ALD Conference, San Diego, CA, USA

31st July 2013

Room-Temperature ALD of Al_2O_3, TiO_2, SiO_2 and SiN_x Enabled by Energy-Enhanced ALD Techniques

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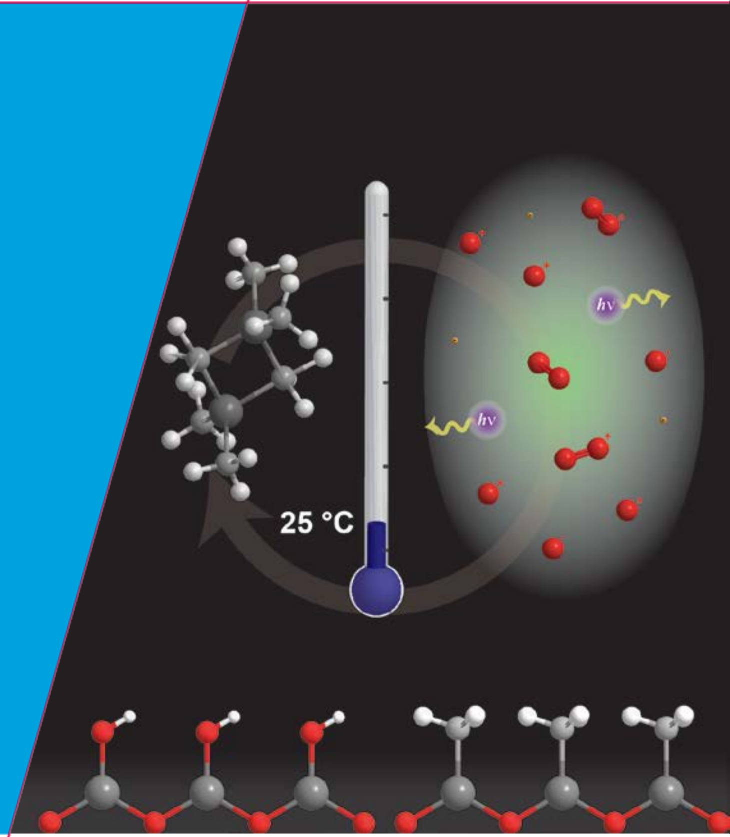
Eindhoven University of Technology, The Netherlands

Viljami Pore and Suvi Haukka

ASM Microchemistry, Finland



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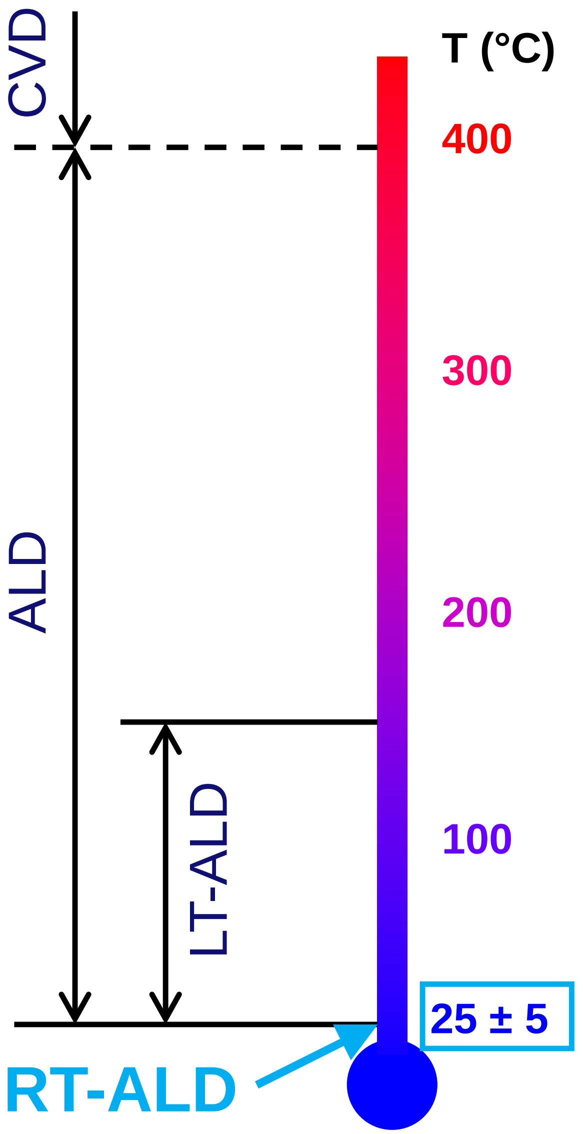
Where innovation starts

Outline

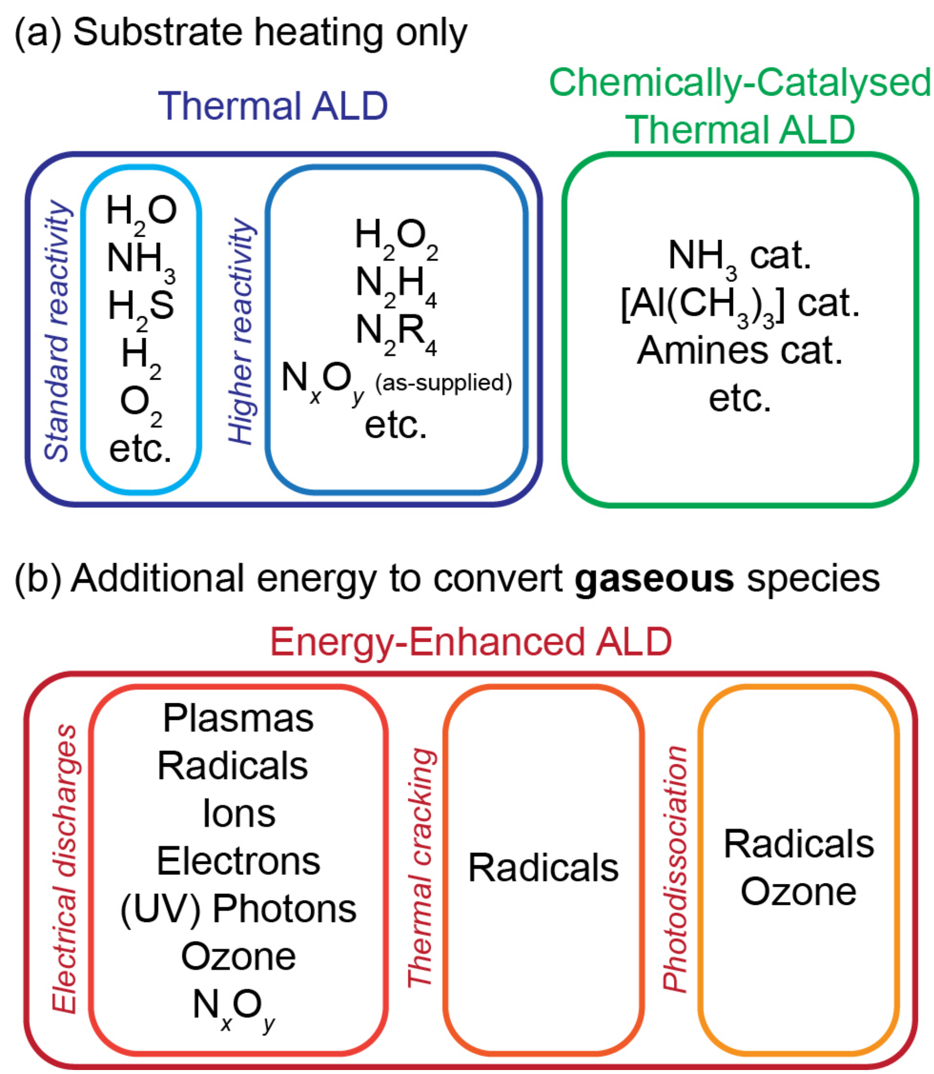


- **Requirements for room-temperature ALD (RT-ALD)**
- **RT-ALD of metal oxides**
  - Growth of
    - Al_2O_3
    - TiO_2
    - SiO_2
  - Importance of surface groups
- **Novel SiN_x RT-ALD process**
- **Conclusions**

Energy-Enhanced ALD

S. E. Potts & W. M. M. Kessels, *Coordination Chemistry Reviews*, **advance article now online** (2013).

- **Co-reactants have different levels of reactivity.**
- **Energy-enhanced ALD**
  - Additional energy
  - Conversion of gaseous species
    - Short lifetime
    - High reactivity



Requirements for Room-Temperature ALD

Desirable

- Metalorganic precursors with a high vapour pressure (≥ 5 Torr at RT).
- Short purge times.

