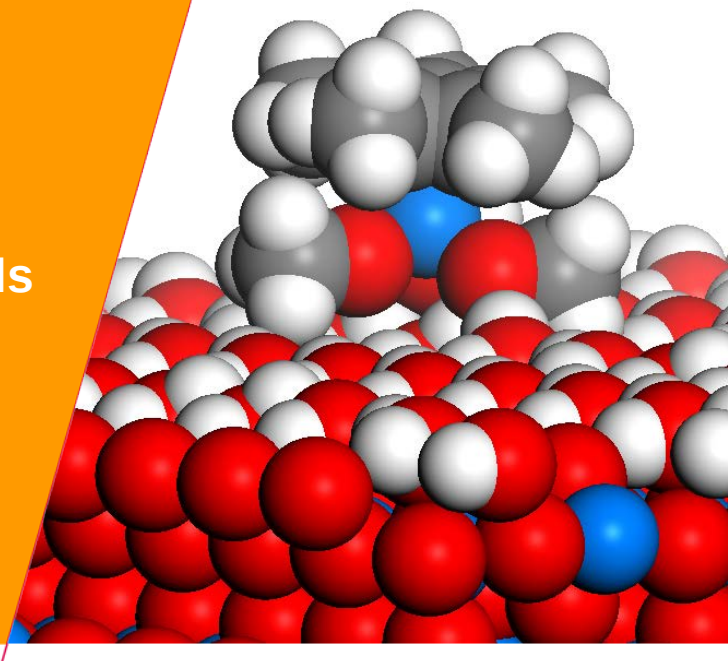
Plasma-Enhanced ALD of TiO_2 using Cp-Based Precursors:
Experiments and DFT Calculations



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ALD 2011, Cambridge, MA, USA, 28th June 2011

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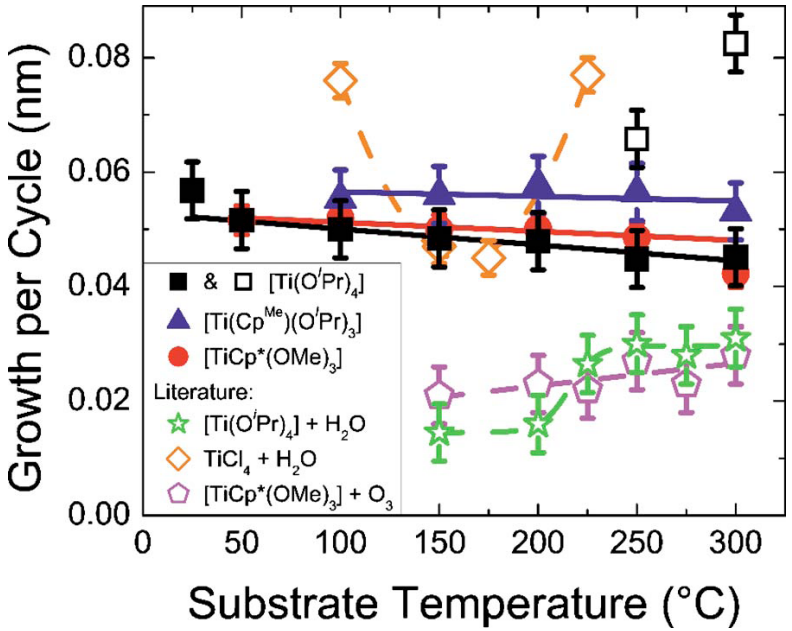
Where innovation starts

Motivation

Mixed (ternary) oxides

- $SrTiO_3$ and $BaSrTiO_3$
- Ultra-high-*k* dielectric.
- Ti-Cp precursors are stable alternatives.
- TiO_2 ALD is “complex”.



Better understanding of the plasma-enhanced ALD of TiO_2

- Plasma step:
  How do different plasma compositions affect growth?
- Precursor step:
  Can DFT calculations help us understand growth?

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

Outline

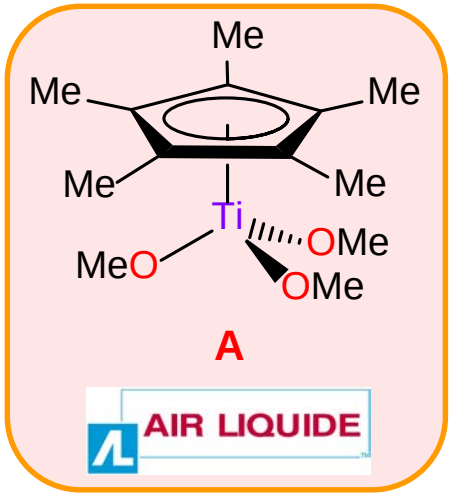
- Motivation

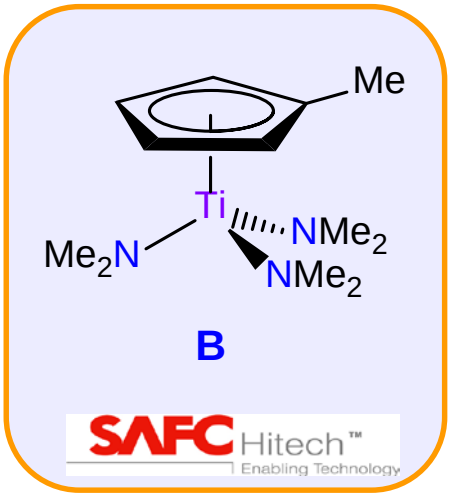
- **Plasma-Enhanced ALD using Cp-Based Precursors**
  - $Ti(Cp^*)(OMe)_3$ (**A**) and $Ti(Cp^{Me})(NMe_2)_3$ (**B**)
  - O_2, N_2O and N_2-O_2 plasmas

