Low Temperature Plasma-Enhanced ALD of Metal Oxide Thin Films

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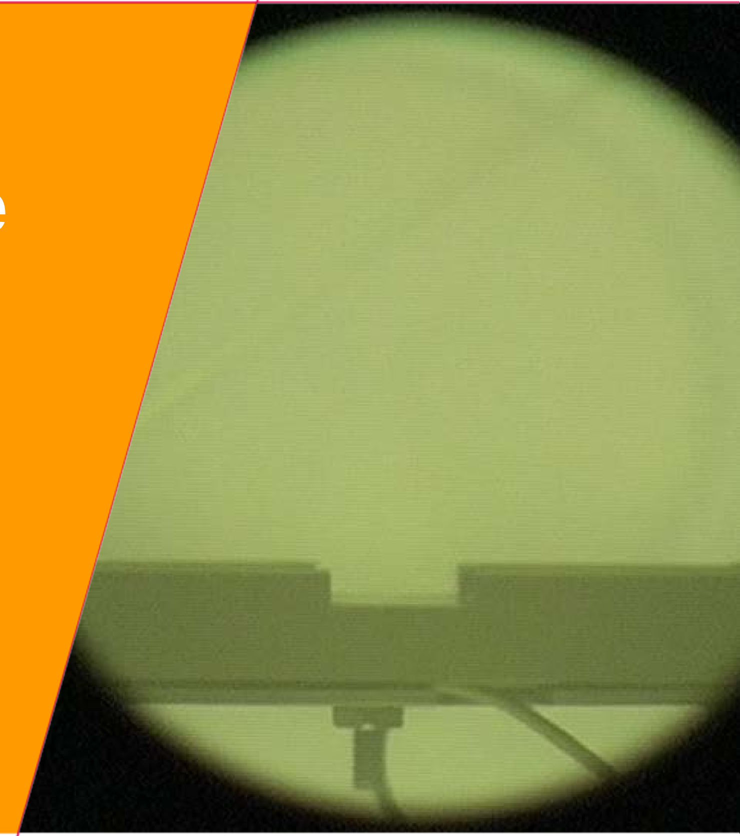

PLASMA & MATERIALS PROCESSING

SEVENTH FRAMEWORK PROGRAMME

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Where innovation starts

Outline

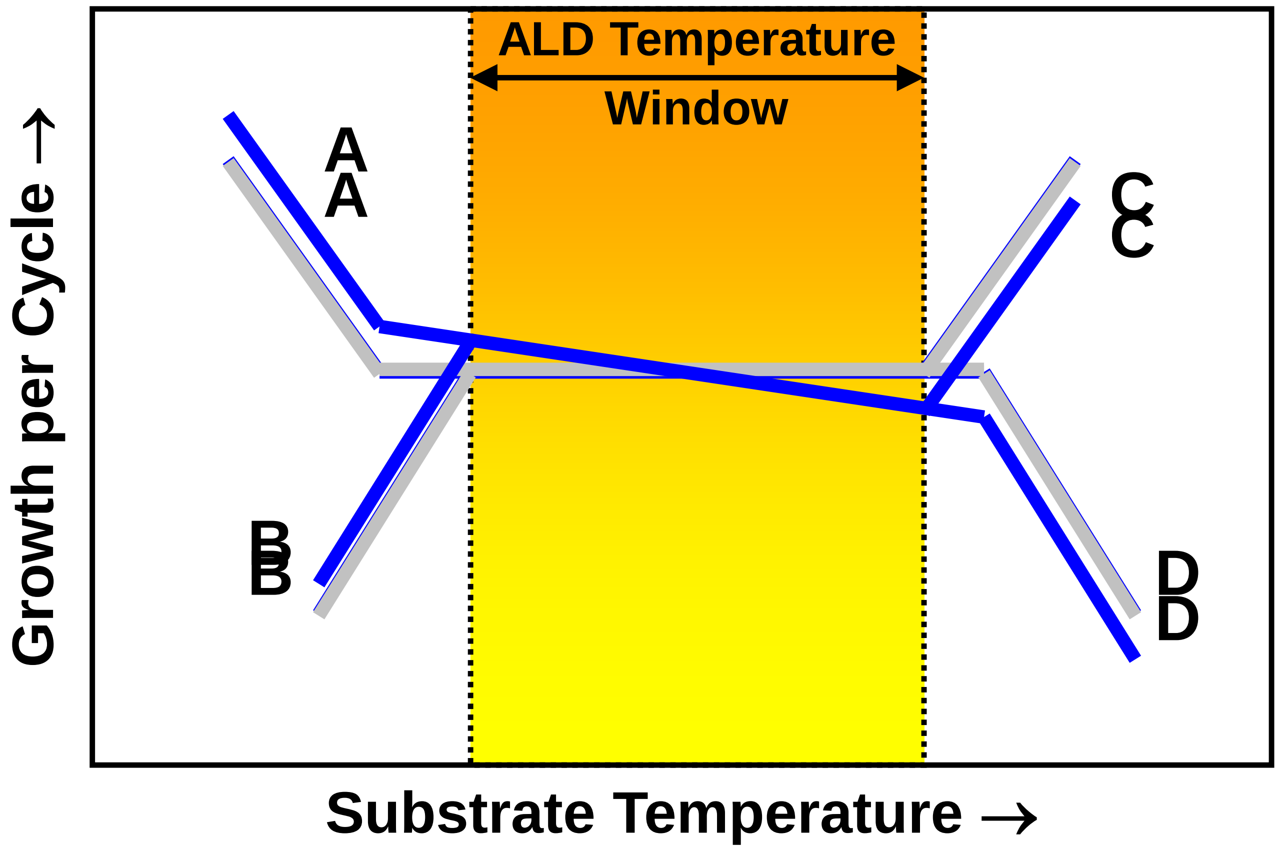
- **The ALD temperature window**
- **Why low temperature plasma-enhanced ALD?**
- **ALD Reactors**
- **Film characterisation**
  - spectroscopic ellipsometry and Rutherford backscattering
- **Overview of low temperature plasma-enhanced ALD of metal oxides**
  - Comparison with thermal procedures and literature
  - Growth per cycle
  - Atoms deposited per cycle
  - Film composition
- **Conclusions**

