Room-Temperature ALD of Metal Oxide Thin Films by Energy-Enhanced ALD

Stephen E. Potts, Harald B. Profijt,
Robin Roelofs and Erwin Kessels

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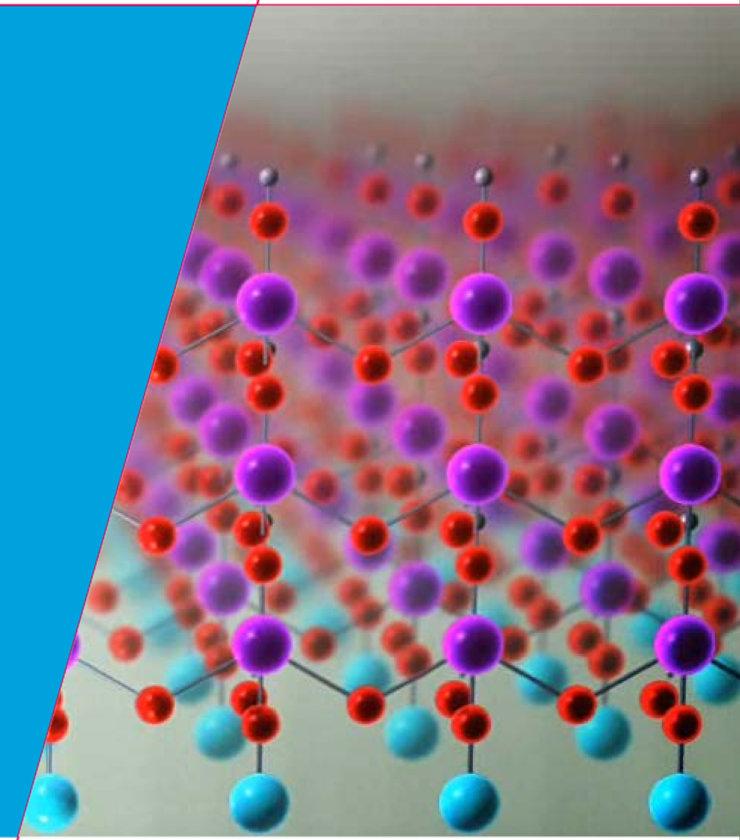
8th October 2012



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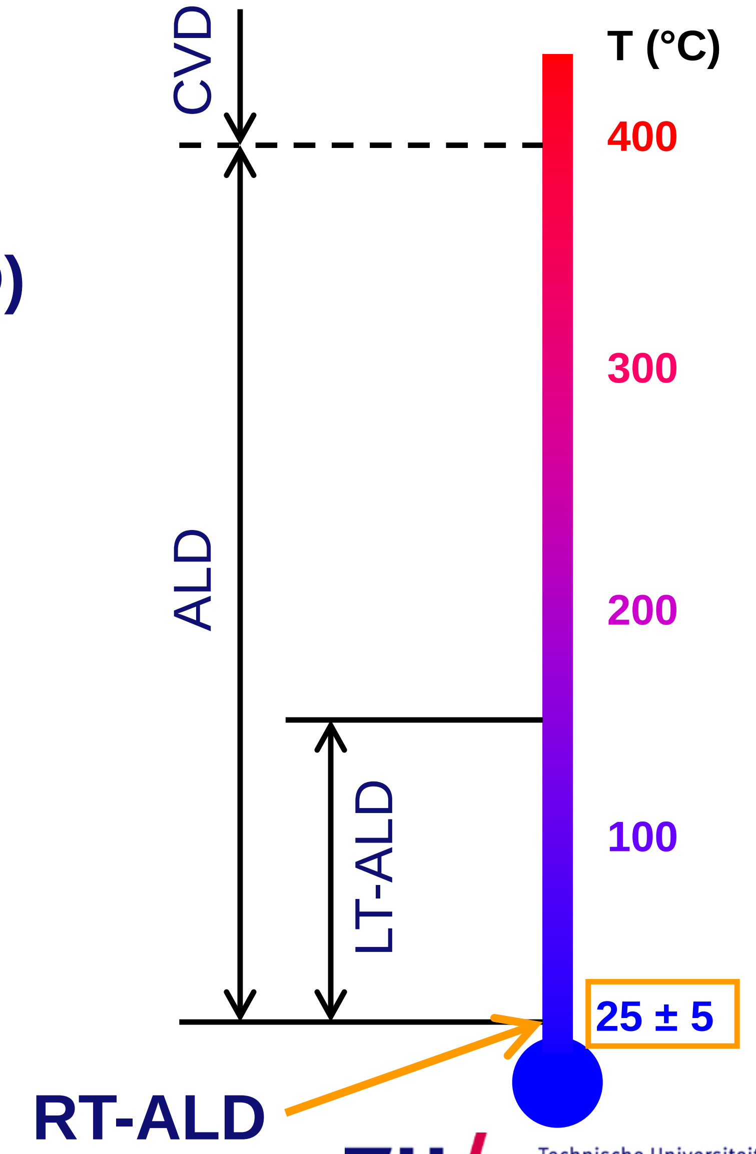
Where innovation starts

