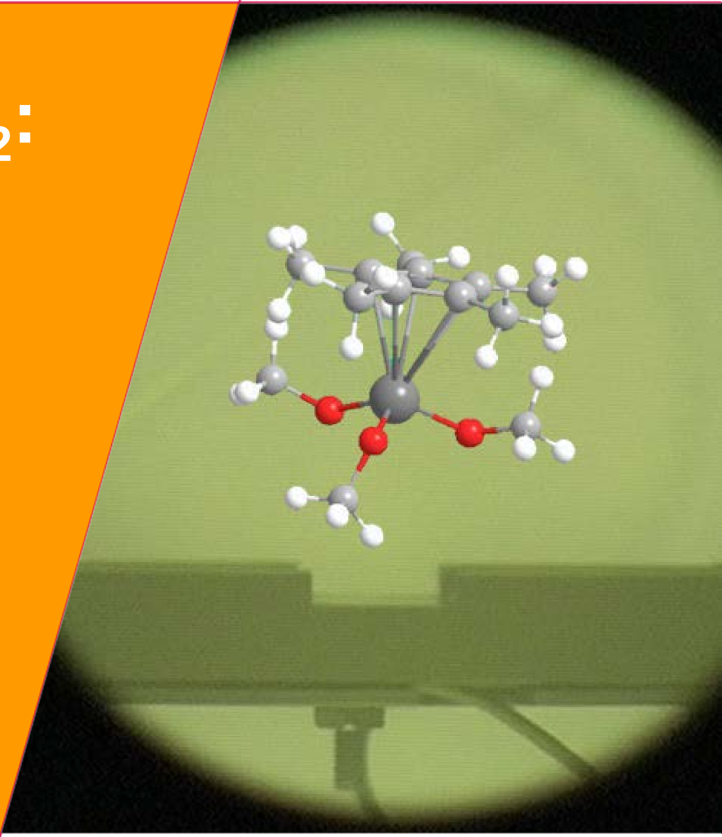
Plasma-Enhanced ALD of TiO_2: From Ligands to Layers



<u>Stephen E. Potts</u>, Wytze Keuning,
Erik Langereis, Anitha Sarkar,
Richard van de Sanden and Erwin Kessels

ALD 2010, Seoul, South Korea
23rd June 2010

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

- **Motivation**
- **Experimental**
  - ALD reactors & diagnostics (spectroscopic ellipsometry, RBS)
  - Available precursors for TiO_2
- **Results**
  - Growth per cycle as a function of substrate temperature
    1. $[Ti(O^iPr)_4]$
    2. $[Ti(Cp^{Me})(O^iPr)_3]$
    3. $[Ti(Cp^*)(OMe)_3]$
    4. $[Ti(Cp^{Me})(NMe_2)_3]$
  - Film composition and overview
  - Reactivity of ligands and possible reaction mechanism
- **Conclusions**

Technische Universiteit Eindhoven University of Technology

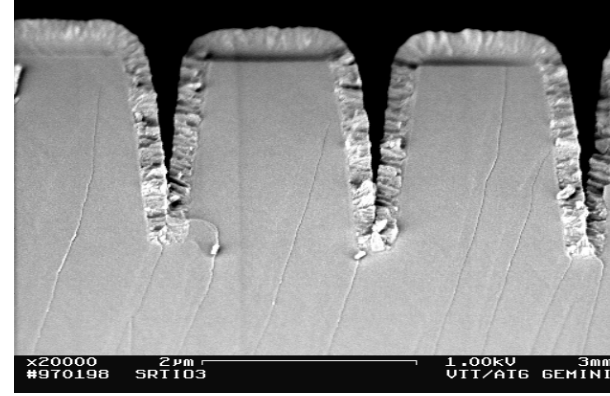
Motivation

- **Many applications require TiO_2**

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

- **Requirements**
  - Ultra-thin films
  - Good conformality
  - Wide range of deposition temperatures
  - Control of stoichiometry/atomic composition