Essential

- Reactivity with surface groups at room temperature.

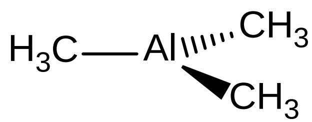
Energy-enhanced ALD plays a significant role in obtaining viable RT-ALD processes

- Plasma-enhanced ALD
- Ozone-based ALD

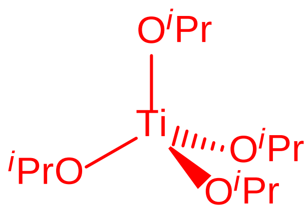
H. B. Profijt *et al.*, *J. Vac. Sci. Technol. A*, **29**, 050801 (2011).
S. E. Potts & W. M. M. Kessels, *Coord. Chem. Rev.*, **online** (2013).

Room-Temperature ALD Growth of Oxides

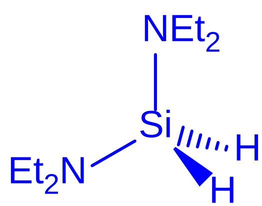
TMA

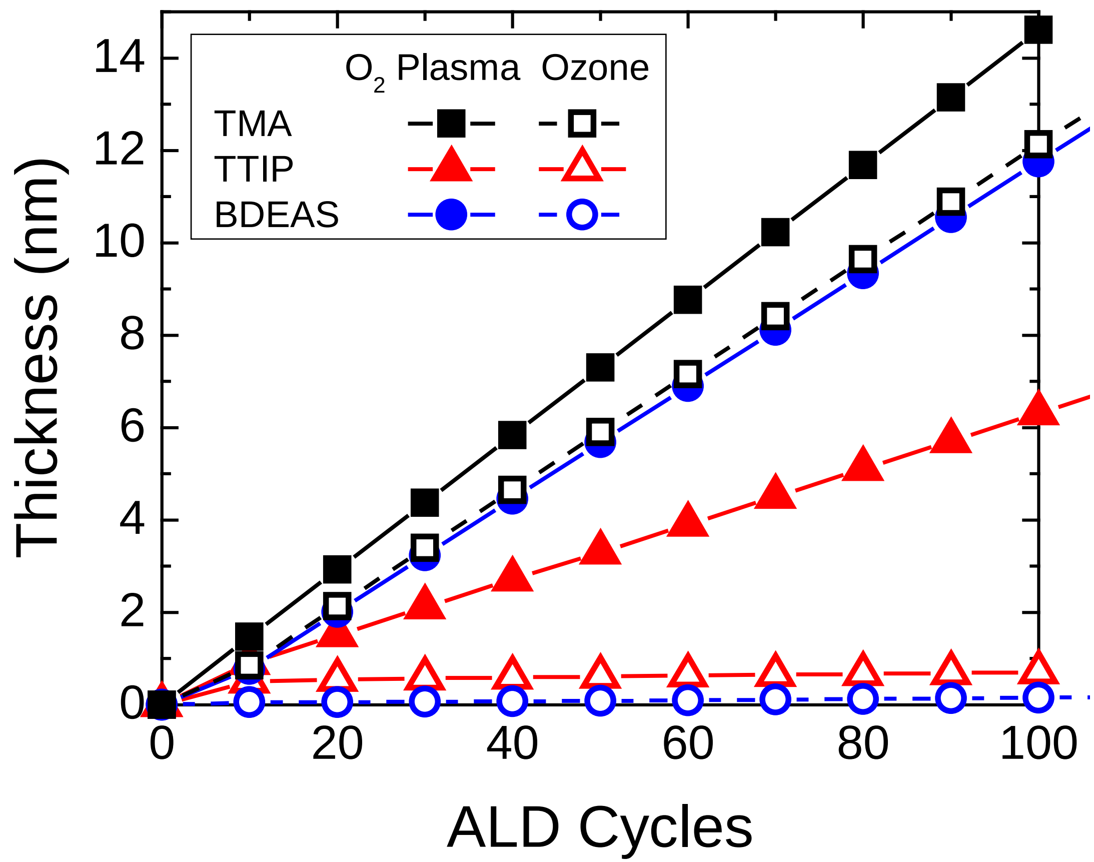


TTIP



BDEAS



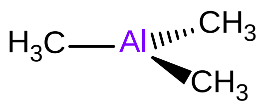


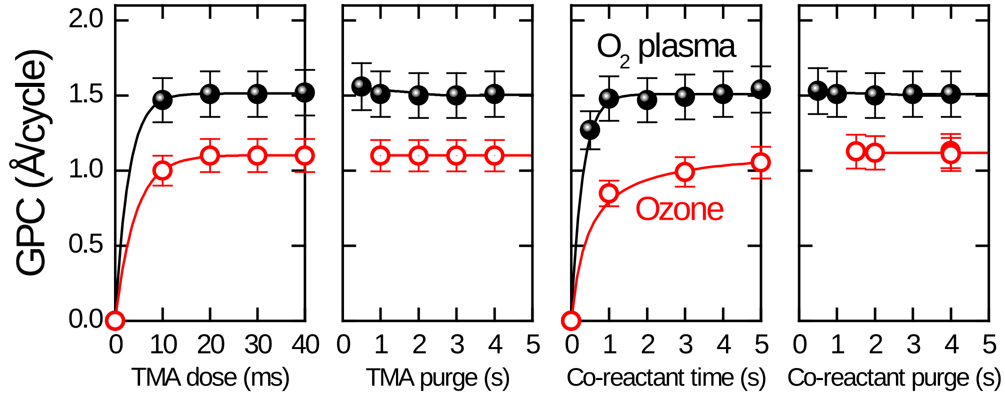
- *In situ* spectroscopic ellipsometry: linear growth at room temperature.
- Suggests neither a significant CVD component nor condensation.

S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).