Outline

- **Why low-temperature ALD?**
- **Room-temperature ALD (RT-ALD) of metal oxides**
  - Precursor vapour pressure
  - Purge times
  - Surface groups
- **Conclusions**

Al_2O_3
SiO_2
TiO_2

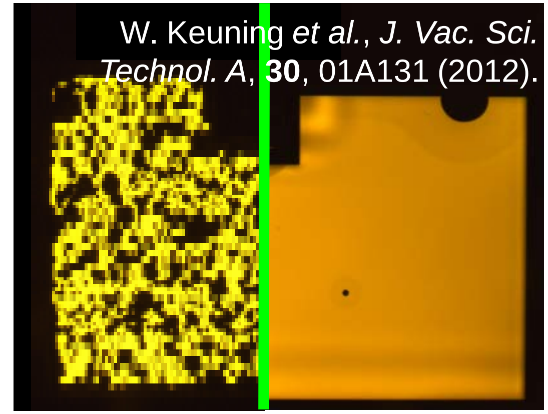


Why Low Temperature ALD?

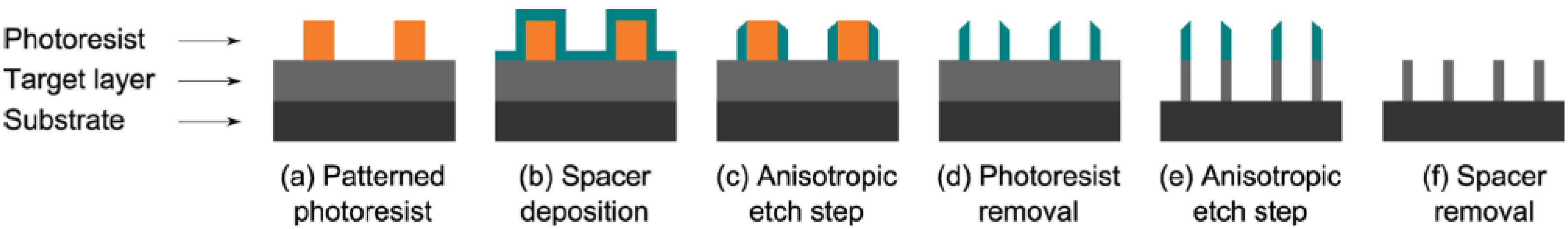
Applications requiring temperature-sensitive substrates.

Polymer Substrates

- Flexible electronics
- Encapsulation
    - Solid-state lighting
    - Organic LEDS



Nanopatterning (direct spacer-defined double patterning)



J. Beynet *et al.*, *Proc. SPIE*, **7520**, 75201J (2009).

Use of room-temperature ALD (RT-ALD) to avoid substrate heating?

S. E. Potts *et al.*, *J. Electrochem.Soc.*, **157**, P66 (2010).
H. B. Profijt *et al.*, *J. Vac. Sci. Technol. A*, **29**, 050801 (2011).

Requirements for RT-ALD

Desirable

- Organometallic precursors with a high vapour pressure ($\geq$ 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

- Application of energy to a gas to form a reactive species
- Plasma-enhanced ALD
- Ozone-based ALD

Room-Temperature ALD in the Literature

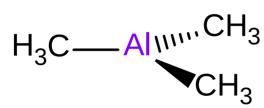
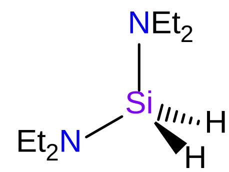
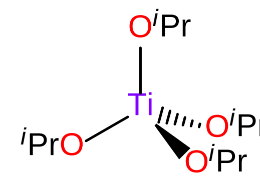
Material	Precursor	Co-Reactant	Reference
Al_2O_3	$Al(CH_3)_3$	H_2O	Groner, Nam
	$Al(CH_3)_3$	**O_3**	Kim, **this work**
	$Al(CH_3)_3$	**O_2 plasma**	Kessels, Niskanen, Tang, **this work**
	$[Al(CH_3)_2(O^iPr)]_2$	O_2 plasma	Potts
B_2O_3	BBr_3	H_2O	Putkonen
SiO_2	**$Si(OEt)_4$**	**$H_2O + NH_3$ cat.**	**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**

Me = methyl, Et = ethyl, ^{i}Pr = isopropyl, ^{t}Bu = *tert*-butyl

For full reference list, see
S. E. Potts *et al.*, ECS Trans., **50**, xx (2012).