$SrTiO_3$ on an Si trench structure.*



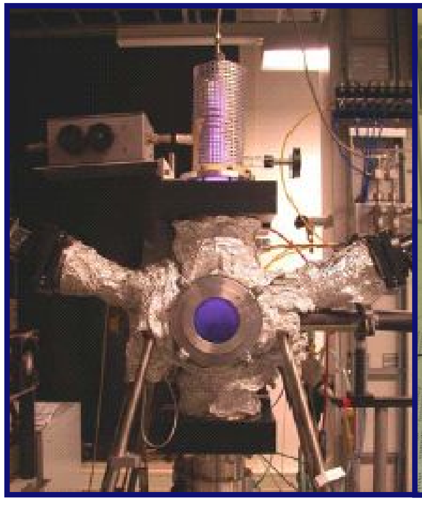
*From: M. Vehkamäki *et al.*, *Electochem. Solid-State Lett.*, **2**, 504 (1999).

Plasma-Enhanced ALD

Why use a plasma?

- **Increased reactivity (radicals, electrons, ions)**
- **Allows for depositions at low temperatures**
- **A wider range of precursors can be used,** e.g. [Ti(Cp^x)L_3]

Remote Plasma ALD Reactors



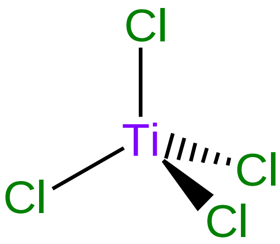
ALD-I (home-built)

FlexAL™

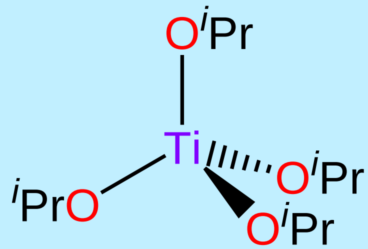
- **100 mm n-type Si{100} substrates**
- ***In situ* spectroscopic ellipsometry (SE)**
  - Film thickness & growth per cycle (GPC)
- **RBS and ERD (H)**
  - Absolute areal density (atoms cm^{-2})

TU/e Technische Universiteit Eindhoven University of Technology

Ti Precursors

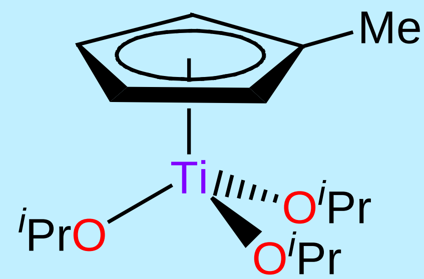


Halides
- Film contamination
- Corrosive by-products (HX)



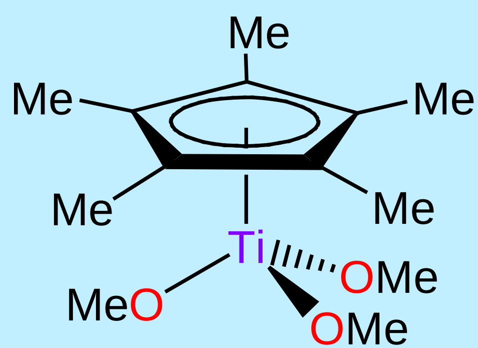
1

Homoleptic Alkoxides

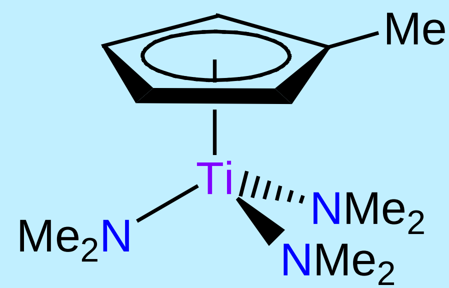


2

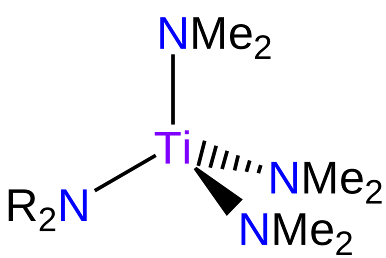
Heteroleptic Cp-Compounds
(2-4)