Room-Temperature ALD Saturation: Oxides

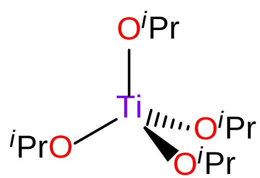
Al_2O_3

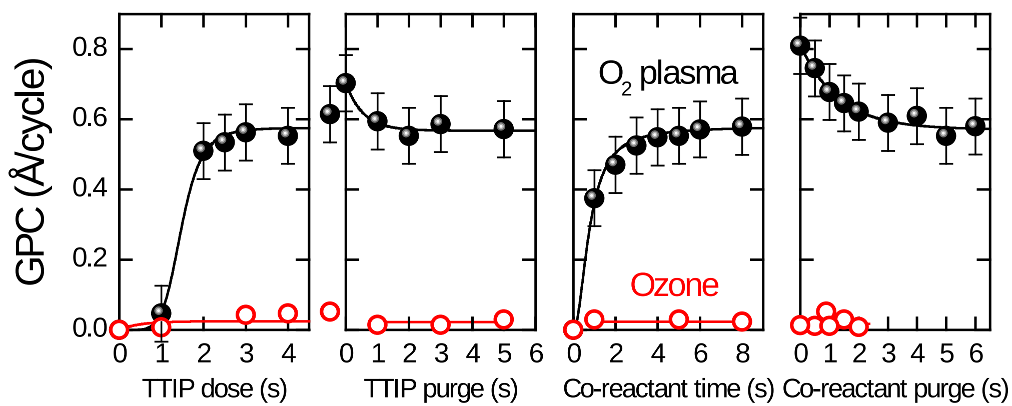




- V.P. = 13 Torr
- No heating
- No bubbling

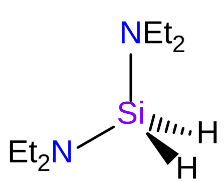
TiO_2

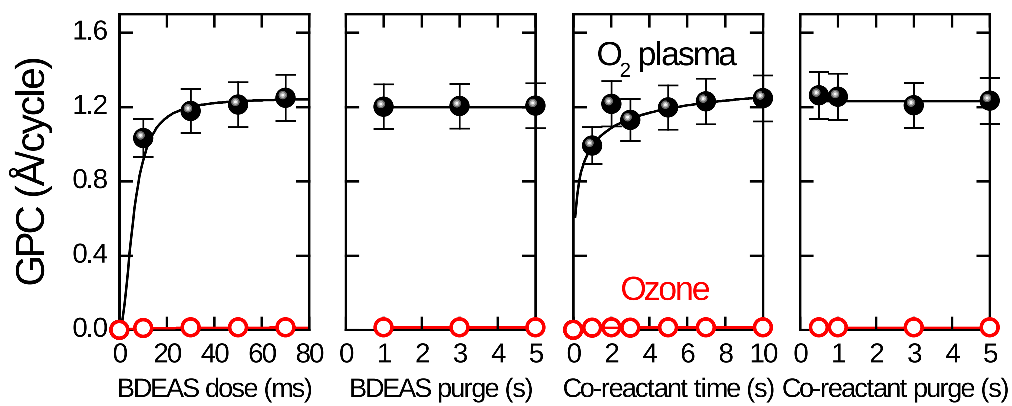




- V.P. = 0.13 Torr (at RT)
- Heating, 45 °C
- Bubbling, 50 sccm Ar

SiO_2





- V.P. = 2 Torr (at RT)
- Heating, 50 °C
- No bubbling

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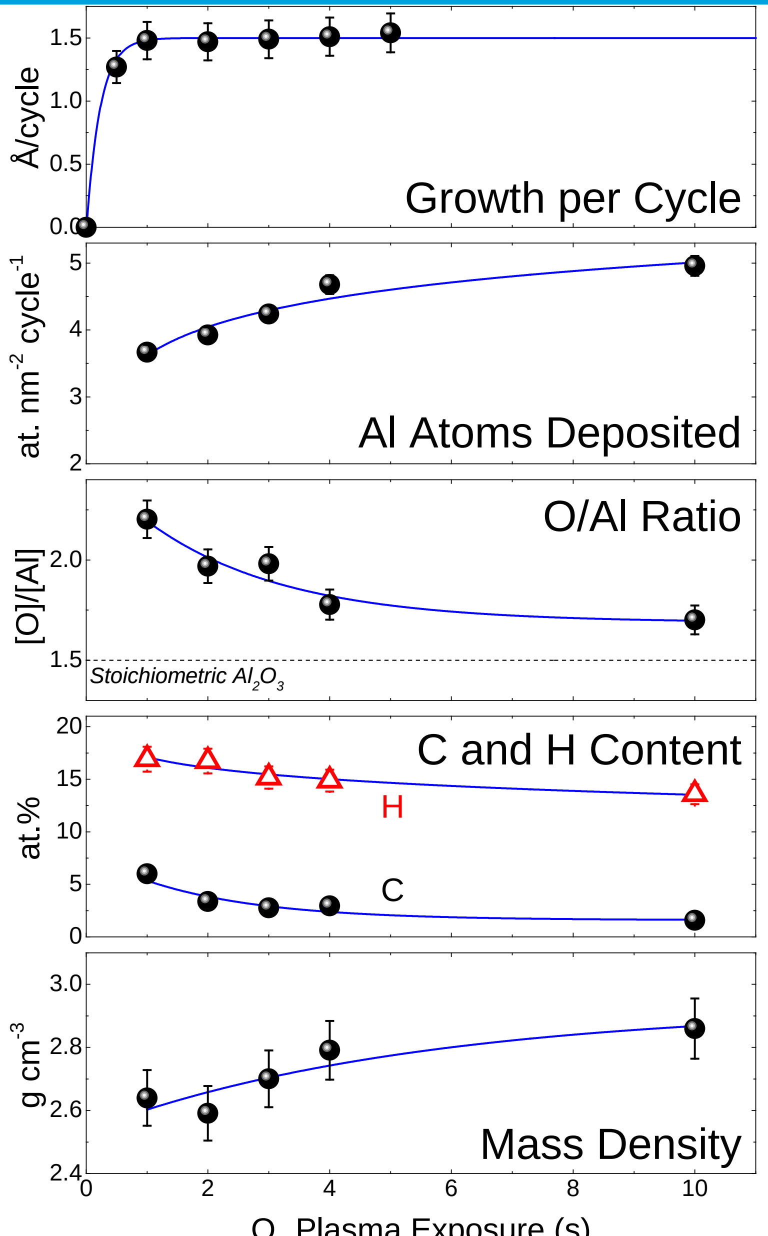
Plasma-Enhanced RT-ALD of Al_2O_3
Variation of Film Composition with Plasma Time



- **Saturation of growth per cycle does not correspond to saturation of film quality.**
- **A longer O_2 plasma leads to**
  - An increase in Al atoms deposited.
  - A reduction of C, H and excess O.
  - An increase in film density.
- **RT-ALD films with 10 s plasma**
  - equivalent to films grown at 100 °C using standard process (2 s plasma).

S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).

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Requirements for Room-Temperature ALD

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- Reactivity with surface groups at room temperature.

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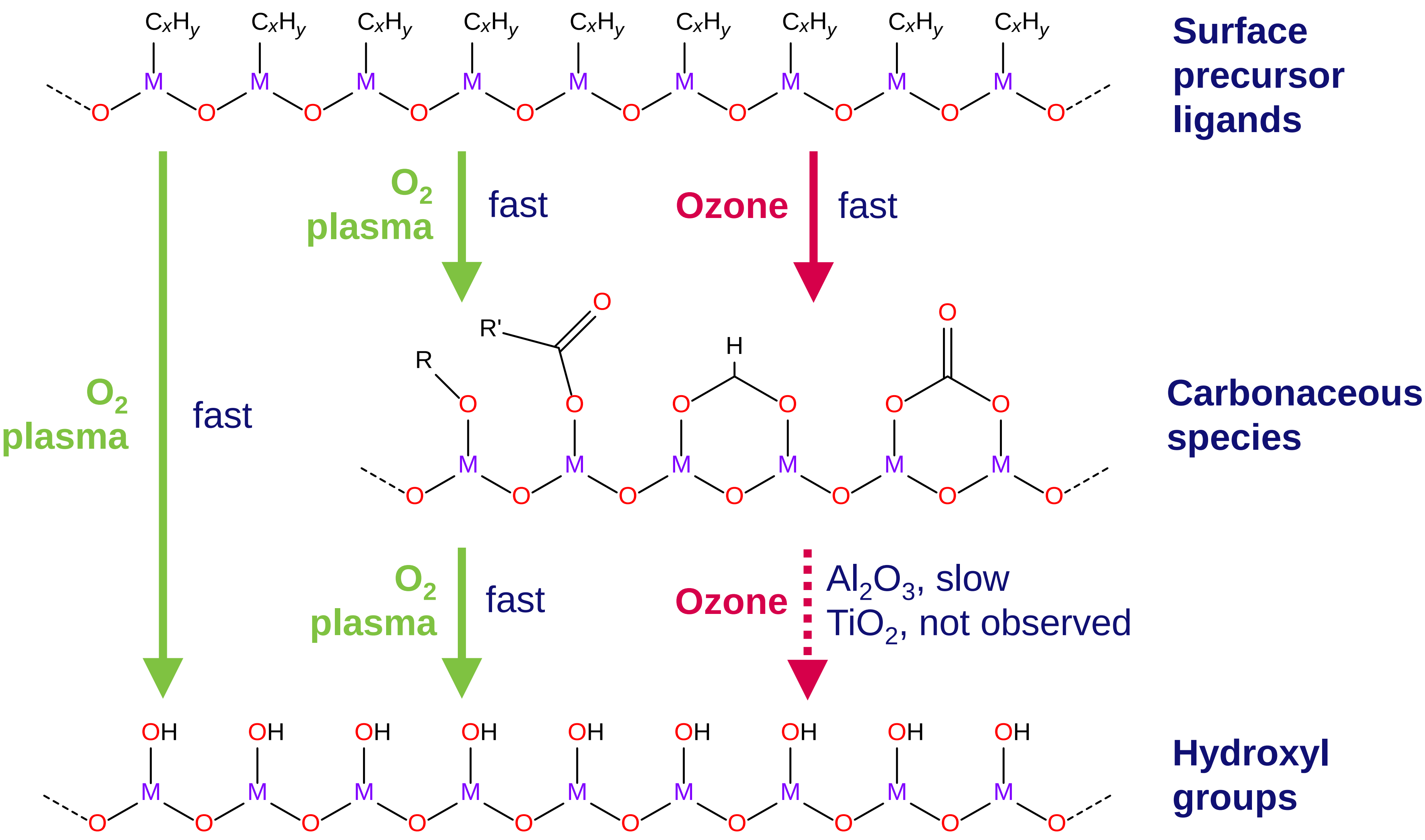
S. E. Potts & W. M. M. Kessels, *Coord. Chem. Rev.*, **online** (2013).