Al_2O_3

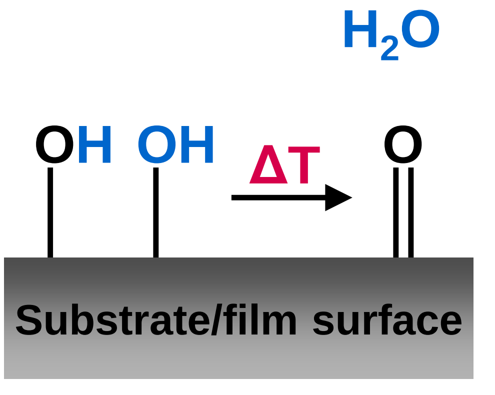
TiO_2

Ta_2O_5

The ALD Temperature Window



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

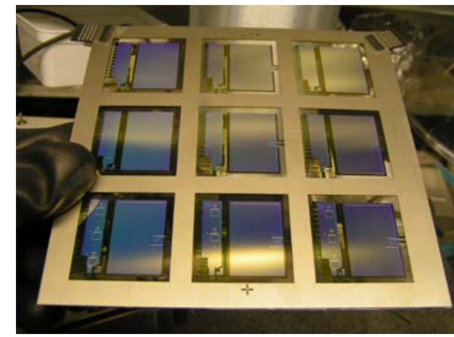


- **Assumption: a sub-monolayer of material is deposited**
- **Loss of surface groups with increasing temperature**

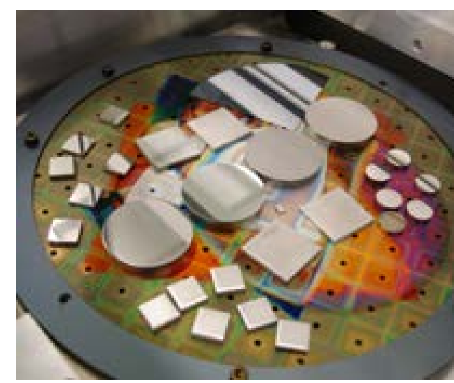
T. Suntola, *Mater. Sci. Rep.*, **4**, 261 (1989).

Why Low Temperature ALD?

- **Some applications require high film quality but the substrates required are temperature-sensitive.**
- **Dense, defect-free films required.**
- **Organic substrates**
  - Moisture permeation barriers in OLEDs
  - Thin film transistors
- **Metals (or polymers) requiring a corrosion-resistant barrier layer**
  - Higher temperatures can alter the metal's mechanical properties



OLEDs at TU/e



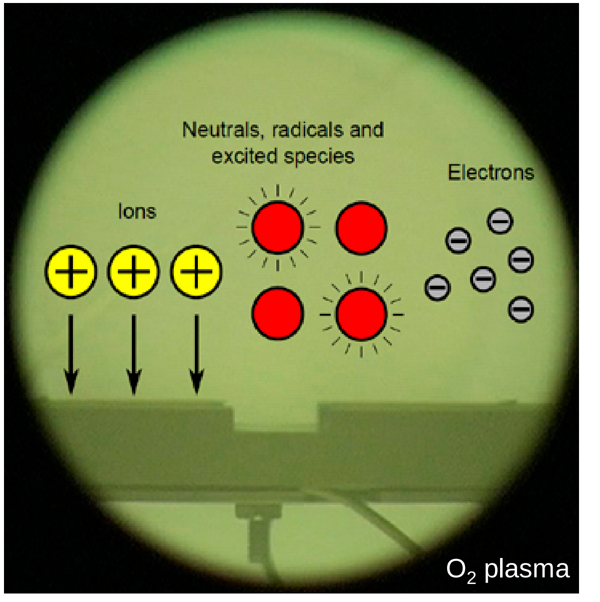
Coating metal substrates at TU/e

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.*, **25**, 233 (2009).

Why Plasma-Enhanced ALD?

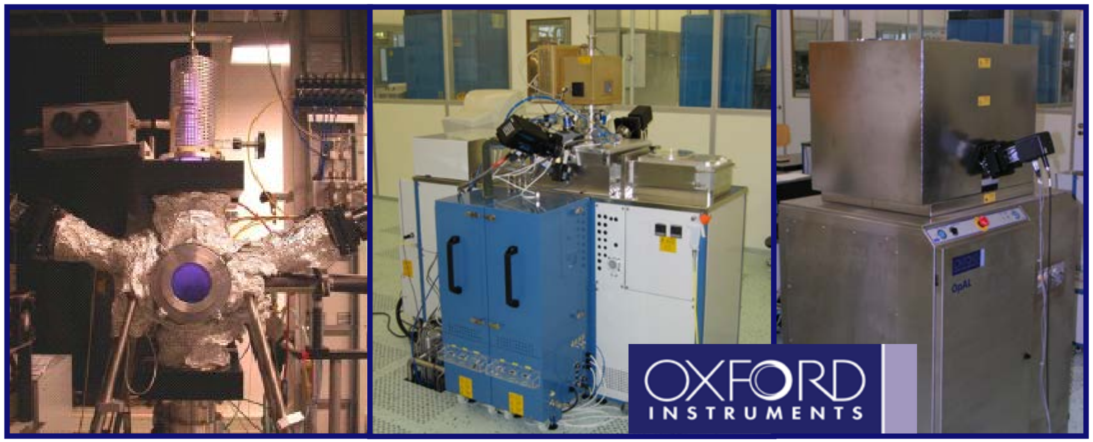


- **Gas ionised by electrical energy**
  - Ions
  - Electrons
  - Neutral species including radicals
- **Radicals react with surface groups**
- **Ion energy and ion flux**
  → surface ion bombardment
  - Can lead to denser films
- **Increased reactivity**
- **Extension of temperature window down to room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