3



4

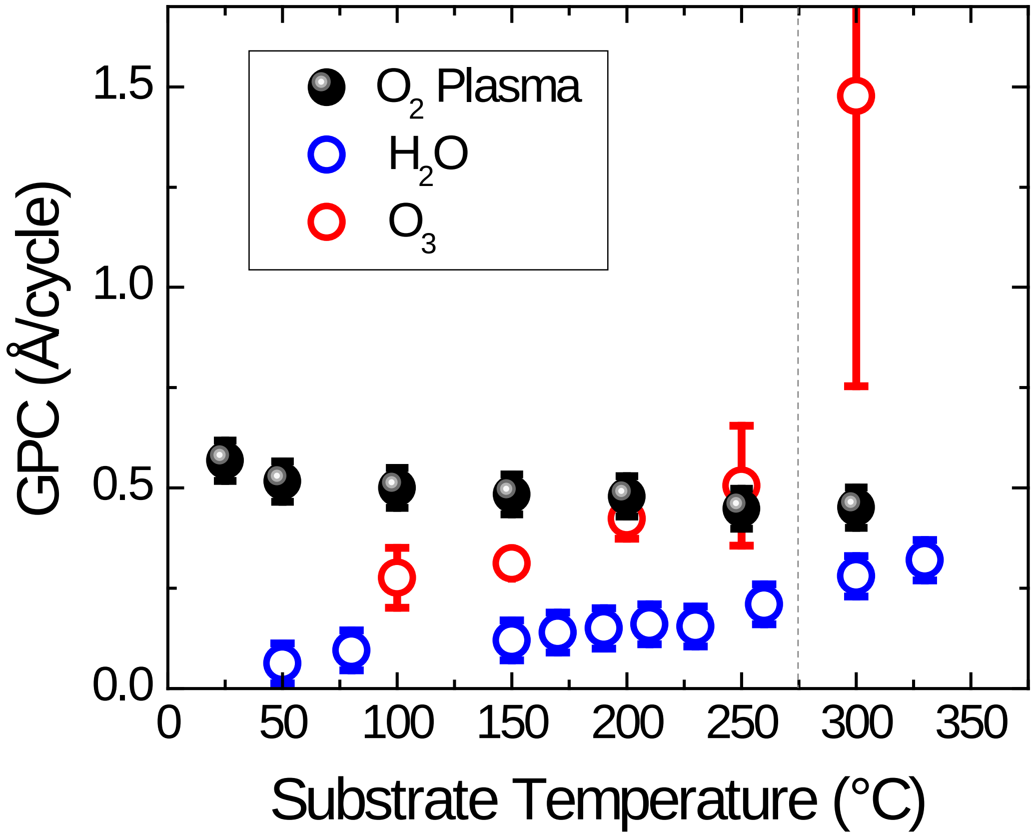


Homoleptic Amides
- Low stability

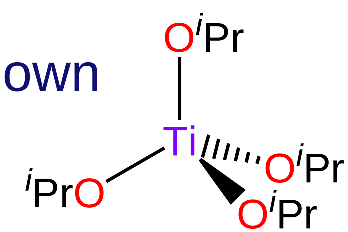
For more on ligand possibilities, see: N. Blasco *et al.*, *Sr and Ti Precursors Development for Next Generation Thin Film Application*, 216th ECS Meeting, Vienna (2009).

Growth per Cycle (GPC) • 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 down to room temperature.