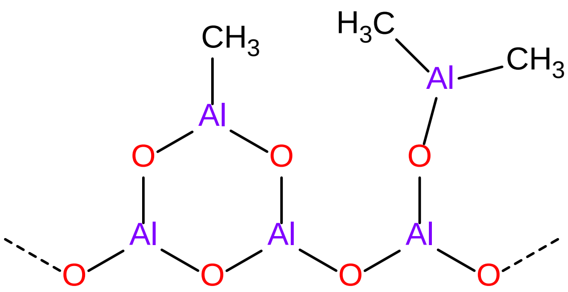
Surface Groups during RT-ALD
After the Co-Reactant Pulse



D. M. Goldstein *et al.*, *J. Phys. Chem. C*, **112**, 19530 (2008).
V. R. Rai *et al. J. Phys. Chem. C*, **112**, 9552 (2008).

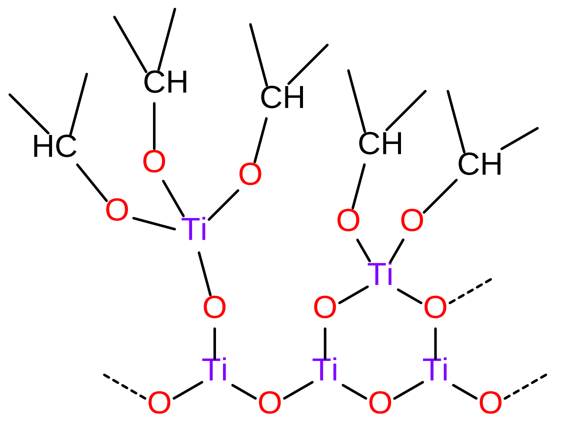
Surface Groups during RT-ALD
After the Metal Precursor Pulse

TMA, Al(CH_3)$_3$



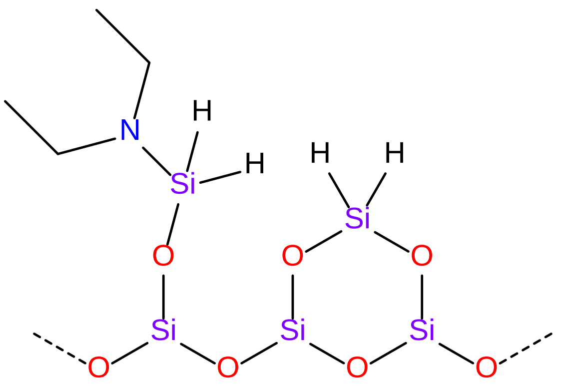
- Highly reactive Al–C bonds.
- Easily removed by O_2 plasma and ozone.

TTIP, Ti(O^{i}Pr)$_4$



- Ti–O bond already relatively strong.
- Easily removed by O_2 plasma.
- No or negligible reactivity with ozone?

BDEAS, SiH_2(NEt$_2$)$_2$

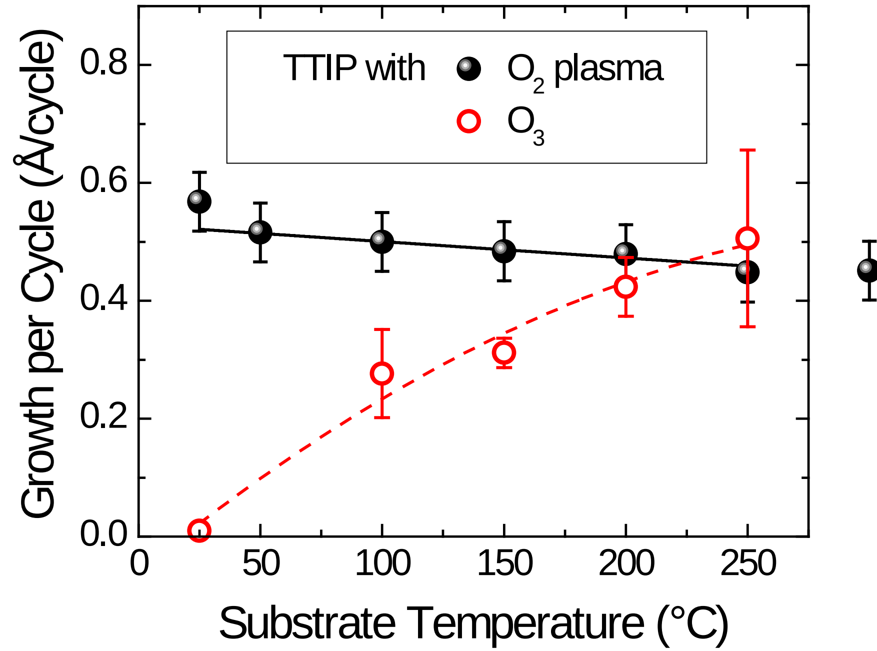


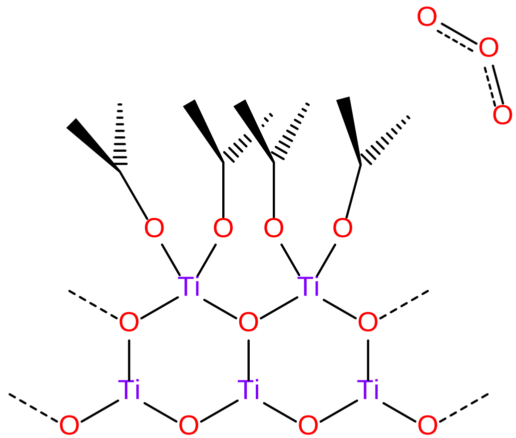
- s-H predominates.
- Easily removed by O_2 plasma.
- No or negligible reactivity with ozone?

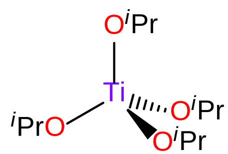
S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).
S. E. Potts & W. M. M. Kessels, *Coord. Chem. Rev.*, **online** (2013).

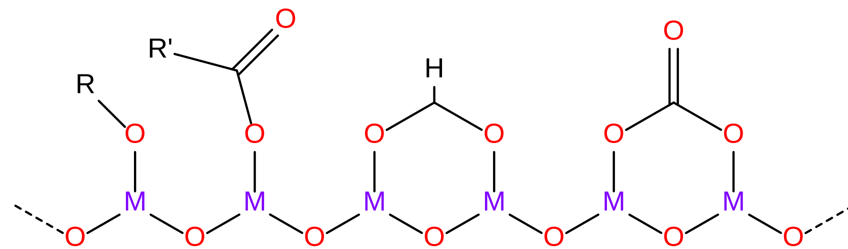
Surface Groups during RT-ALD
TTIP + Ozone

- **ALD process has a thermal activation component.**
- **TTIP surface groups/ozone simply unreactive at RT.**



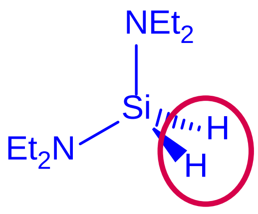




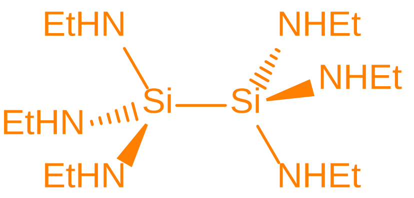


O_2 plasma: S. E. Potts *et al.*, *J. Electrochem.Soc.*, **157**, P66 (2010).
O_3: P. Williams *et al.* at ALD Conference 2008, Bruges.
O_3 (RT): S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).