- **DFT Calculations**
  - Reactions of **A**, **B** and $Ti(OMe)_4$ with hydroxylated TiO_2
  - Hydrogen-bonding to surface sites
  - Towards the elimination of by-products

- **Conclusions**

Experimental Details: ALD





Oxford Instruments FlexAL™ reactor

Atomic Layer Deposition

- Remote ICP plasma
  - 200 W RF power
  - O_2, N_2O, N_2/O_2 (4:1)
- 100 mm n-type Si(100) with native oxide

Diagnostics

- Spectroscopic ellipsometry
- Rutherford backscattering spectrometry

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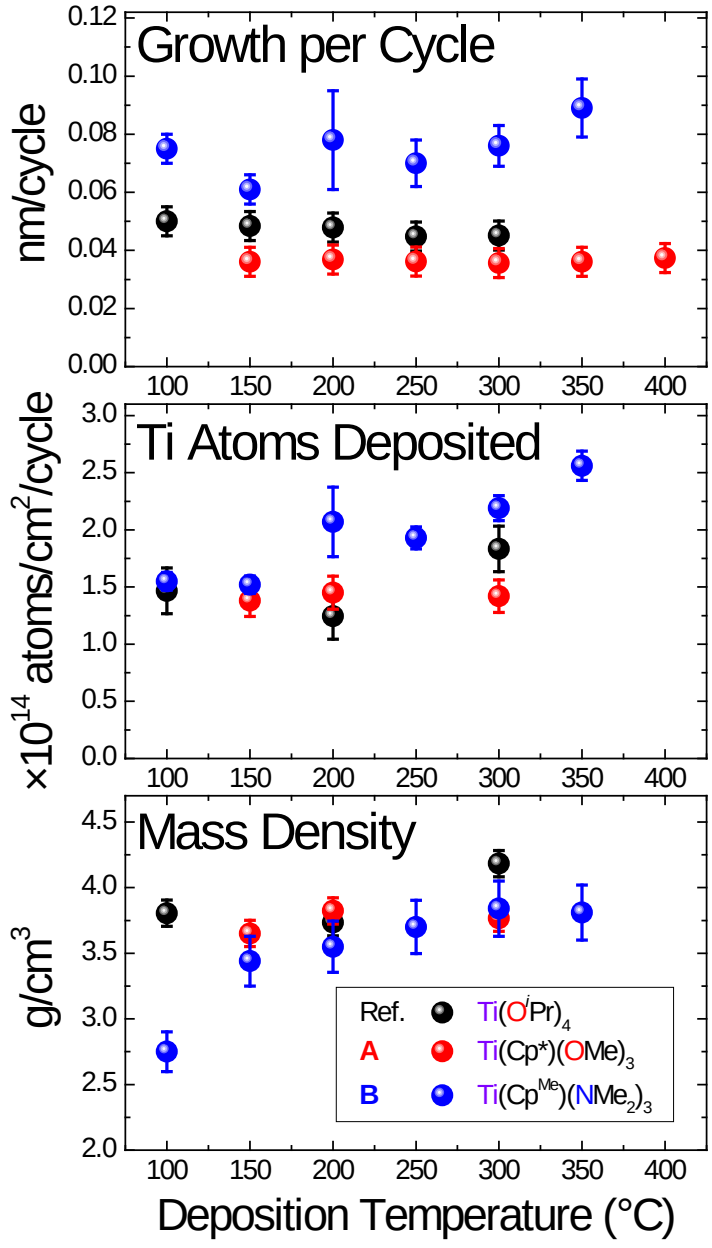
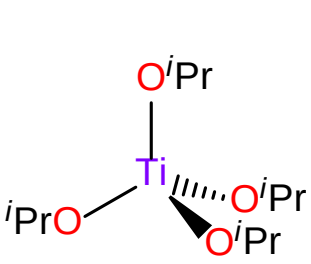
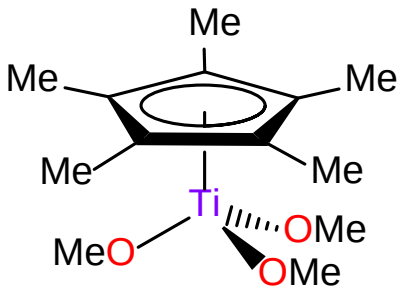
Plasma-Enhanced ALD of TiO_2



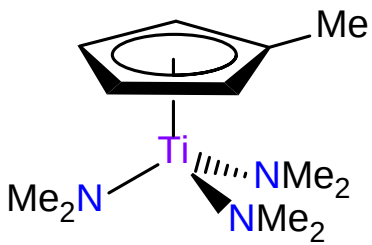
- Two similar precursors in the same reactor with $Ti(O^iPr)_4$ as a reference.
- **B** deposited more Ti atoms/cycle.
- **B** shows signs of thermal activation.
- Nitrogen in **B** a cause of this?
  - Presence of N in the plasma?
  - Decomposition?