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

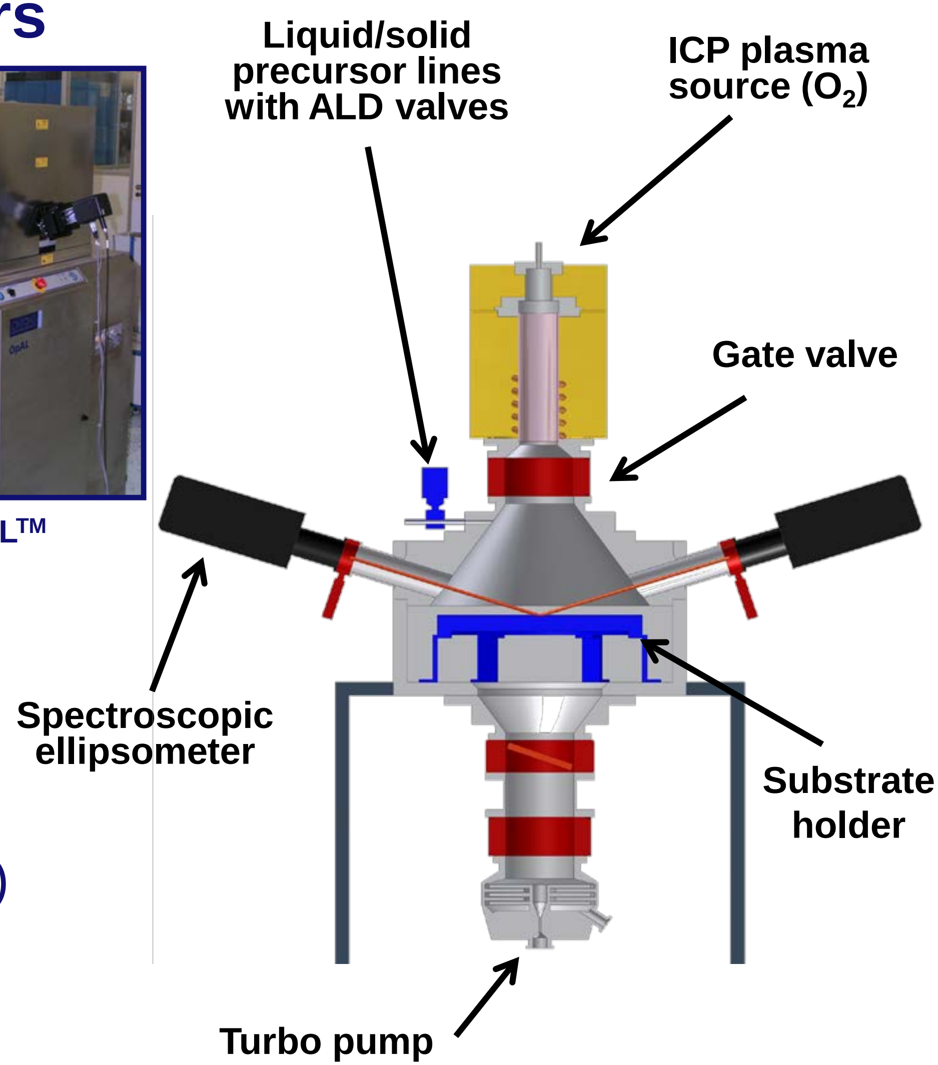
Experimental Details (Plasma & Thermal ALD)

Remote Plasma ALD Reactors



ALD-I (home-built) | FlexAL™ | OpAL™

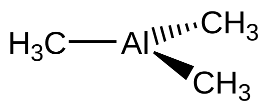
- **p-type Si{100} substrates**
- **Diagnostics**
  - Film thickness:
    - Spectroscopic ellipsometry (SE)
  - Film composition
    - RBS and ERD (H)



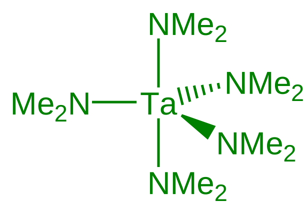
E. Langereis *et al.*, *J. Phys. D: Appl. Phys.*, **42**, 073001 (2009).