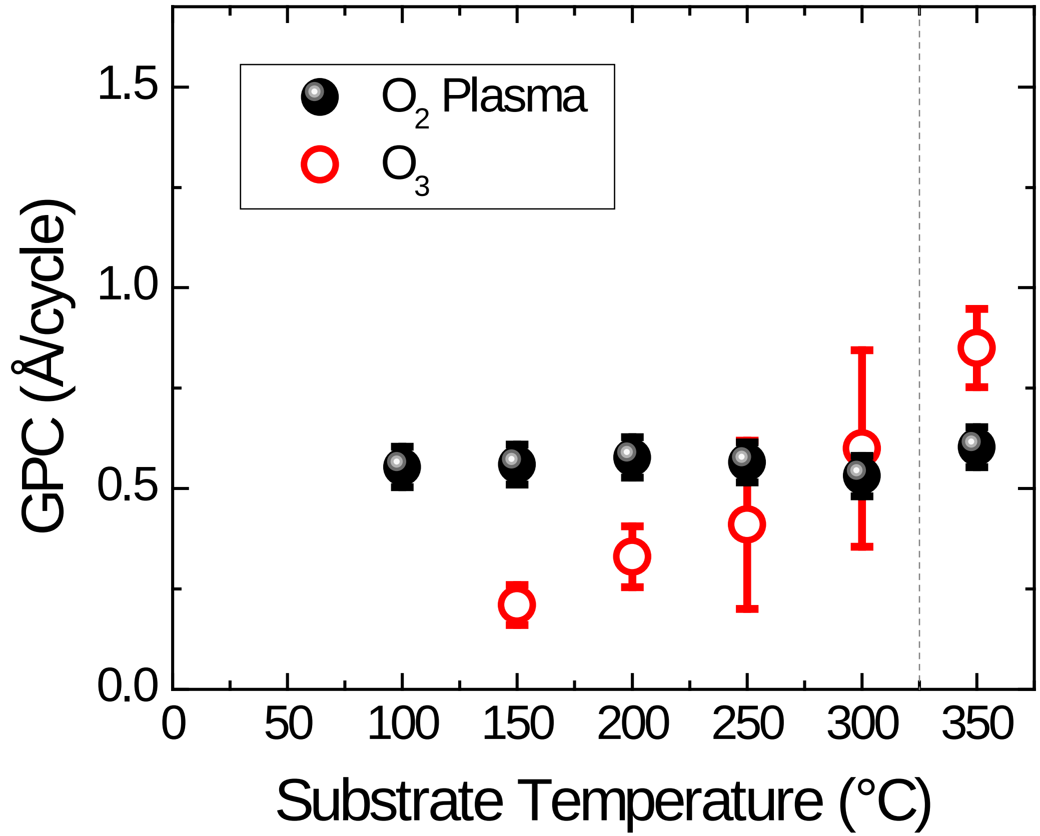
Precursor decomposition at T_s > dashed line.



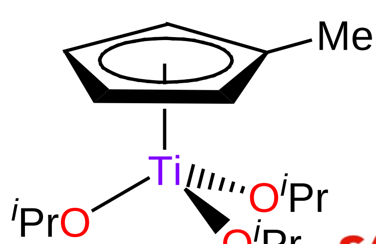
H_2O process: Q. Xie *et al.*, *J. Appl. Phys.*, **102**, 083521 (2007).
O_3 process: P. Williams at ALD 2008, Bruges, Belgium.

Growth per Cycle (GPC) • 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.