Ref.



A



B

[A + Ref.] S. E. Potts *et al.* at the ALD Conference, Seoul, 2010.
[B] A. Sarkar *et al.*, *ECS Trans.*, **33**, 385 (2010).

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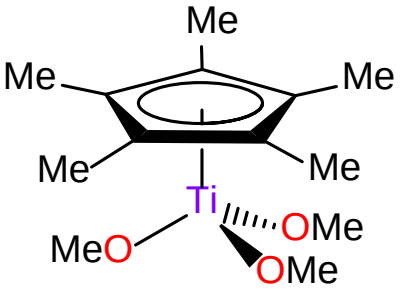
Addition of N_2 to the O_2 Plasma

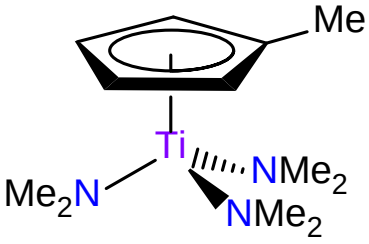
- Addition of N_2 to an ozone generator can have a significant effect on growth.

  A. Delabie *et al.*, *Electrochem. Solid-State Lett.*, **13**, H176 (2010).

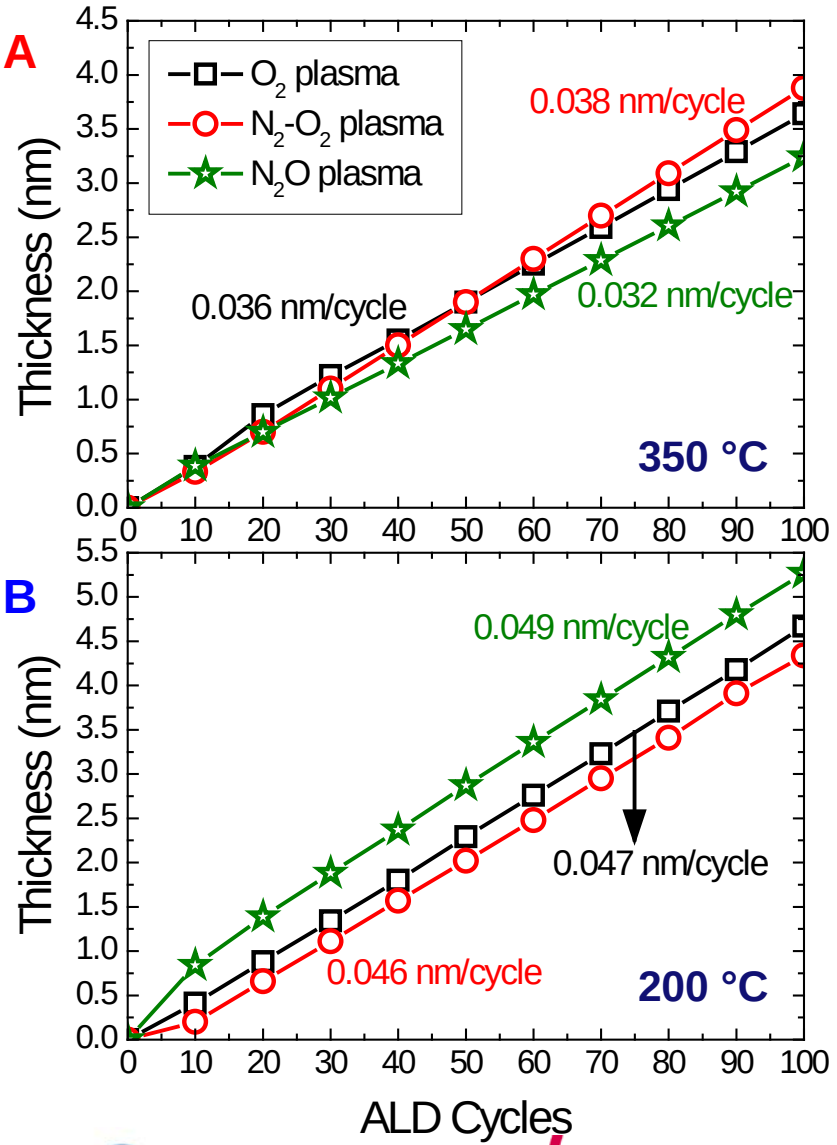
- All growths per cycle are the same, within experimental error.
- Independent of the plasma gas composition.