Precursors for RT-ALD

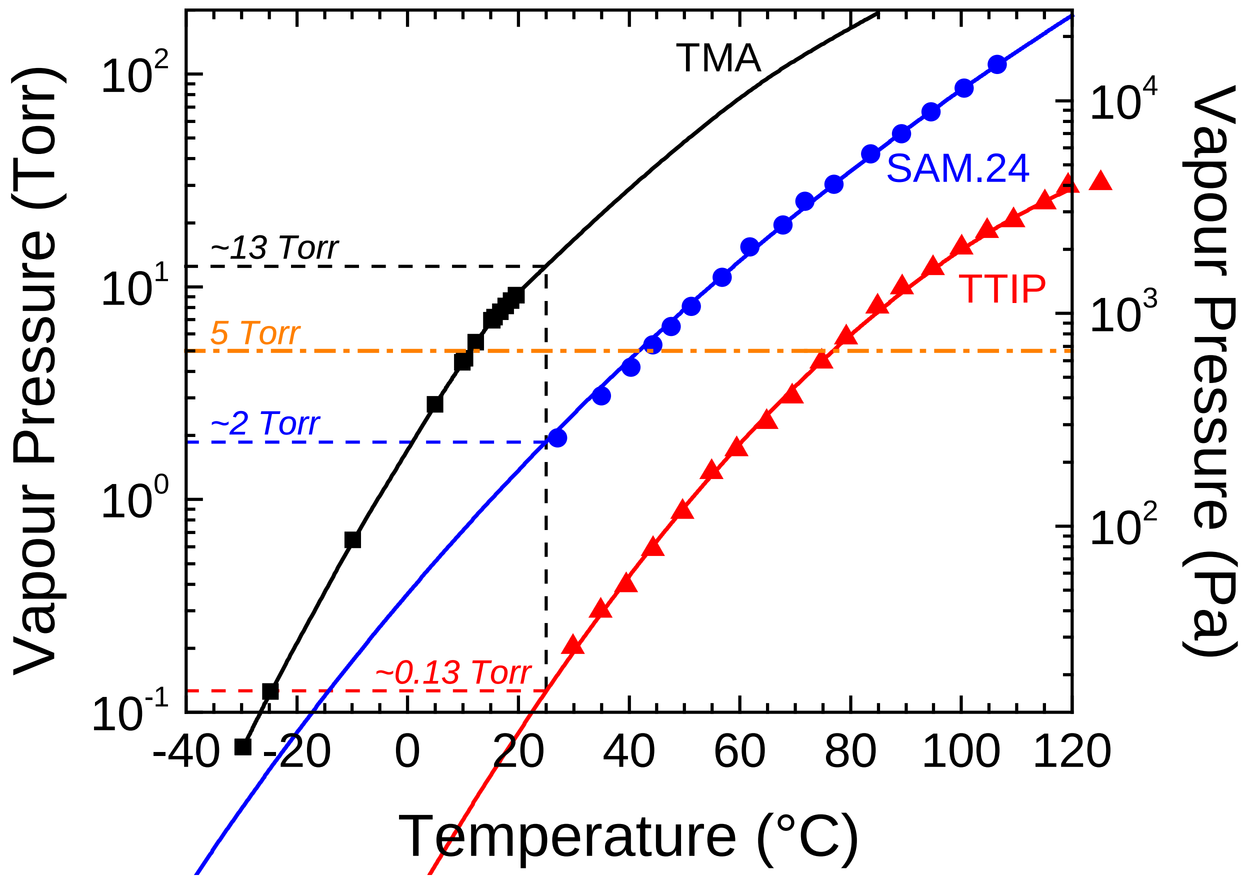
- O_2 plasma and ozone

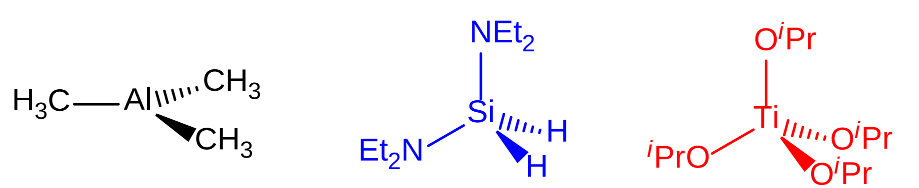
Property	TMA Al_2O_3	SAM.24 (BDEAS) SiO_2	TTIP TiO_2
Structural Formula	 AkzoNobel	 AIR LIQUIDE	 SIGMA-ALDRICH
Melting Point	15 °C	<-10 °C	14 °C
Boiling Point	125 °C	188 °C	232 °C
Vapour Pressure (25 °C)	~13 Torr	~2 Torr	~0.13 Torr

- Oxford Instruments FlexAL^{TM} reactor
- Substrate: Si wafer with native oxide
- Thickness by spectroscopic ellipsometry (SE)

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.