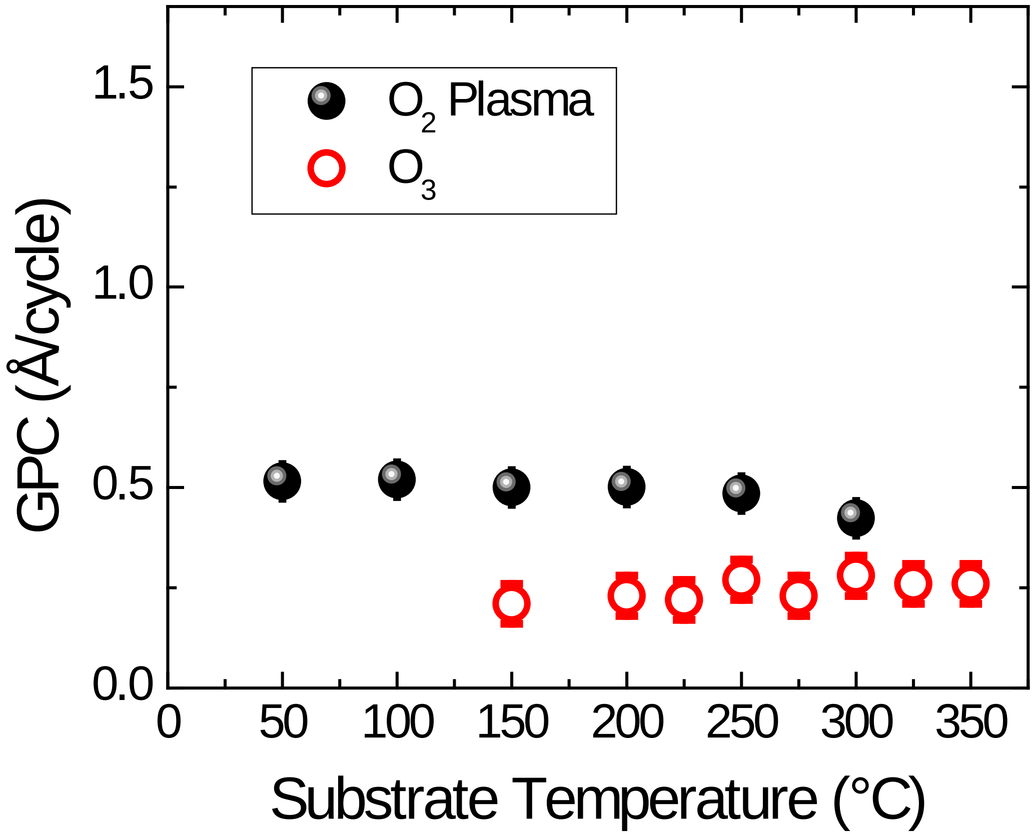
O$_3$ process: P. Williams at ALD 2008, Bruges, Belgium.

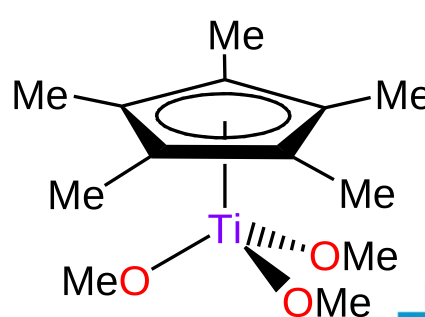
SAFC Hitech™ Enabling Technology

TU/e Technische Universiteit Eindhoven University of Technology

Growth per Cycle (GPC) • 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.