A



B



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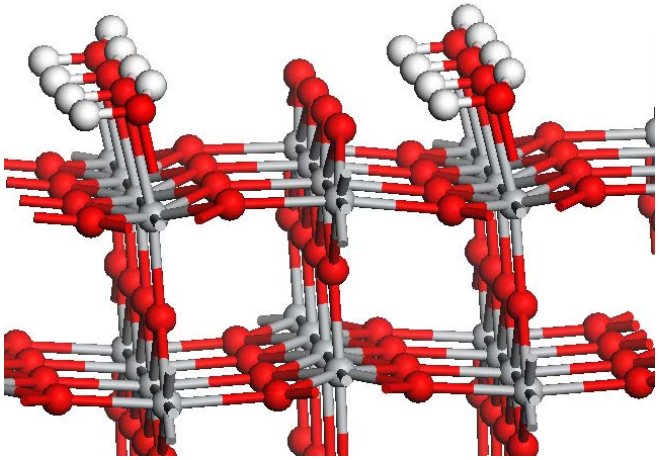
Experimental Details: DFT Calculations

- **Comparison of A and B with Ti(OMe)$_4$**
- **Surface**
  - Rutile (110)
  - Water molecules bound to rutile surface
  - E_{ads} = -0.79 eV per water molecule



- Periodic plane wave density functional theory (DFT),
- VASP package,
- For the surface model, 1 × 2 × 1 k-point sampling grids were used for the (4 × 2) surface expansions,
- Core-valence interaction treated using projector augmented wave (PAW) gradient-corrected density functional PBE,
- Plane-wave basis <396 eV,
- The molecular geometries of the precursor molecules, Ti(OMe)$_4$, **A**, **B**, Cp*H, MeOH, HNMe$_2$ and water were individually relaxed in a box of dimensions 20 × 20 × 20 Å, with a 396 eV cutoff energy and Γ-point sampling.

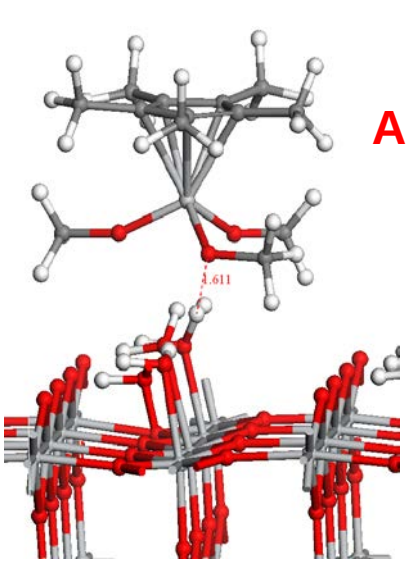
G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, **6**, 15 (1996).

Initial Reaction: Hydrogen Bonding

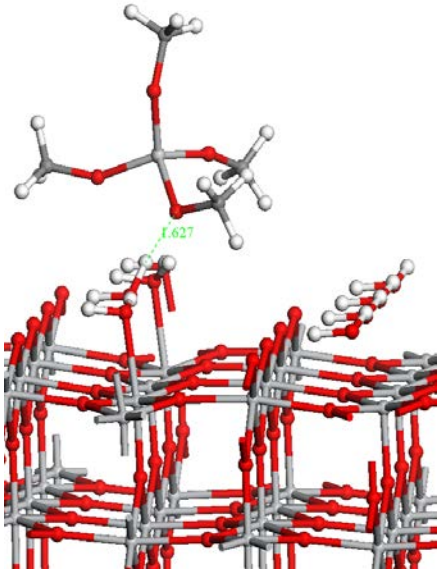
Prior to full ligand exchange

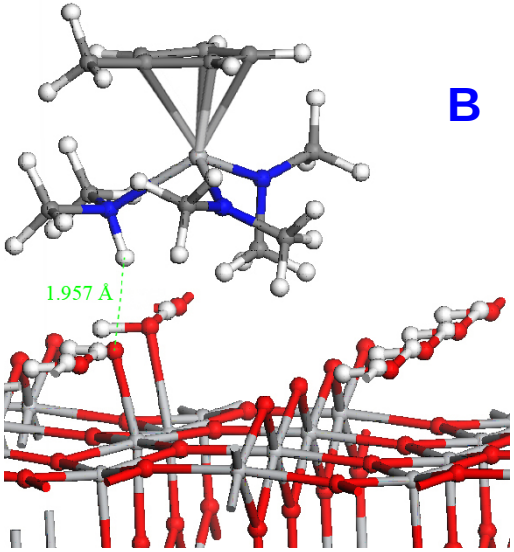
Ti H C O N

$Ti(Cp^*)(OMe)_3$ $Ti(OMe)_4$ $Ti(Cp^{Me})(NMe_2)_3$



A





B

E_{ads} = -0.35 eV > E_{ads} = -0.48 eV > E_{ads} = -0.70 eV

- H-bonding favourable for all precursors.
- Stronger bonding than expected.
- **B** most likely to H-bond: quantum mechanics show instantaneous proton transfer.