Plasma-Enhanced ALD of Metal Oxides

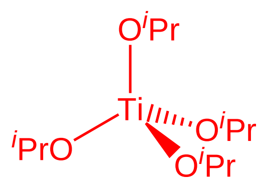
1. $[Al(CH_3)_3]$
TMA



2. $[Ta(NMe_2)_5]$
PDMAT

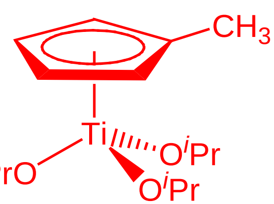


3. $[Ti(O^iPr)_4]$
TTIP



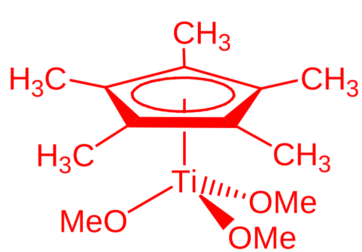
4. $[Ti(Cp^{Me})(O^iPr)_3]$

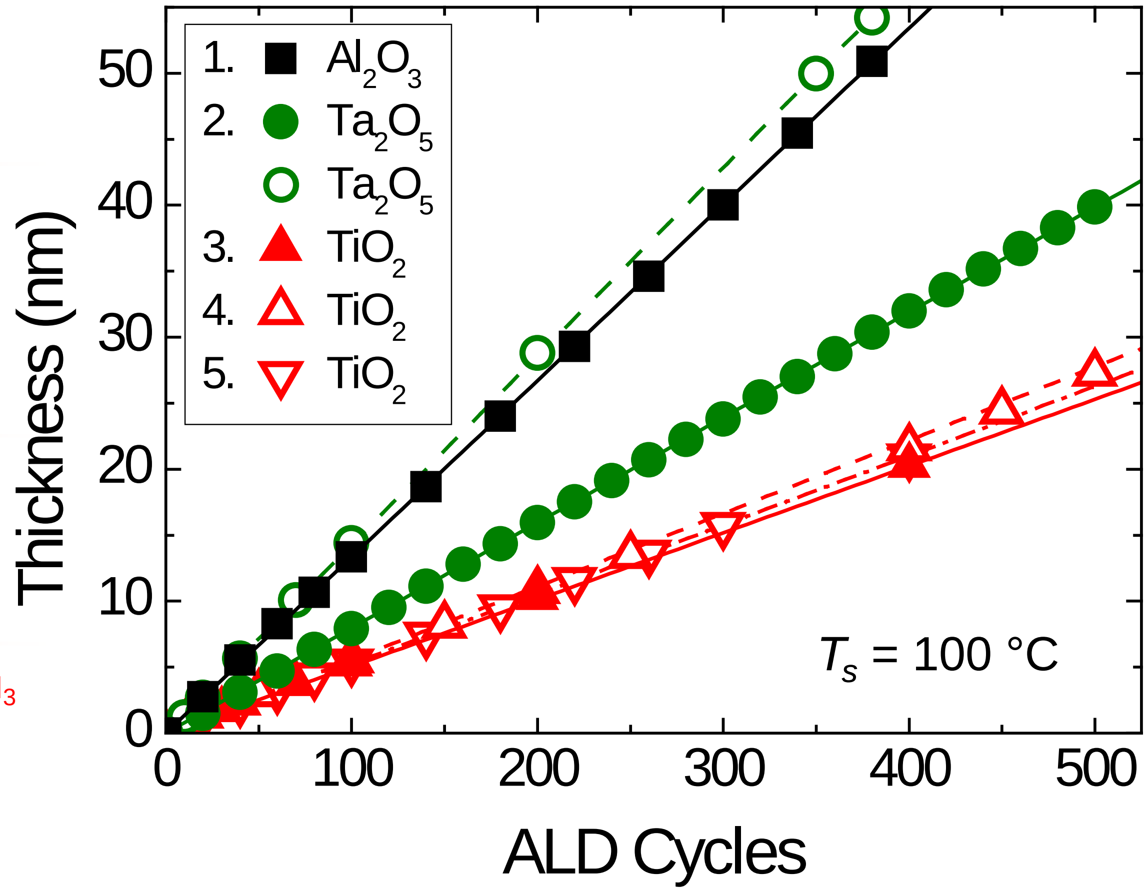
SAFC Hitech™ Enabling Technology



5. $[TiCp^*(OCH_3)_3]$

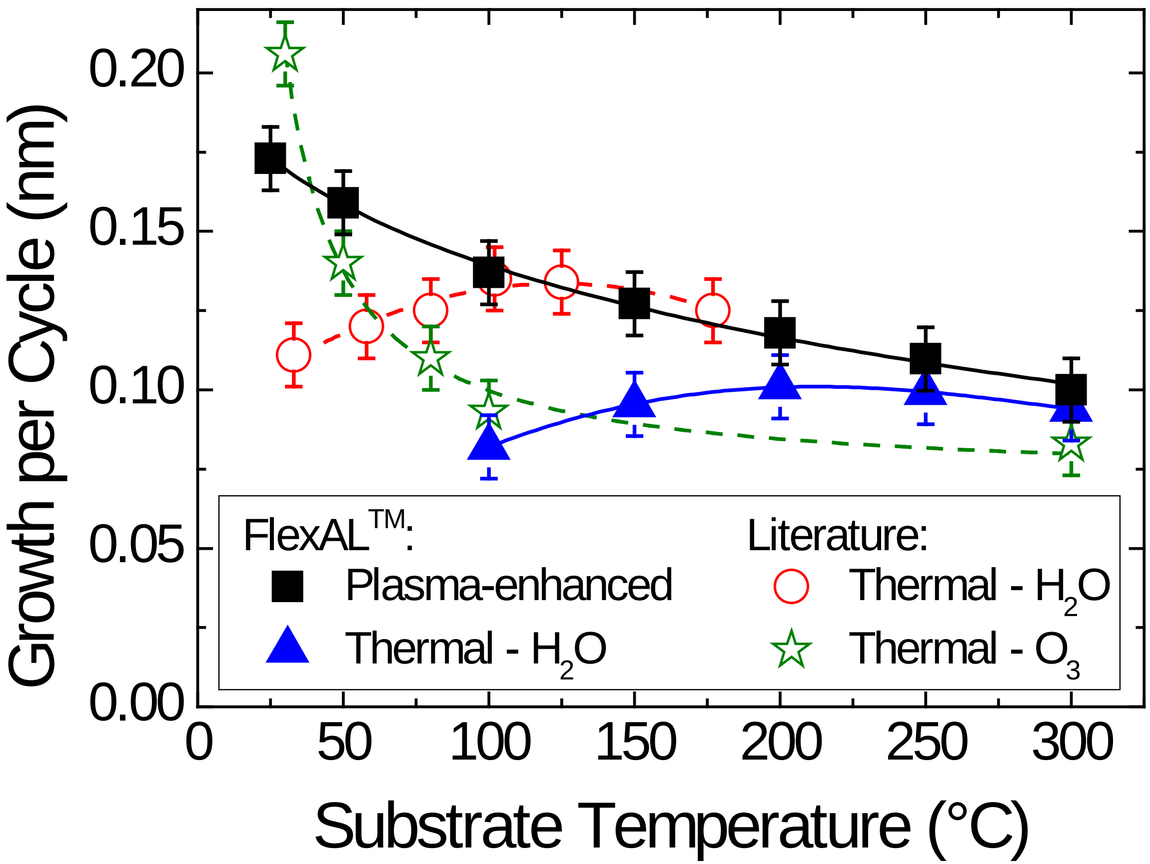
AIR LIQUIDE





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

Al_2O_3: Growth per Cycle

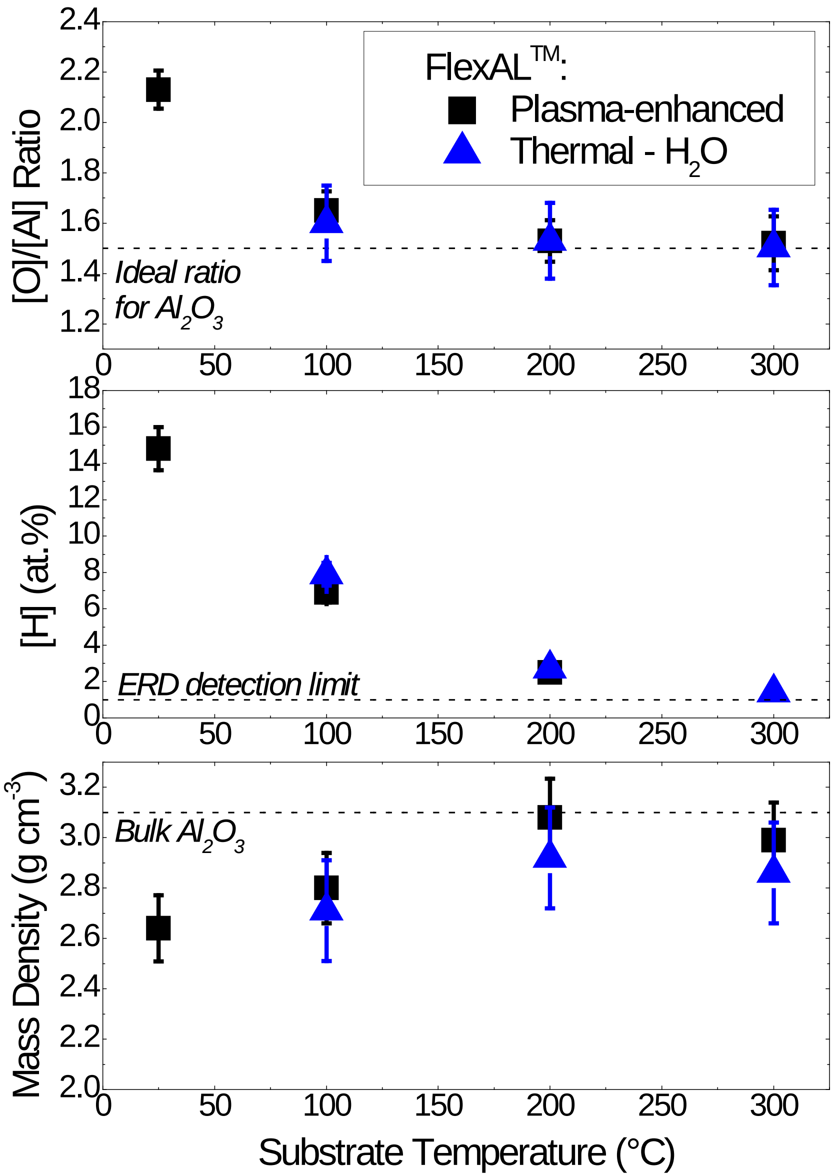


- **Water processes: lower growths per cycle at low temperatures**
- **Ozone process: many extra surface groups at T_s < 100 °C.**
- **Reduction in growth per cycle with increasing T_s → dehydroxylation.**

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).