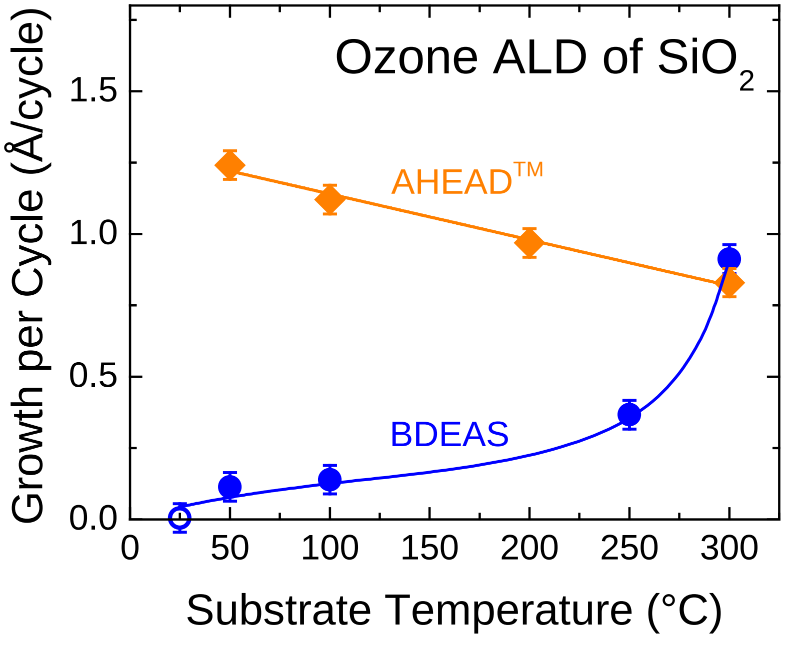
Surface Groups during RT-ALD
BDEAS + Ozone



BDEAS



AHEAD™

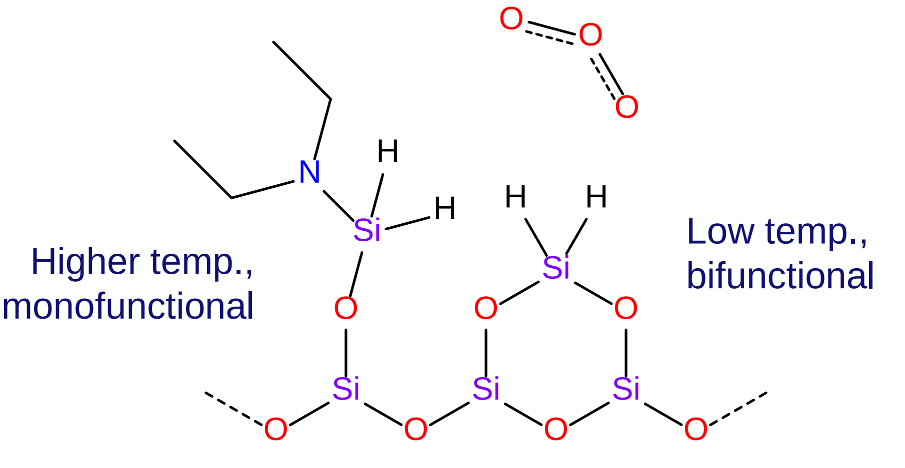


Two possible explanations

1. Insufficient thermal energy
2. Reactivity with surface OH:

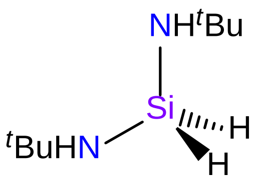
   Si–NEt_2 >> Si–H

- Si^{IV}–H unreactive with ozone at room temperature.



S. Haukka, at Baltic ALD 2010, Hamburg.
C. K. Fink *et al.*, *J. Phys.: Condens. Mater.*, **21**, 183001 (2009).

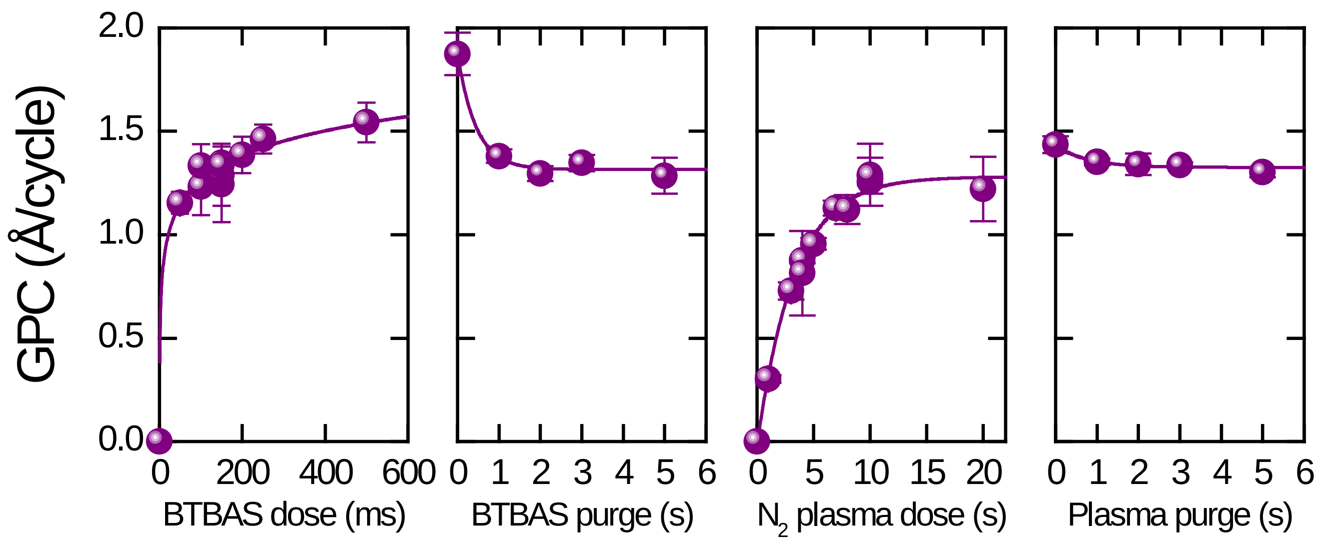
Plasma-Enhanced RT-ALD of SiN_x



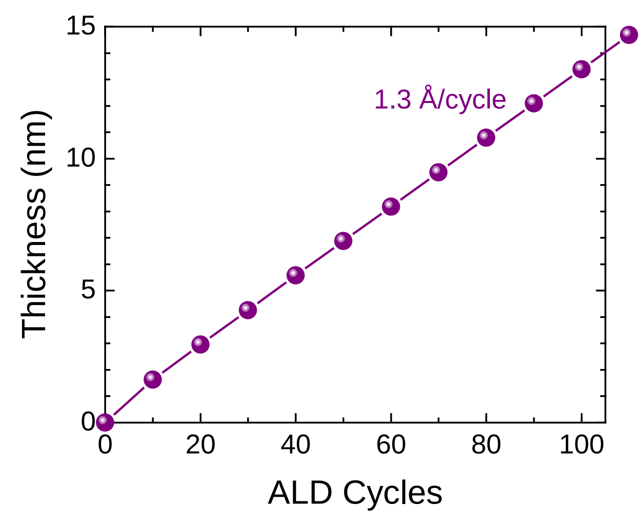
BTBAS

N_2 plasma

600 W, 40 mTorr



- **Reasonable saturating behaviour**
- **Linear increase in thickness with cycles**
- **Plasma saturation requires times >10 s (c.f. 5 s at 100 °C)**