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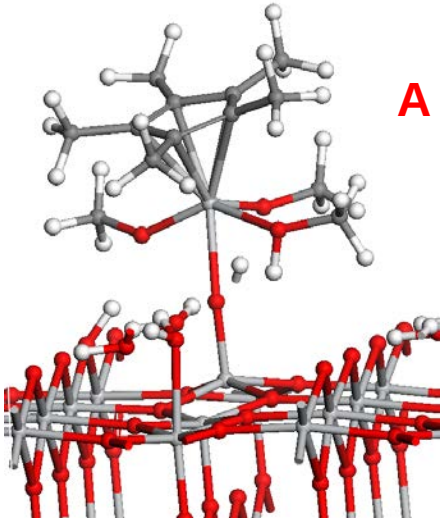
Energy of Adsorption

Towards elimination of MeOH or $HNMe_2$

Ti H C O N

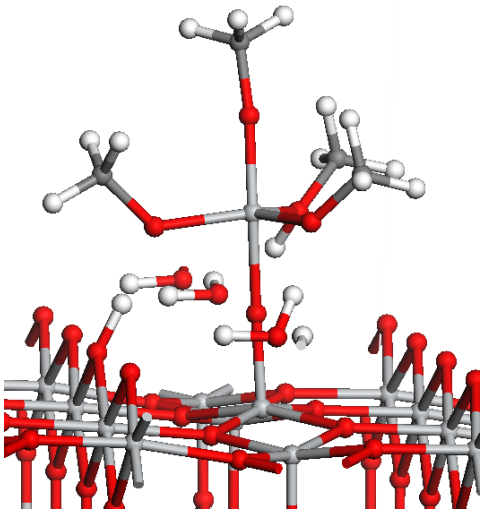
$Ti(Cp^*)(OMe)_3$



A

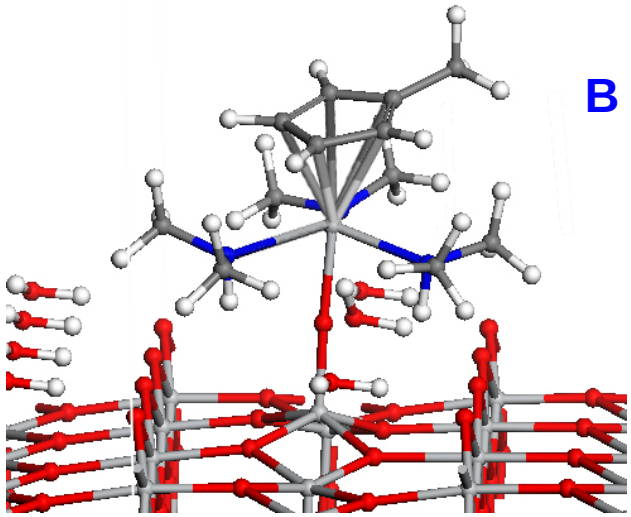
E_{ads} = +0.79 eV
unfavourable

$Ti(OMe)_4$



E_{ads} = -0.62 eV

$Ti(Cp^{Me})(NMe_2)_3$



B

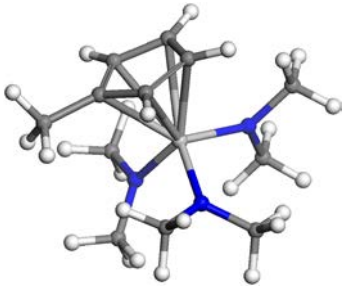
E_{ads} = +0.11 eV
unfavourable

- Formation of Ti–O bond and ligand loss for **A** and **B** unfavourable.
- Cp compounds sterically crowded → would not expect ALD growth.
- $Ti(OMe)_4$ has room to rotate → allows for a full reaction.

Example Decomposition of Precursor B

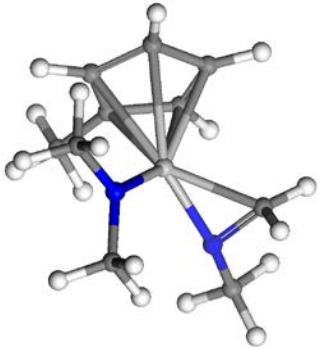
One of many possibilities…

Ti H C O N

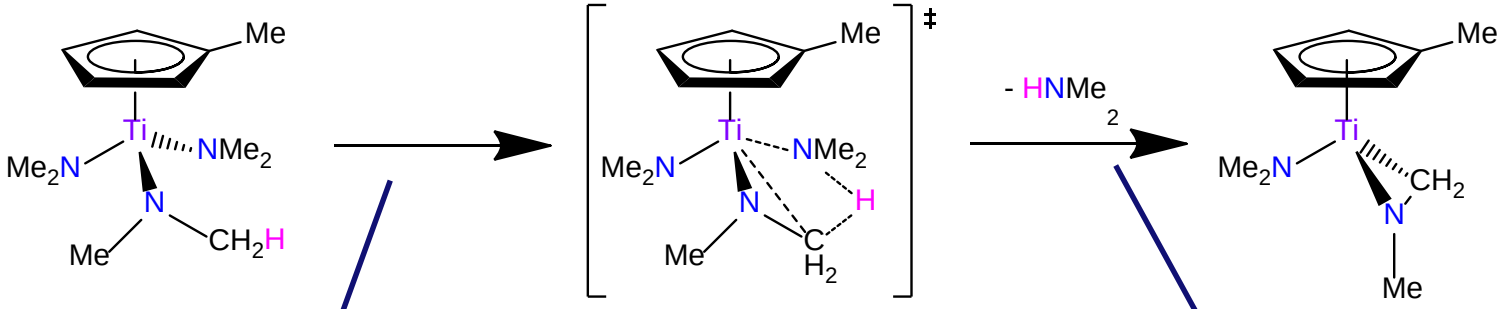


Reactant

Transition State



Product



E_a = +130 kJ/mol
(+1.35 eV/molecule)