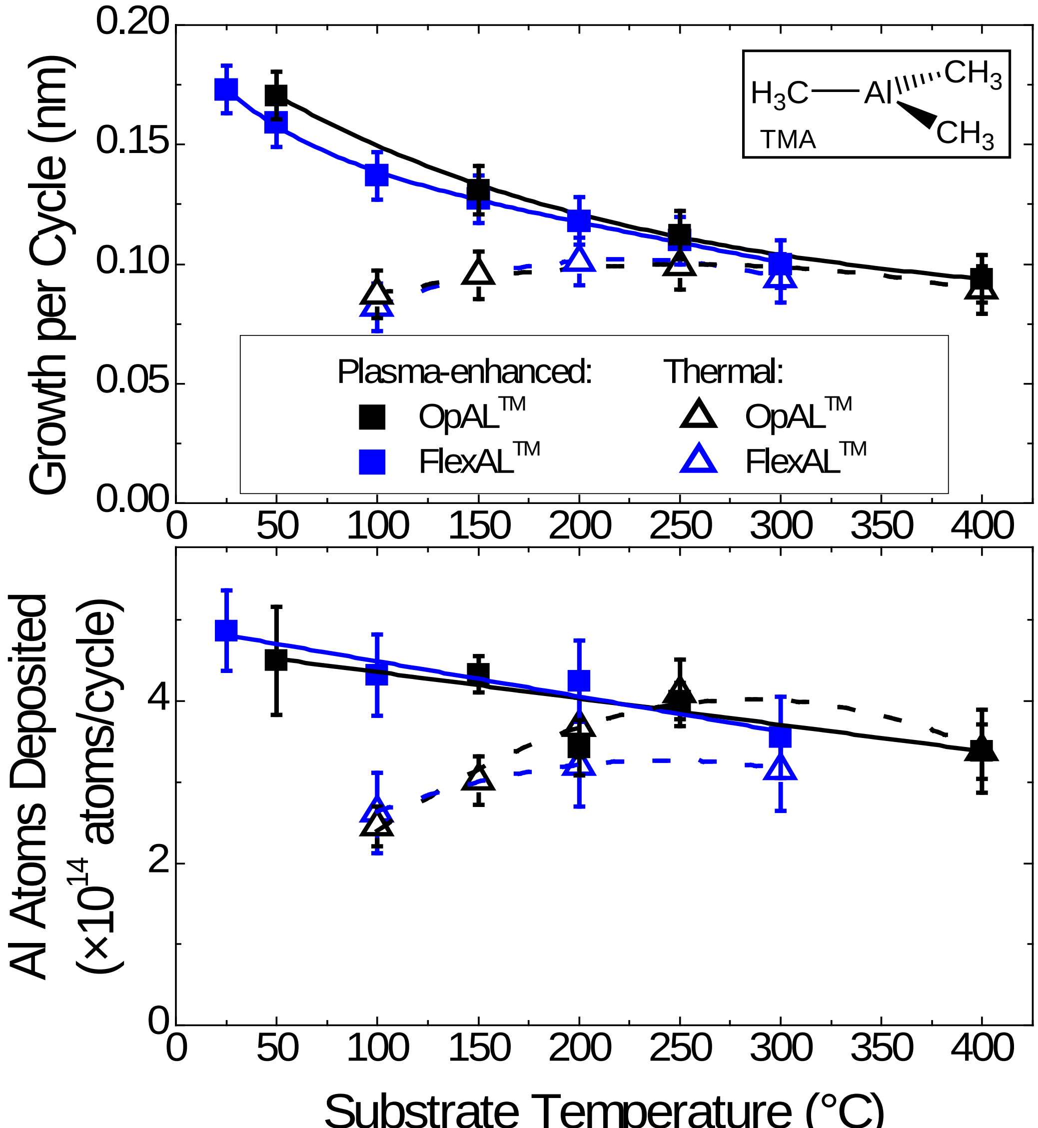
Al_2O_3: Film Composition



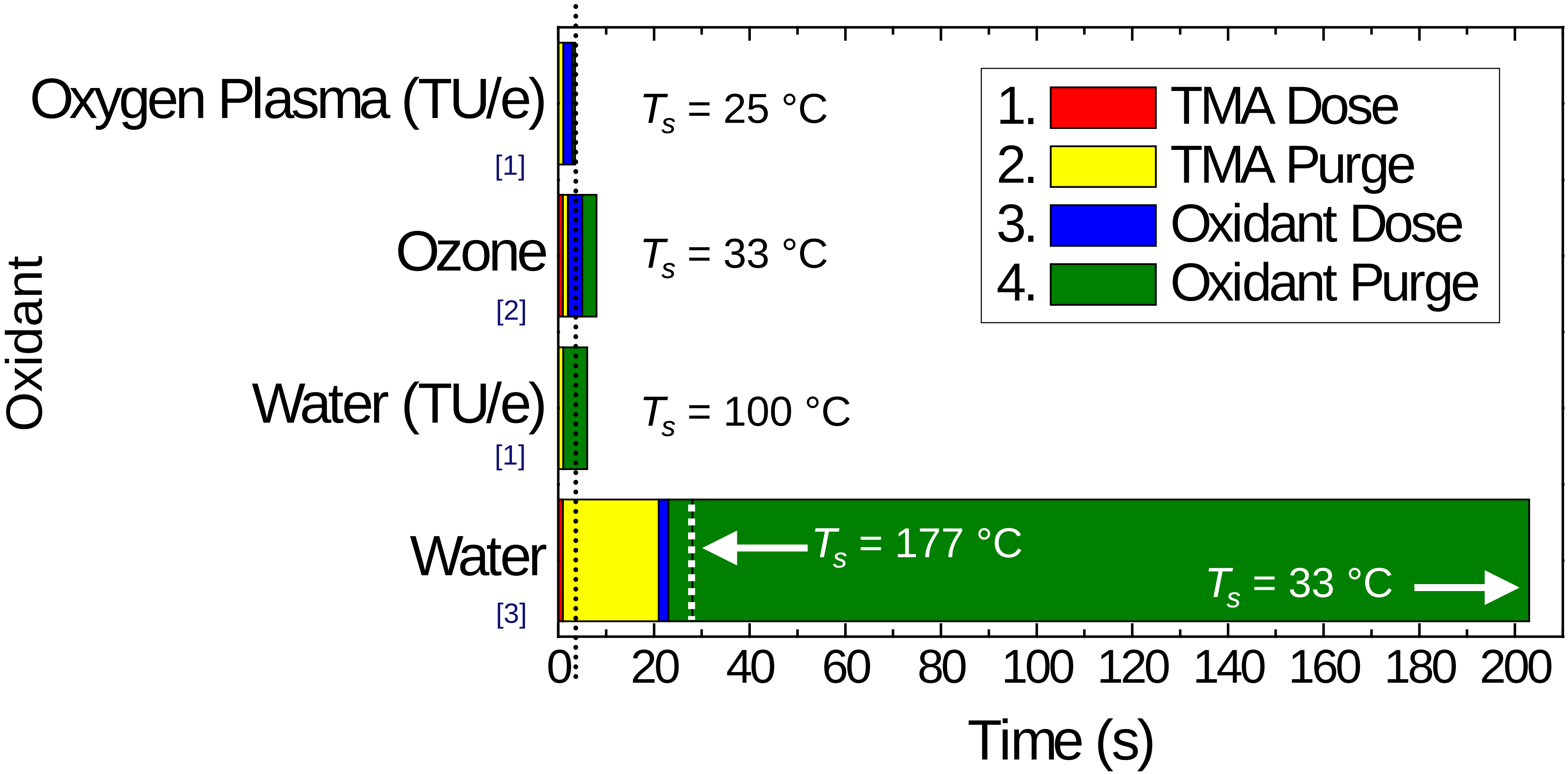
- **[C] < 1 at.% in each case.**
- **–OH is prominent at lower temperatures.**
- **Leads to increasing mass density of the films with deposition temperature.**
- **No significant composition difference between plasma and thermal ALD.**

Al_2O_3: Al Atoms Deposited