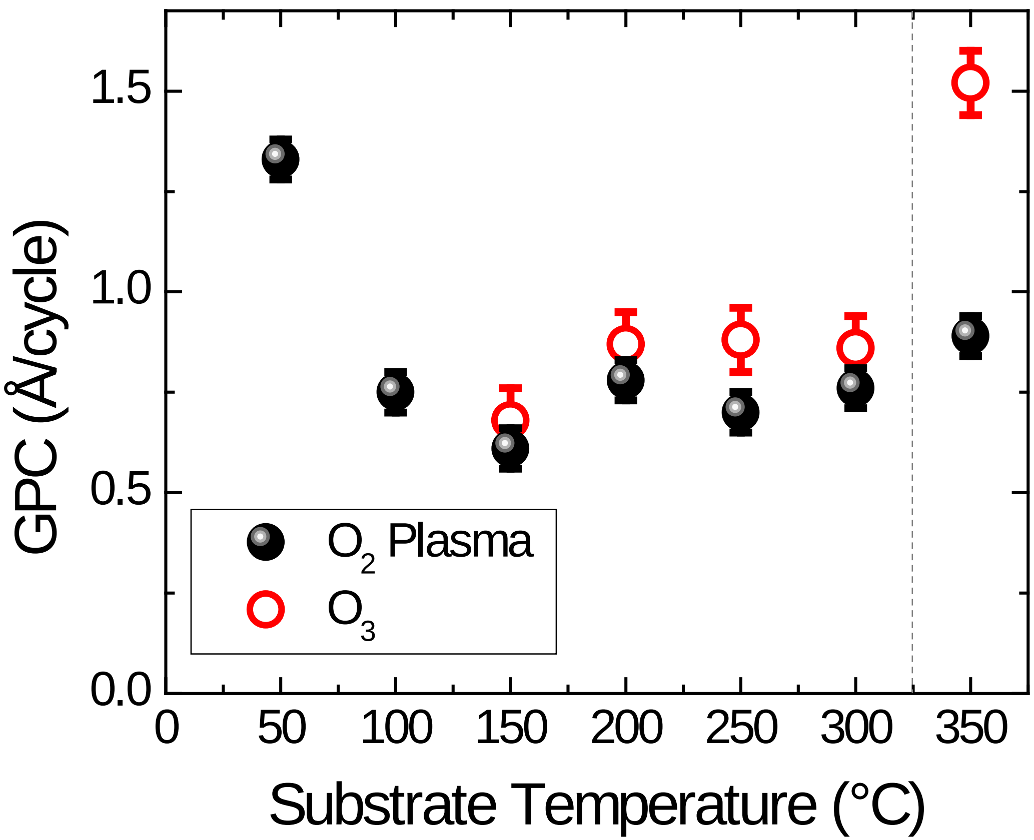




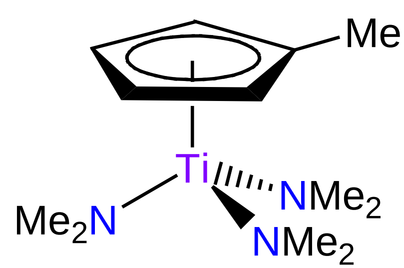
O_3 process: R. Katamreddy *et al.*, *ECS Trans.*, **25**, 217 (2009).
*S. D. Elliott *et al.* at ALD 2010, 22nd June.

Growth per Cycle (GPC) • 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.