$\Delta E = (E_{products} - E_{reactant})$ = +126 kJ/mol
(+1.31 eV/molecule)

- Endothermic overall, so thermodynamically unlikely.
- Less coordinative saturation – "opens up" metal centre.

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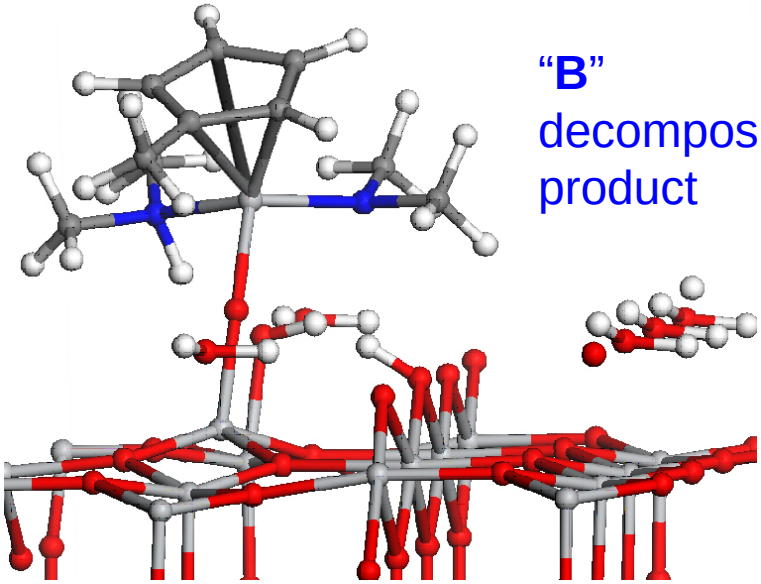
Energy of Adsorption: Decomposition Product

Towards elimination of $HNMe_2$

Ti H C O N

$Ti(Cp^{Me})(NMe_2)(CH_2NMe)$

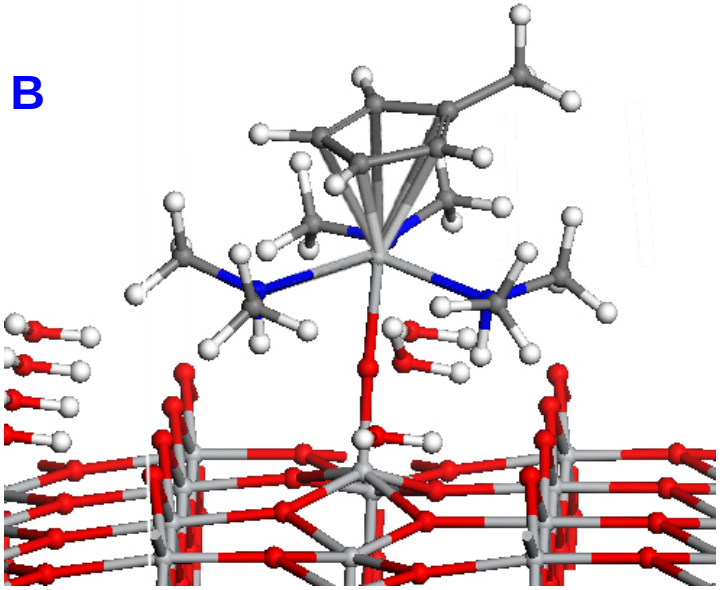


"**B**" decomposition product

E_{ads} = -1.25 eV

$Ti(Cp^{Me})(NMe_2)_3$

B



E_{ads} = +0.11 eV

- Full adsorption favoured for decomposition product of **B**.
- Less-crowded ligand coordination sphere.