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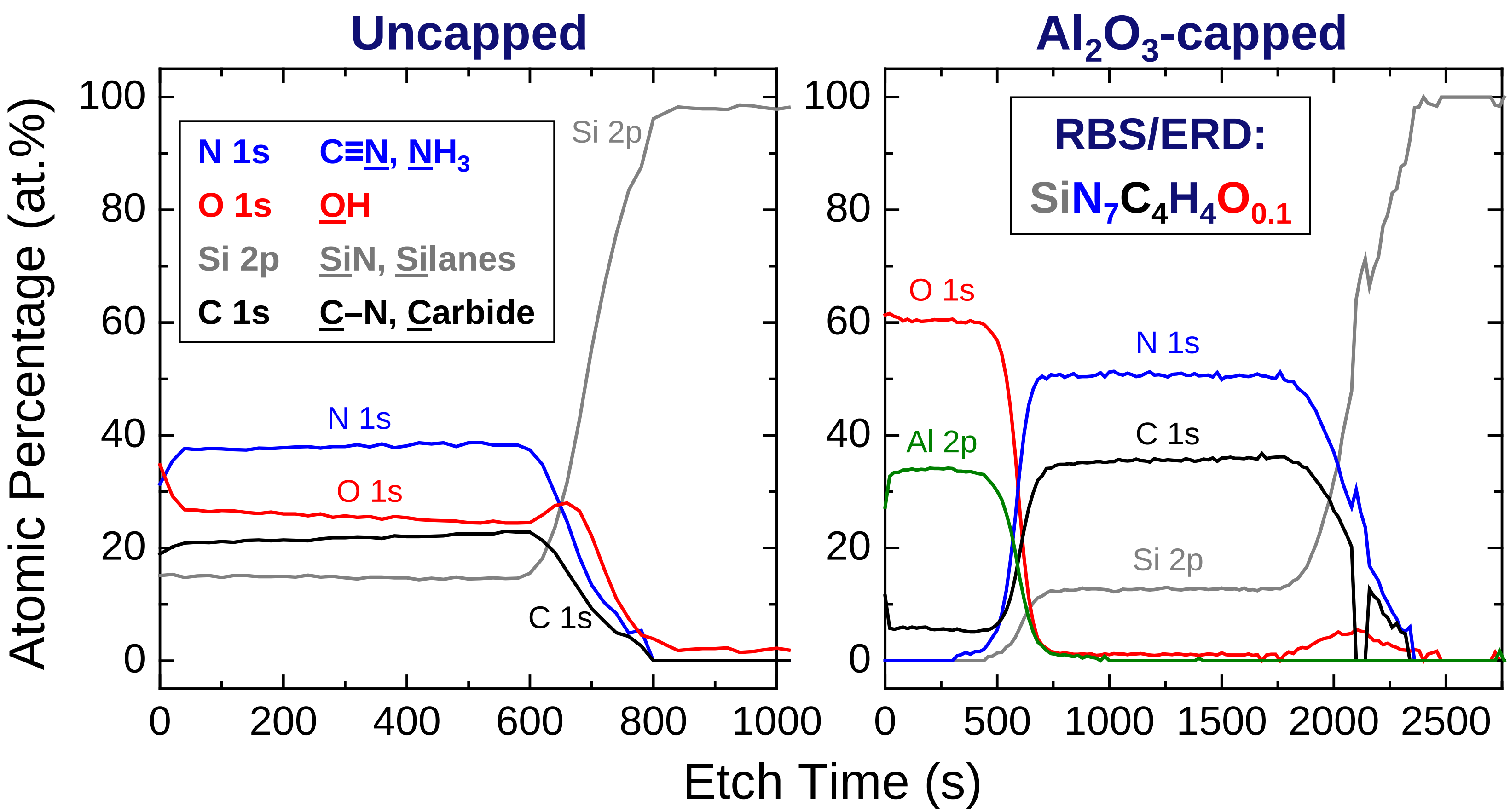
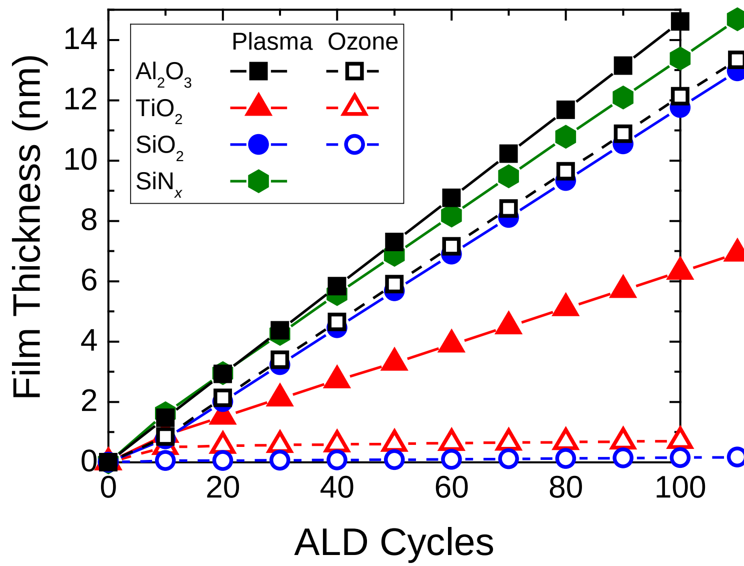
Plasma-Enhanced RT-ALD of SiN_x



- **N- and C-rich films**
- **Air-sensitive but can be protected by a barrier layer**
- **Capped: exceptionally low O content (~1 at.%), even after 2 months**

Summary/Conclusions

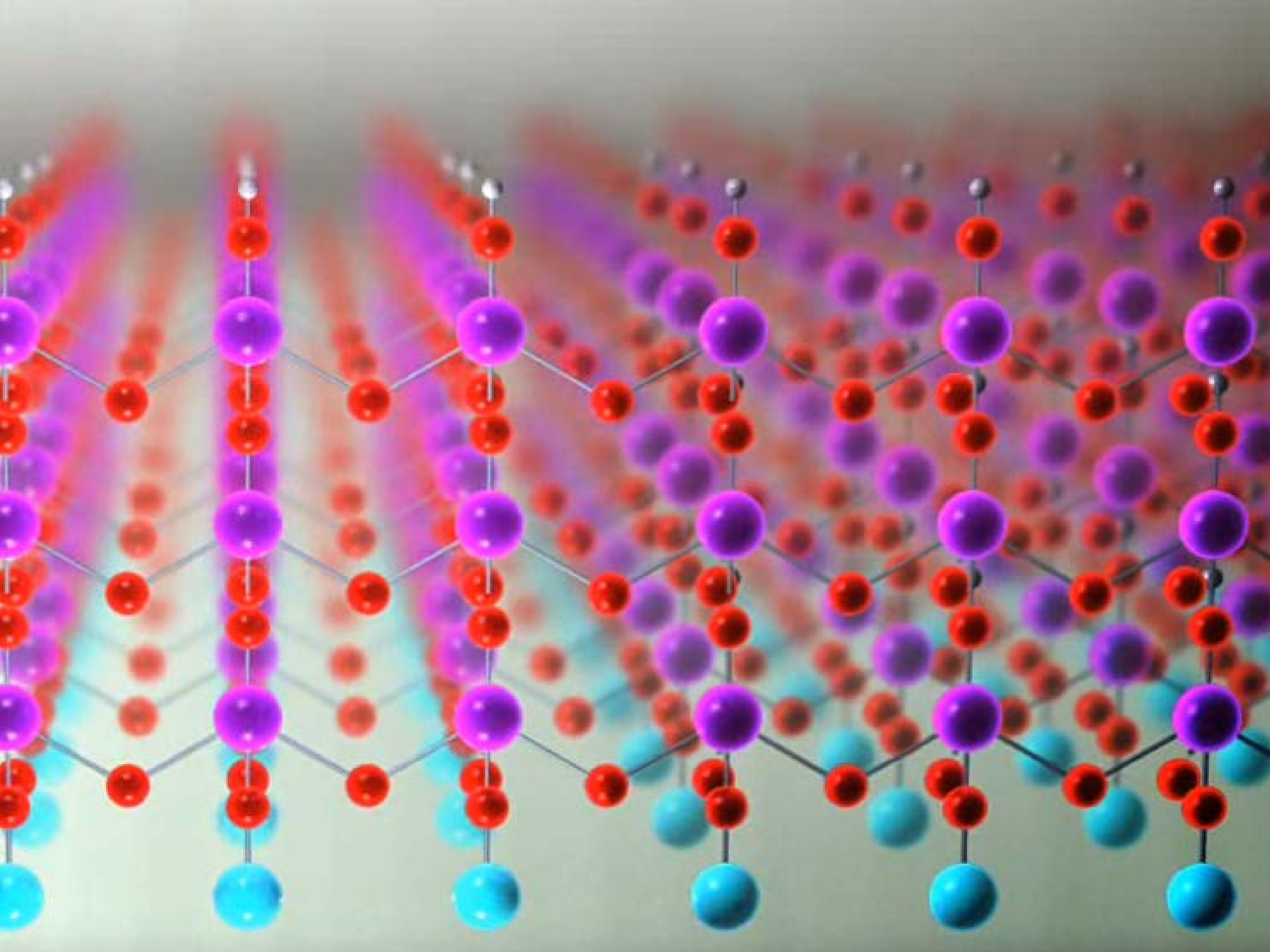
RT-ALD?	Al_2O_3 TMA	TiO_2 TTIP	SiO_2 BDEAS	SiN_x BTBAS
O_2 plasma	✓	✓	✓	
Ozone	✓	✗	✗	
N_2 plasma				✓



- **RT-ALD of metal oxides**
  - Strongly dependent on surface-groups
  - Plasmas give growth
  - Ozone not always sufficiently reactive (carbonaceous species)

- **RT-ALD of silicon nitride**
  - Shows saturating behaviour

S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).
S. E. Potts & W. M. M. Kessels, *Coord. Chem. Rev.*, **online** (2013).



