 2.5**
- **Lit. PDMAT = 2.6**
- **Lit. $TaCl_5$ = ~2 ± 0.1**

- **[C] and [N] < 1 at.% in all cases for PDMAT**
- **[H] detected but < 5 at.%**
- **From $TaCl_5$ [Cl] up to 6 at.%**

- **Difference in growth per cycle due to different reactors?**

[■] S. B. S. Heil *et al.*, *J. Vac. Sci. Technol. A*, **26**, 472 (2008).
[○] W. J. Maeng *et al.*, *J. Vac. Sci. Technol. B*, **24**, 2276 (2008).
[☆] W. J. Maeng and H. Kim, *Electrochem. Solid-State Lett.*, **9**, G191 (2006).
[◇] K. Kukli *et al.*, *Thin Solid Films*, **260**, 135 (1995).

Conclusions

- **Plasma-enhanced and thermal ALD routes compared**
- **Advantages of plasma-enhanced ALD dependant on process:**
- **Al_2O_3 from TMA**
  - Higher growth per cycle down to room temperature than the thermal process with water
  - Higher quality films at low temperatures than the ozone process
  - Reduced cycle times
- **TiO_2 from $[Ti(O^iPr)_4]$ or $[Ti(Cp^{Me})(O^iPr)_3]$**
  - Pure, stoichiometric films down to 50 °C.
  - Higher growth per cycle than $[Ti(O^iPr)_4]$ with water.
- **Ta_2O_5 from PDMAT**
  - High purity, stoichiometric films down to 100 °C.