Conclusions

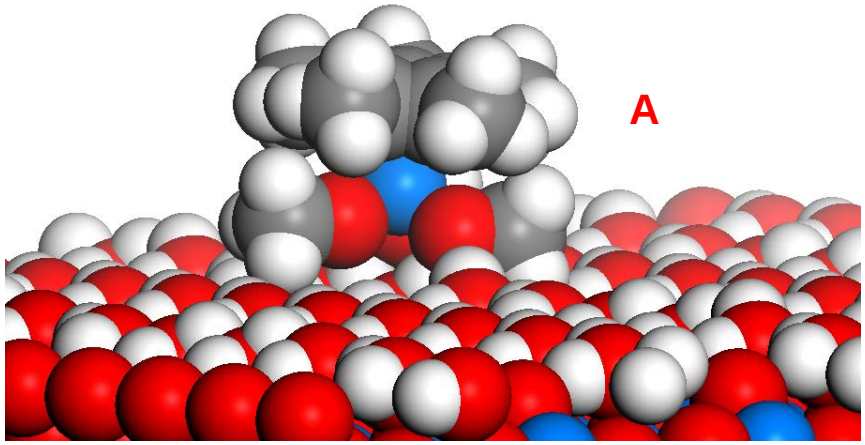
Addition of N_2 to an O_2 plasma

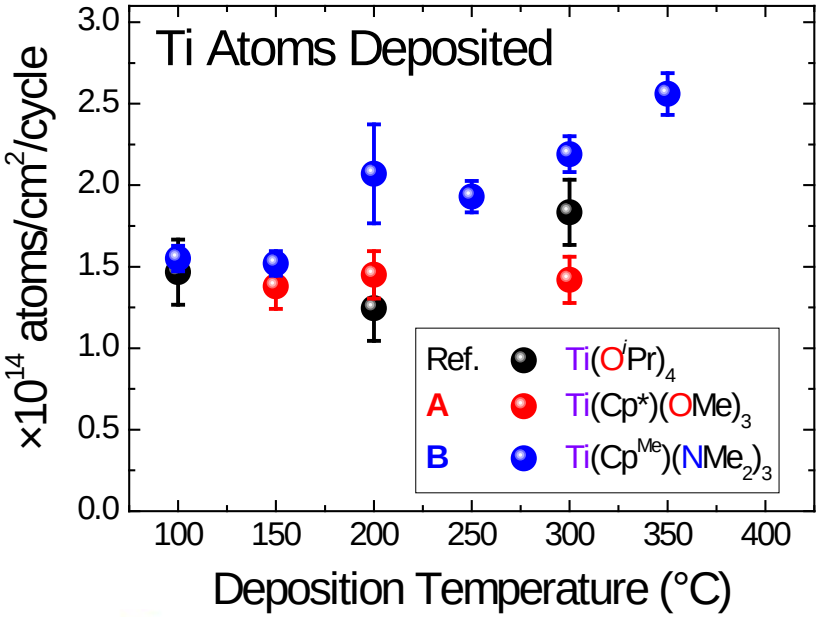
- No significant effect on the growth per cycle of TiO_2 from **A** and **B**.

DFT calculations of Ti-Cp compounds

- Very crowded ligand sphere
- Elimination of by-products not favourable
- Cannot do more than H-bond
- Possible decomposition of **B** affords a more-reactive species.

  → More Ti atoms/cycle.