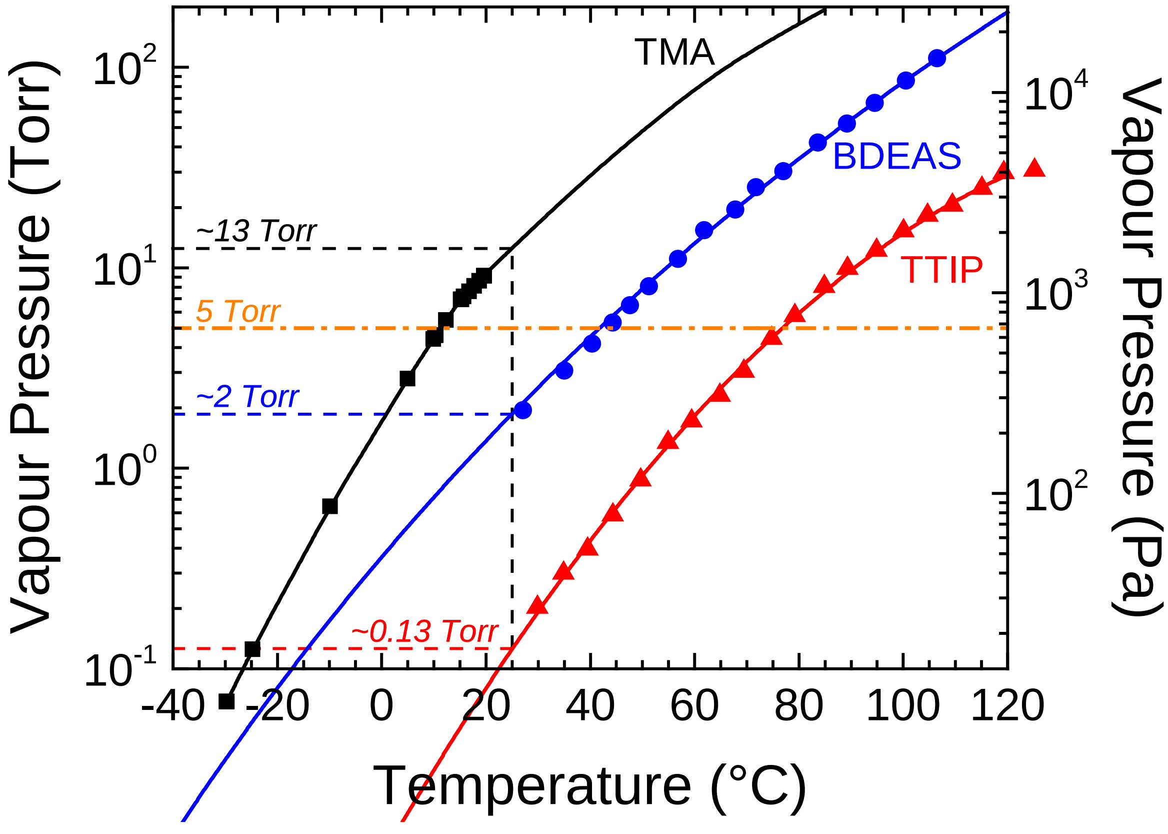
Room-Temperature ALD in the Literature

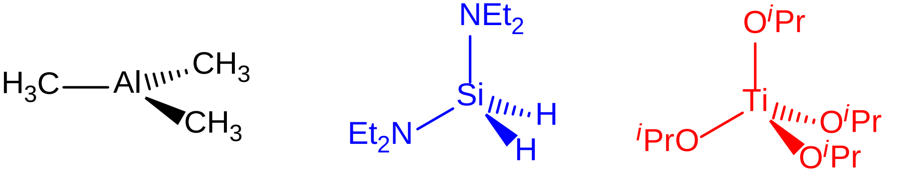
Material	Precursor	Co-Reactant	Reference
Al_2O_3	$Al(CH_3)_3$	H_2O	Groner, Nam
	$Al(CH_3)_3$	**O_3**	Kim, **this work**
	$Al(CH_3)_3$	**O_2 plasma**	Kessels, Niskanen, Tang, **this work**
	$[Al(CH_3)_2(O^iPr)]_2$	O_2 plasma	Potts
B_2O_3	BBr_3	H_2O	Putkonen
Pt	**$Pt(Cp^{Me})Me_3$**	**O_2 gas + H_2 plasma or H_2 gas**	**Mackus**
SiO_2	**$Si(OEt)_4$**	**H_2O + NH_3 cat.**	**Ferguson**
	$Si(NCO)_4$	**H_2O**	**Gasser**
	$SiH_2(NEt_2)_2$	**O_2 plasma**	**This work**
TiO_2	**$Ti(O^iPr)_4$**	**O_2 plasma**	Potts, **this work**
	$Ti(NMe_2)_4$	H_2O	Nam
	$Ti(NMe_2)_4$	O_2 plasma	Nam
Ta_2O_5	$Ta(NMe_2)_5$	O_2 plasma	Potts
ZnO	$Zn(CH_2CH_3)_2$	H_2O	Nam, Ku, Chang
	$Zn(CH_2CH_3)_2$	H_2O_2	King
ZrO_2	**$Zr(O^tBu)_4$**	**H_2O + UV light**	**Lee**

For full reference list, see
S. E. Potts *et al.*, Chem. Vap. Deposition, **19**, 125 (2013).

Vapour Pressure Considerations for RT-ALD

- Ideally ≥5 Torr at room temperature.
- Heating to ~50 °C is fine (reactor-dependent).
- Further heating increases risk of condensation on the substrate.
- Bubbling allows even lower vapour pressure precursors to be used.





S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013) and references therein.

Purge Times

- **Quickly pumped from reactor**
  - Precursors with high vapour pressures.
  - Gaseous reaction products.

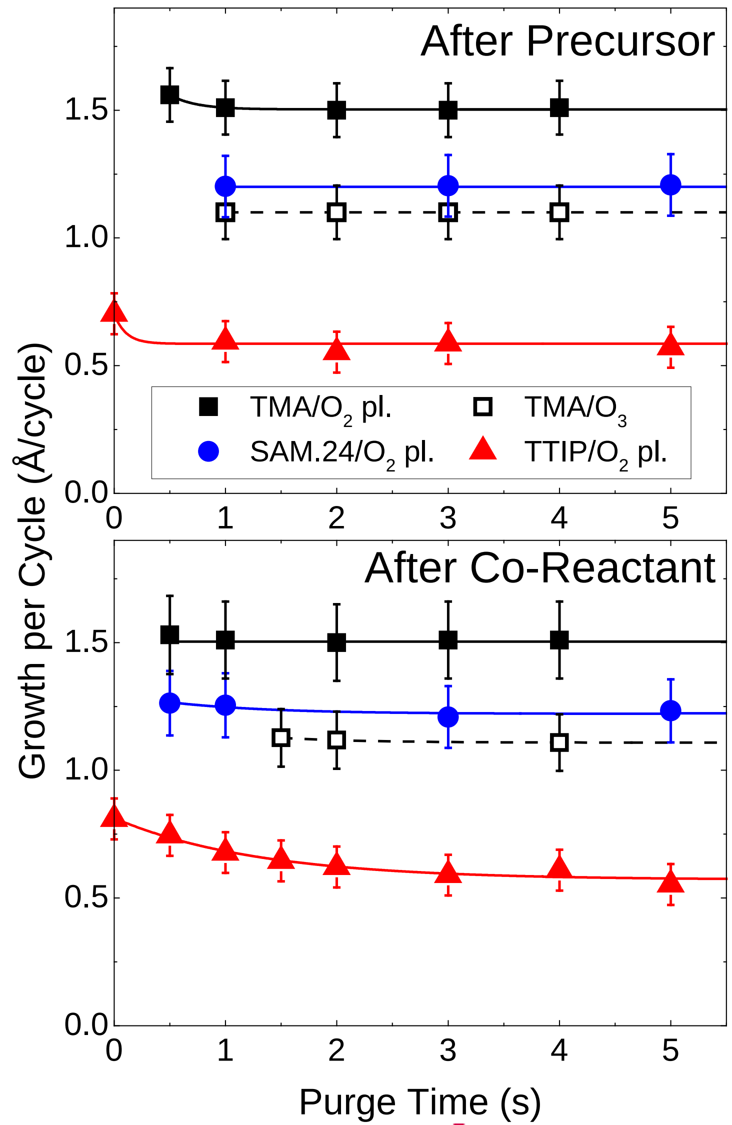
- **Water condenses easily, purging an issue.**

M. D. Groner *et al.*, *Chem. Mater.*, **16**, 639 (2004).
T. Nam *et al.*, *J. Korean Phys. Soc.*, **59**, 452 (2011).

- **Reactive species from energy-enhanced ALD can be 'turned off'**
  - Plasma
    - Ions and electrons disappear almost instantaneously
    - Radicals quickly recombine (surface-dependent)

H. C. M. Knoops *et al.*, *J. Electrochem. Soc.*, **157**, G241 (2010).

  - Ozone is quickly pumped away.