- **GPC decreases with increasing substrate temperature for plasma ALD.**
- **This is less apparent when focussing on the Al atoms deposited per cycle.**
- **Thermal H_2O process deposits fewer atoms below optimisation temperature.**



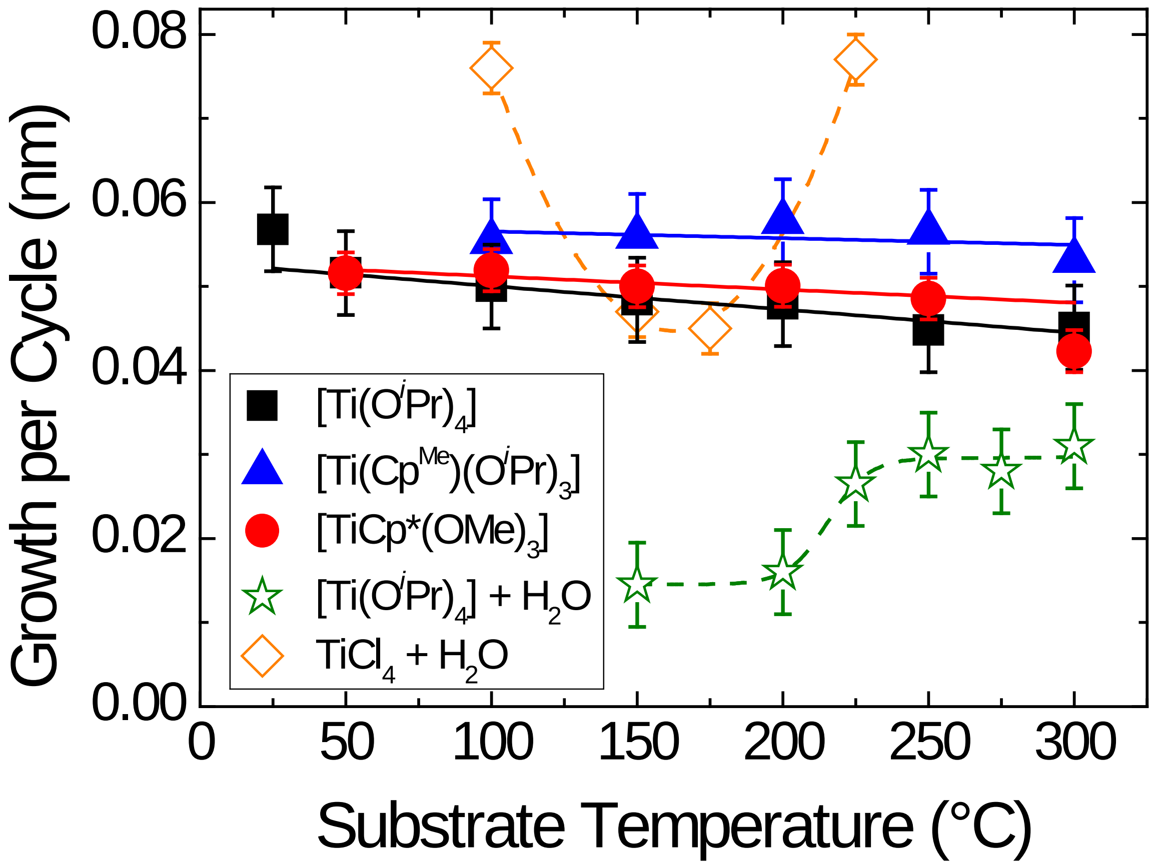
Al_2O_3: Cycle Time



Lower deposition temperatures require a longer oxidant purge for thermal processes.