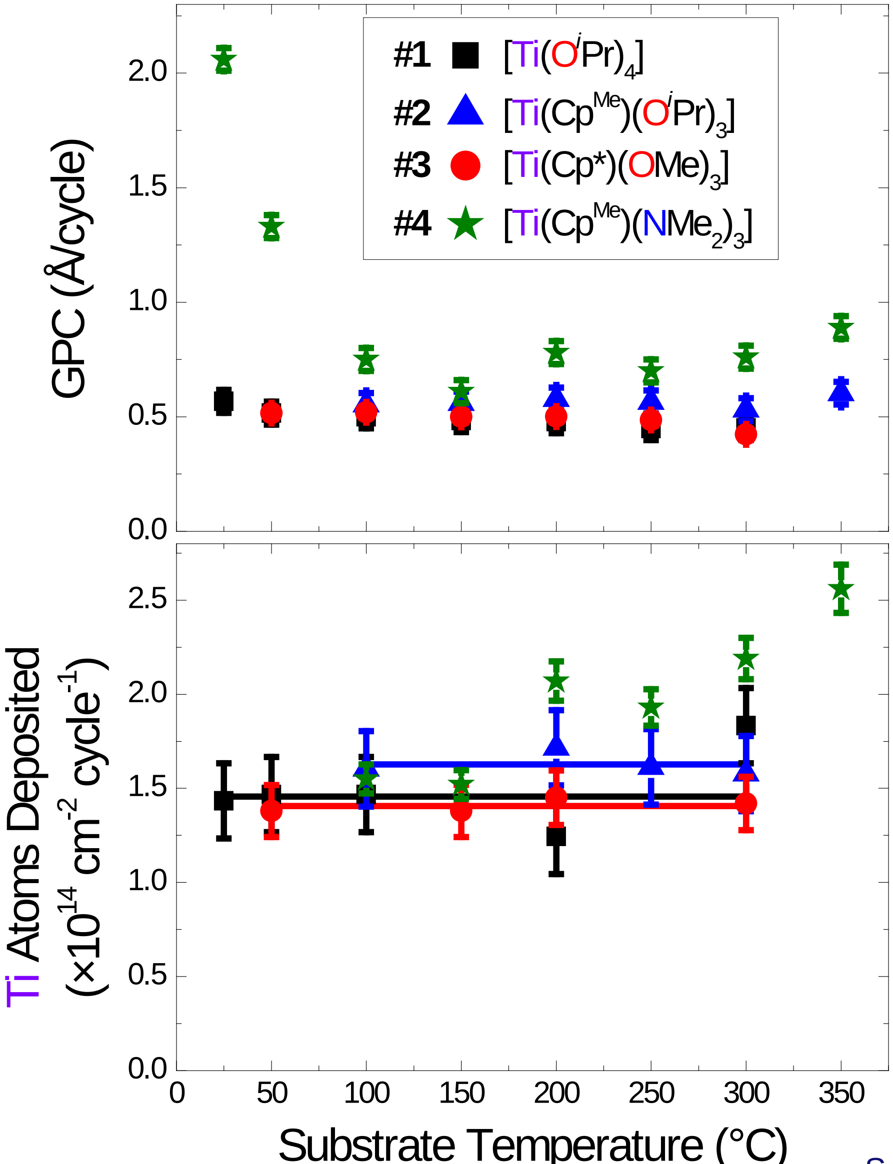


O$_3$ process: P. Williams at ALD 2008, Bruges, Belgium.
See also: A. Sarkar at the 218th ECS meeting, Las Vegas, Oct. 2010.

SAFC Hitech™ Enabling Technology

TU/e Technische Universiteit Eindhoven University of Technology

Overview & Ti Atoms Deposited per Cycle



- **O/Ti ratio = 2.0 ± 0.1**
- **H present**
  - Generally <4 at.%.
  - #4 at 100 °C, ~7 at.%
- **Ti/cycle**
  - Not affected by film density
  - #2 and #3 (Cp/OR) – consistent
  - #4 – increases with temperature
- **OR + Cp^{Me}**
  - most consistent GPCs and Ti/cycles
- **NR$_2$ (+ Cp^{Me})**
  - higher reactivity, increasing with temperature.

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

ALD Reactivity of Ligands Bonded to Ti

- **Ti–OR**
  - GPCs of ~0.5 Å/cycle typically
  - OMe ligand undergoes H-bonding
- **Ti–NR_2**
  - More reactive than alkoxide ligands
  - Full thermal reaction with surface groups at $T_s \geq 200$ °C
- **Ti–Cp^x**
  - No reactivity towards water
  - Low reactivity towards ozone
  - Plasma best option at lower temperatures
  - Cannot H-bond
- **The Ti precursor should have some ligands which are, at least, able to H-bond with the surface.**

TU/e Technische Universiteit Eindhoven University of Technology

Conclusions

- **H_2O, O_3 and an O_2 plasma give very different results for the same ligands.**
- **Two oxide-ALD factors:**
  1. Reactivity of the precursor with the surface groups
  2. Reactivity of the oxidant with the surface groups
- **For plasma ALD, the precursor reactivity with the substrate surface (1) is, in practice, the only limiting step.**
- **More reactive ligands can give a higher growth per cycle.**
- **Reactivity of ligands in Ti compounds towards surface groups at low temperature:**

$$Cp^x < OR < NR_2$$

- **Ability to H-bond with surface groups is key to the reaction mechanism.**
- **Cp-based precursors for microelectronics applications:**
  - Give good ALD behaviour
  - Cp^x ligands provide stability to the precursors

Technische Universiteit Eindhoven University of Technology