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RT-ALD Film Compositions (RBS/ERD)

Material	Co-reactant	T_{dep}	[O]/[M] ratio	[C] (at.%)	[H] (at.%)	Mass density (g cm^{-3})	M deposited (at. nm^{-2} cycle^{-1})
Al_2O_3	O_2 plasma	**RT**	**2.0**	**2.8**	**15.2**	**2.7**	**4.2**
		200 ºC	*1.5*	*< 1*	*2.5*	*3.1*	*3.4*
	Ozone	**RT**	**2.1**	**9.0**	**20.8**	**2.4**	**1.9**
		200 ºC	*1.7*	*< 2*	*8.1*	*3.0*	*2.2*
SiO_2	O_2 plasma	**RT**	**2.0**	**< 5**	**7.8**	**1.9**	**2.8**
		200 ºC	*2.1*	*< 5*	*7.1*	*2.0*	*2.3*
TiO_2	O_2 plasma	**RT**	**2.2**	**4.2**	**16.9**	**2.7**	**0.9**
		200 ºC	*2.0*	*< 1*	*< 5*	*3.7*	*1.2*

SiO_2 process: N was below 5% detection limit.

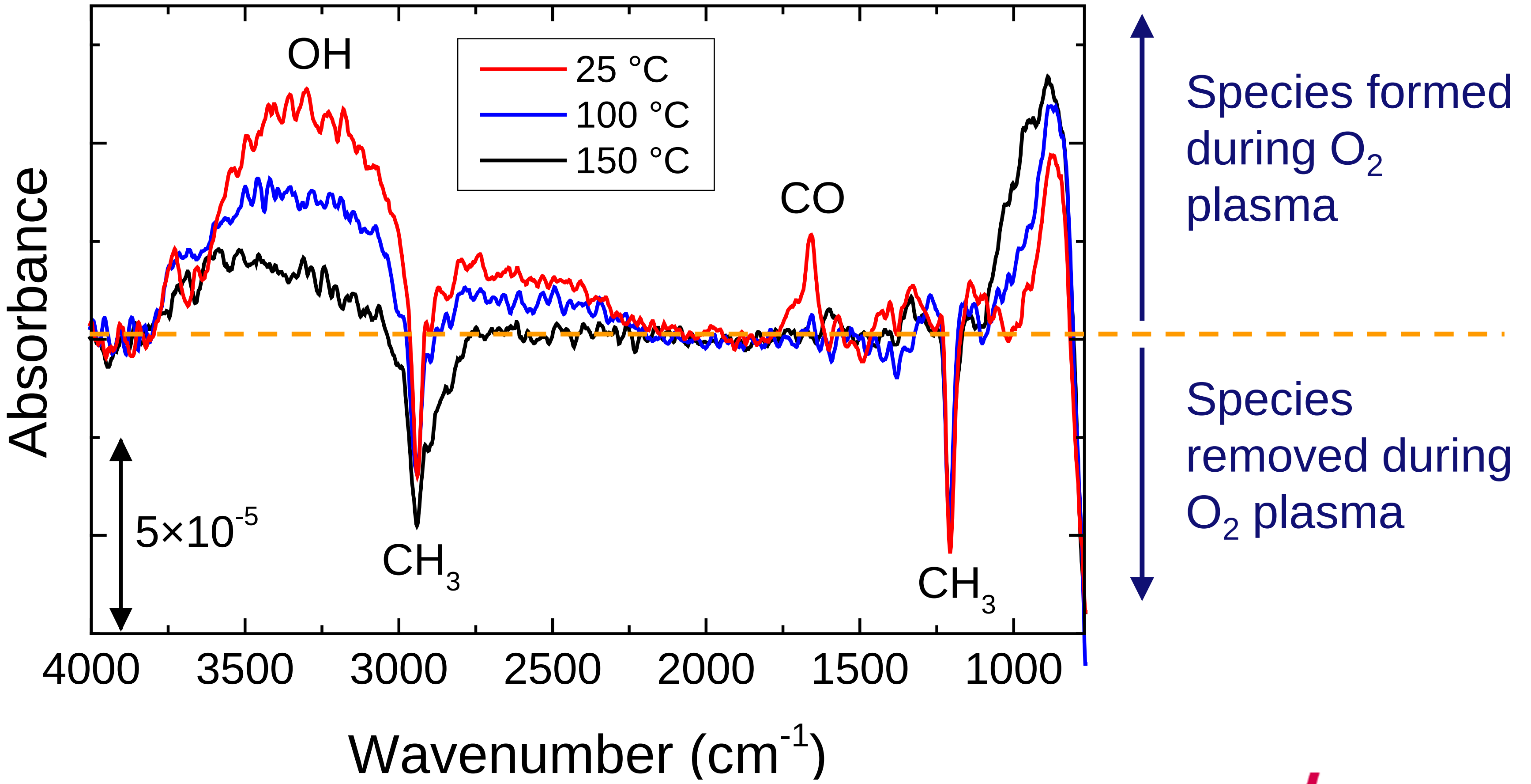
- Al_2O_3 and TiO_2: RT films have lower density and higher O, C, H content than 300 °C films.
- SiO_2: RT and 200 °C (and 300 °C) films are remarkably comparable!

S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).

Surface OH During Plasma-Enhanced ALD

TMA
+
2 s O_2 plasma

- Difference FT-IR spectra
- OH is the dominant species after plasma
- Some carbonaceous species at room temperature.



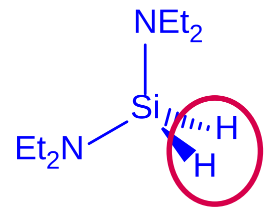
E. Langereis *et al.*, *Appl. Phys. Lett.*, **92**, 231904 (2008).

Surface Groups during RT-ALD

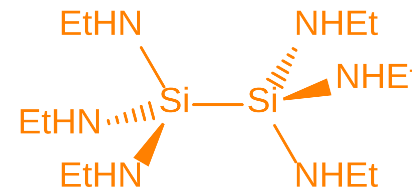
BDEAS/AHEAD + Ozone

- Low reactivity of Si–NEt_2 and Si–H with carbonaceous species.
- Reactivity with surface OH:

  Si–NEt_2 >> Si–H
- High surface [OH] at RT promotes bifunctional binding.
- Si–H remains, unreactive with ozone.



BDEAS



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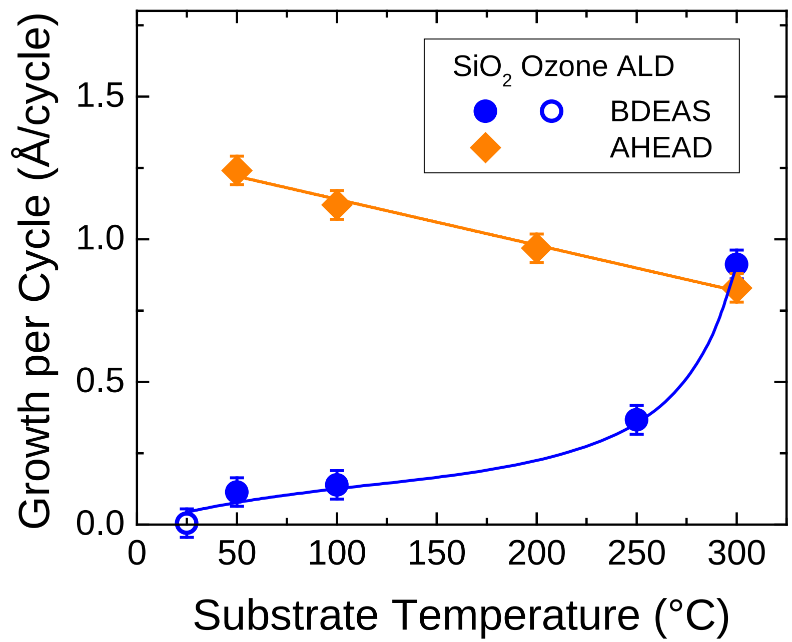
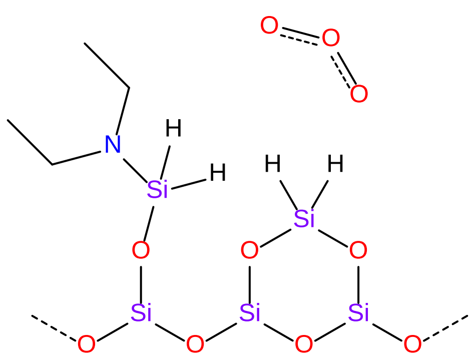


S. Haukka, at Baltic ALD 2010, Hamburg.



S. Haukka *et al.*, *Appl. Surf. Sci.*, **82/83**, 548 (1994).
S. Haukka *et al.*, *Interface Sci.*, **5**, 119 (1997).

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