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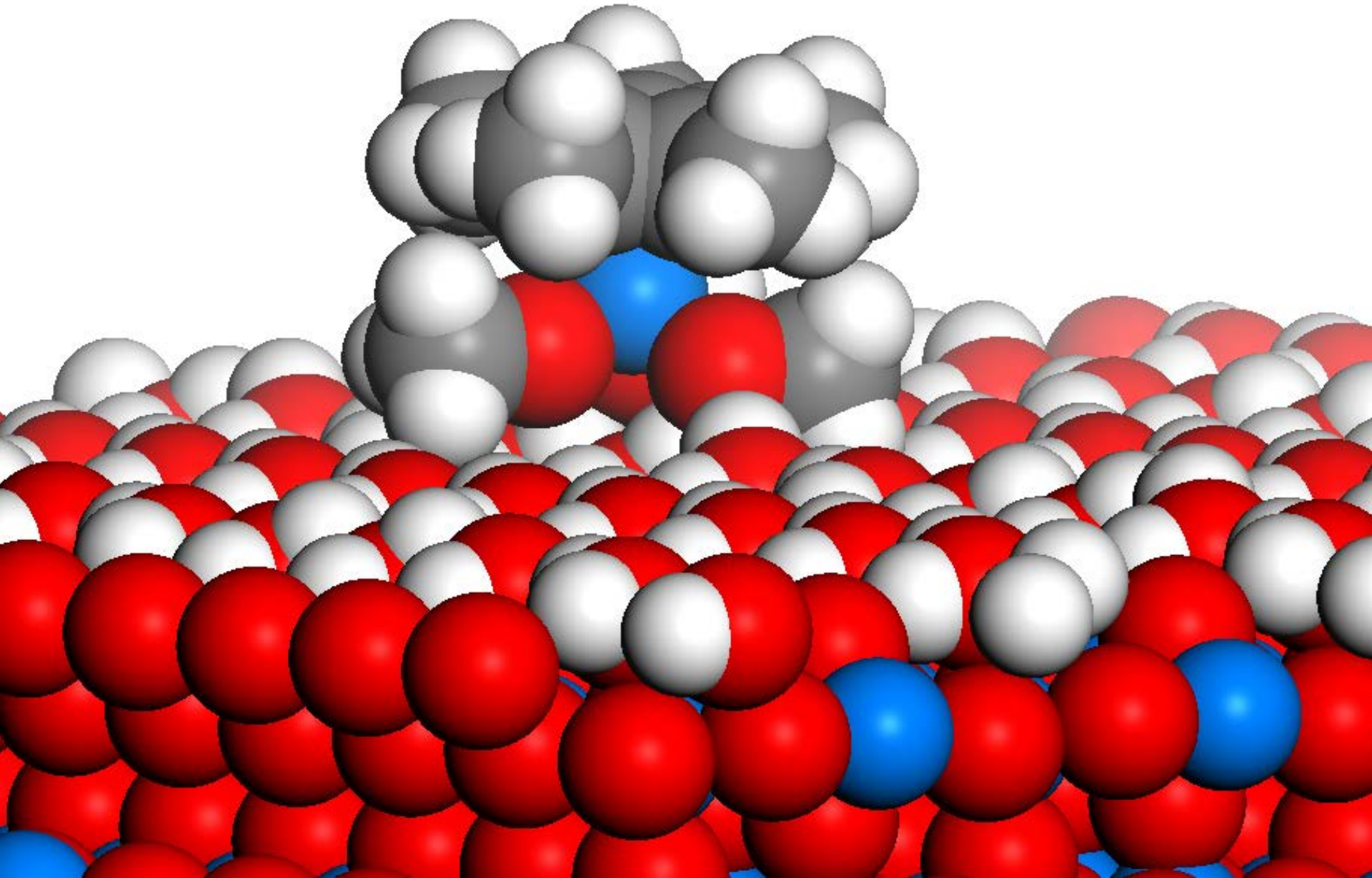
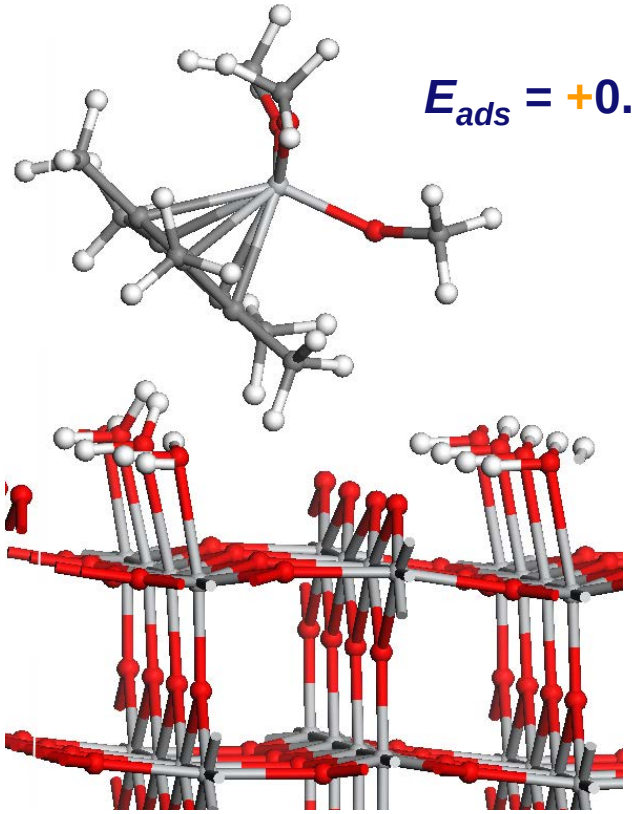
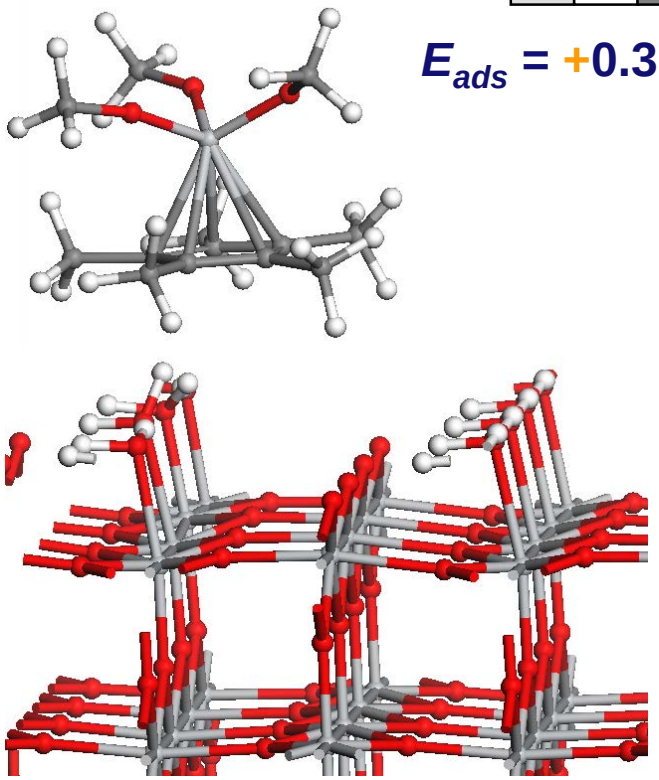


Adsorption *via* Cp* for Precursor A?

Ti H C O N



E_{ads} = +0.60 eV



E_{ads} = +0.37 eV

- Endothermic overall, thermodynamically unlikely.
- Cannot occur *via* H-bonding.
- Cp* not basic enough to undergo an acid-base reaction under these conditions.