[1] L.R. J. G. van den Elzen, G. Dingemans *et al.*, work to be published (2009).
[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

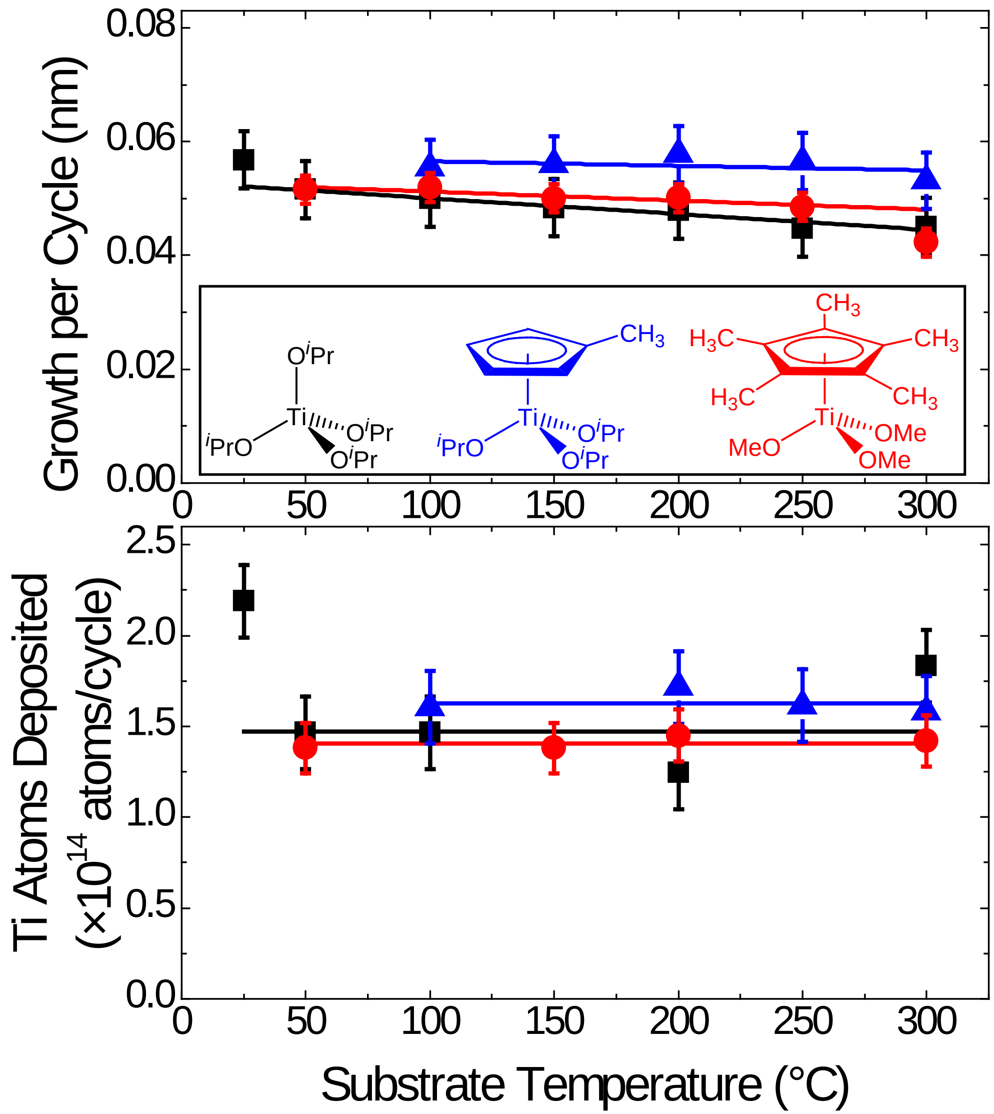
[■] W. Keuning *et al.*, work to be published.
[▲] E. Langereis *et al.*, work to be published.
[●] S. E. Potts *et al.*, work to be published.
[☆] M. Ritala *et al.*, *Chem. Mater.*, **5**, 1174 (1993).
[◇] J. Aarik *et al.*, *J. Cryst. Growth*, **220**, 531 (2000).

TiO_2: Film Composition & Ti Atoms Deposited

- **All 3 Ti precursors: same film composition for $T_s \geq 50$ °C**
  - [O]/[Ti] = **2** (TiO_2)
  - [C] < 1 at.%.
  - [H] below detection limit at $T_s \geq 50$ °C (0.1-5%)
  - –OH groups only seen at $T_s = 25$ °C for [Ti(O^{i}Pr)$_4$]

- **Thermal route [H] ~0.3 at.%**

Reduction in GPC but Ti atoms deposited per cycle are almost constant for Cp precursors.



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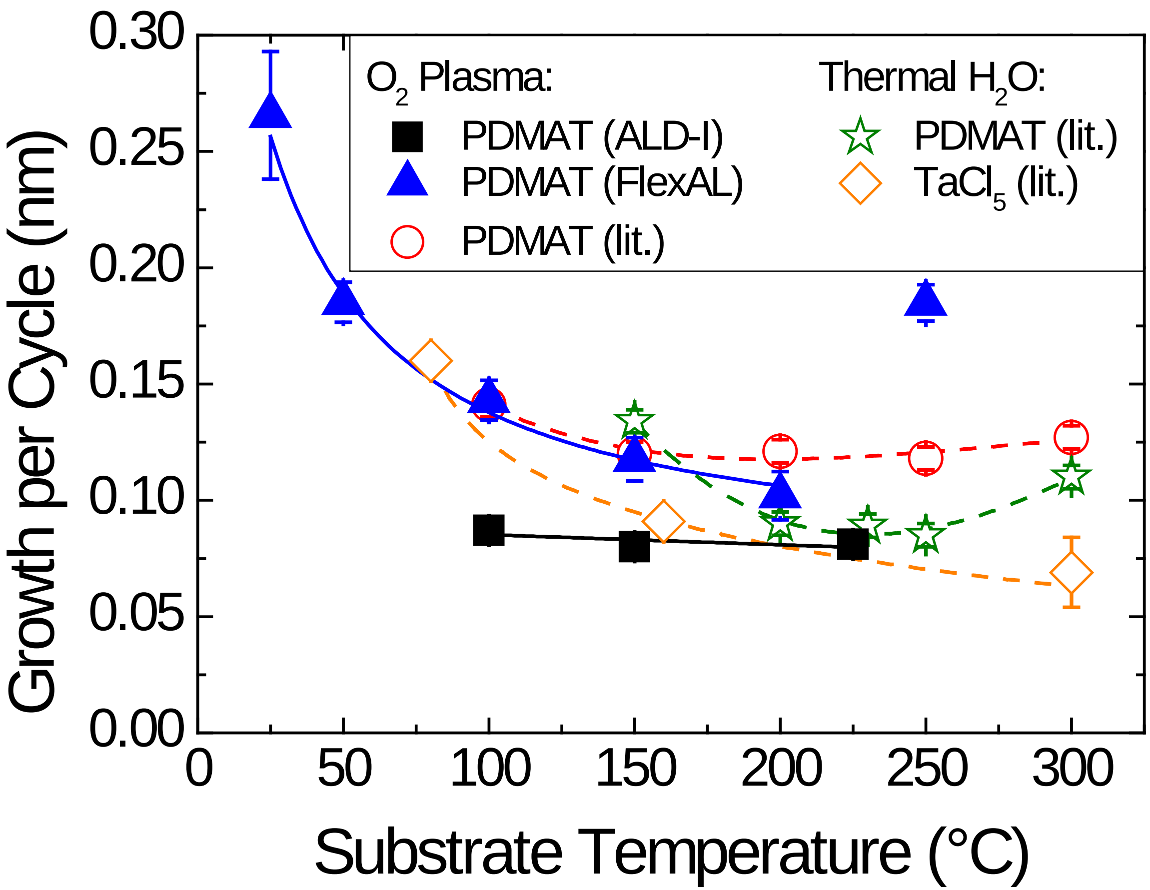
Ta_2O_5: Growth per Cycle



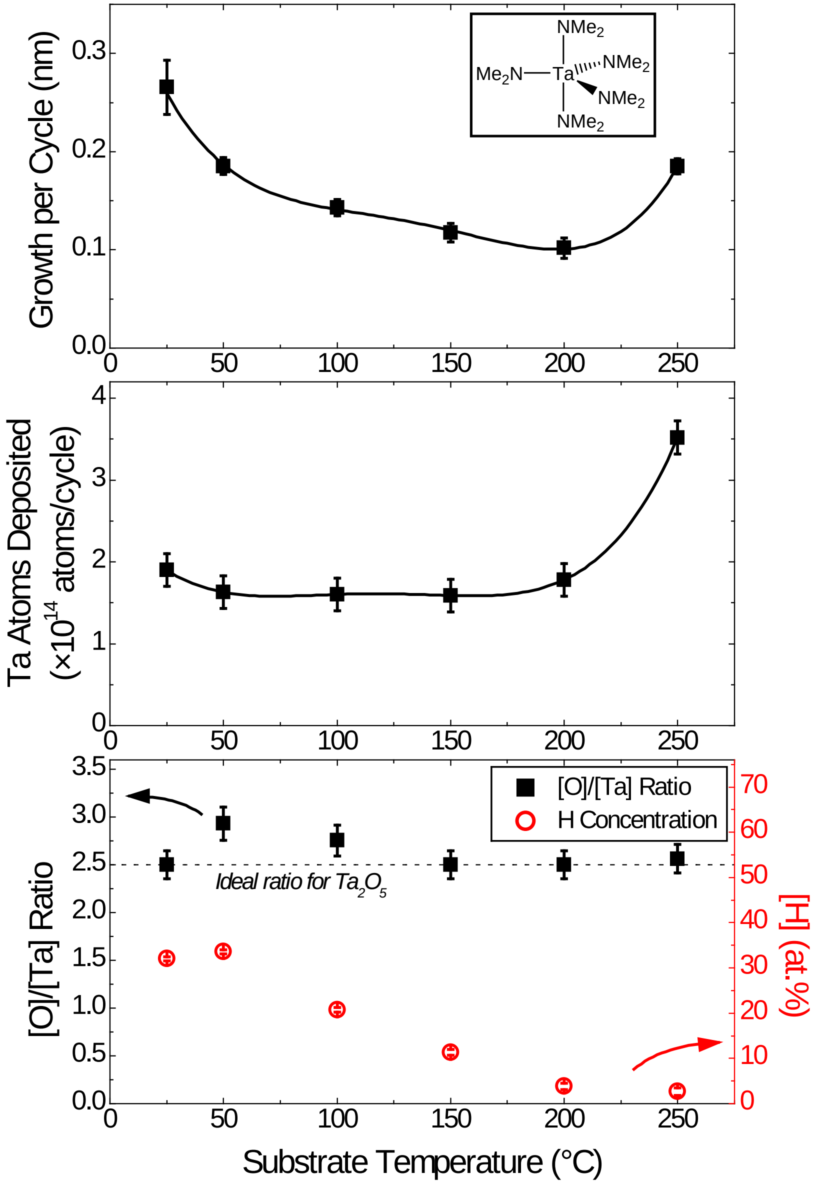
- **[O]/[Ta] Ratio:**
- **ALD-I = 2.5**
- **FlexAL = 2.5-3**
- **Lit. PDMAT = 2.6**
- **Lit. $TaCl_5$ = ~2 ± 0.1**

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

- **Difference in GPC due to different reactors?**

[■] S. B. S. Heil *et al.*, *J. Vac. Sci. Technol. A*, **26**, 472 (2008).
[▲] S. E. Potts *et al.*, work to be published.
[○] 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).

Ta_2O_5: Film Composition & Ta Atoms Deposited



- **Drop in growth per cycle with increasing temperature.**
- **Number of Ta atoms deposited reasonably constant for T_s = 50-200 °C.**
- **A big increase in Ta deposited at 250 °C**
  - decomposition of PDMAT = CVD
- **H decreases with increasing substrate temperature.**

Conclusions

Al_2O_3 from [Al(CH_3)$_3$]

- **Higher growth per cycle down to room temperature** for the plasma process.
- **Higher quality films at low temperatures** for the plasma process compared with the ozone thermal process.
- Al_2O_3 processes more sensitive to surface dehydroxylation compared with TiO_2 and Ta_2O_5.
- **Reduced cycle times** for the plasma process.

Ta_2O_5 from [Ta(NMe_2)$_5$]

- Stoichiometric Ta_2O_5 down to 150 °C.
- CVD at 250 °C.

TiO_2 from [Ti(O^iPr)$_4$], [Ti(Cp^{Me})(O^iPr)$_3$] or [TiCp*(OMe)$_3$]

- **Pure, stoichiometric TiO_2** down to 50 °C.
- **Higher growth per cycle** than for [Ti(O^iPr)$_4$] with water.

- **Benefits of plasma processes depend on the application.**
- **Plasma processes can give high quality films at lower temperatures.**
- **Analysis of atoms/cycle gives additional insight into the ALD temperature window.**