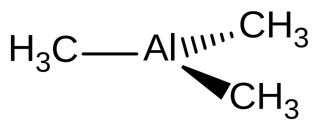




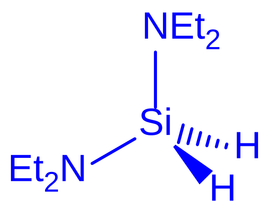
TMA: M. Fulem *et. al.*, *J. Cryst. Growth*, **248**, 99 (2003).
SAM.24: Air Liquide, France.
TTIP: K. L. Siefering and G. L. Griffin, *J. Electrochem. Soc.*, **137**, 1206 (1990).

Room-Temperature ALD Growth

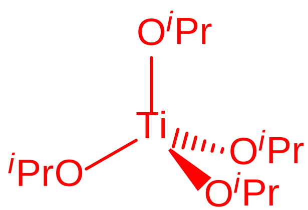
TMA

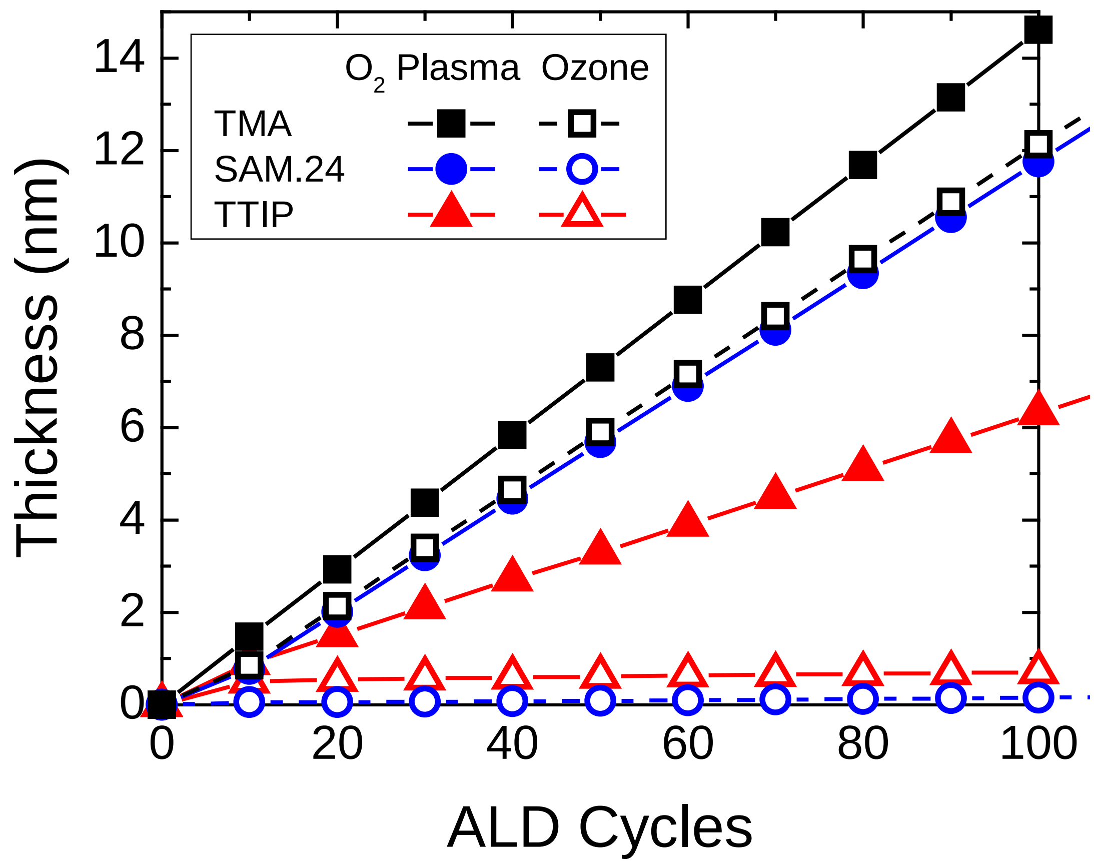


SAM.24



TTIP

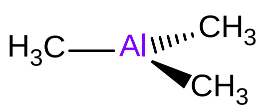




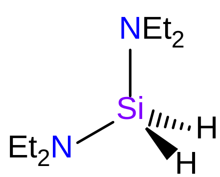
- Linear growth at room temperature.
- Suggests neither a significant CVD component nor condensation.

Room-Temperature ALD Saturation

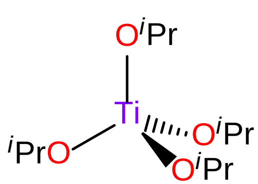
Al_2O_3

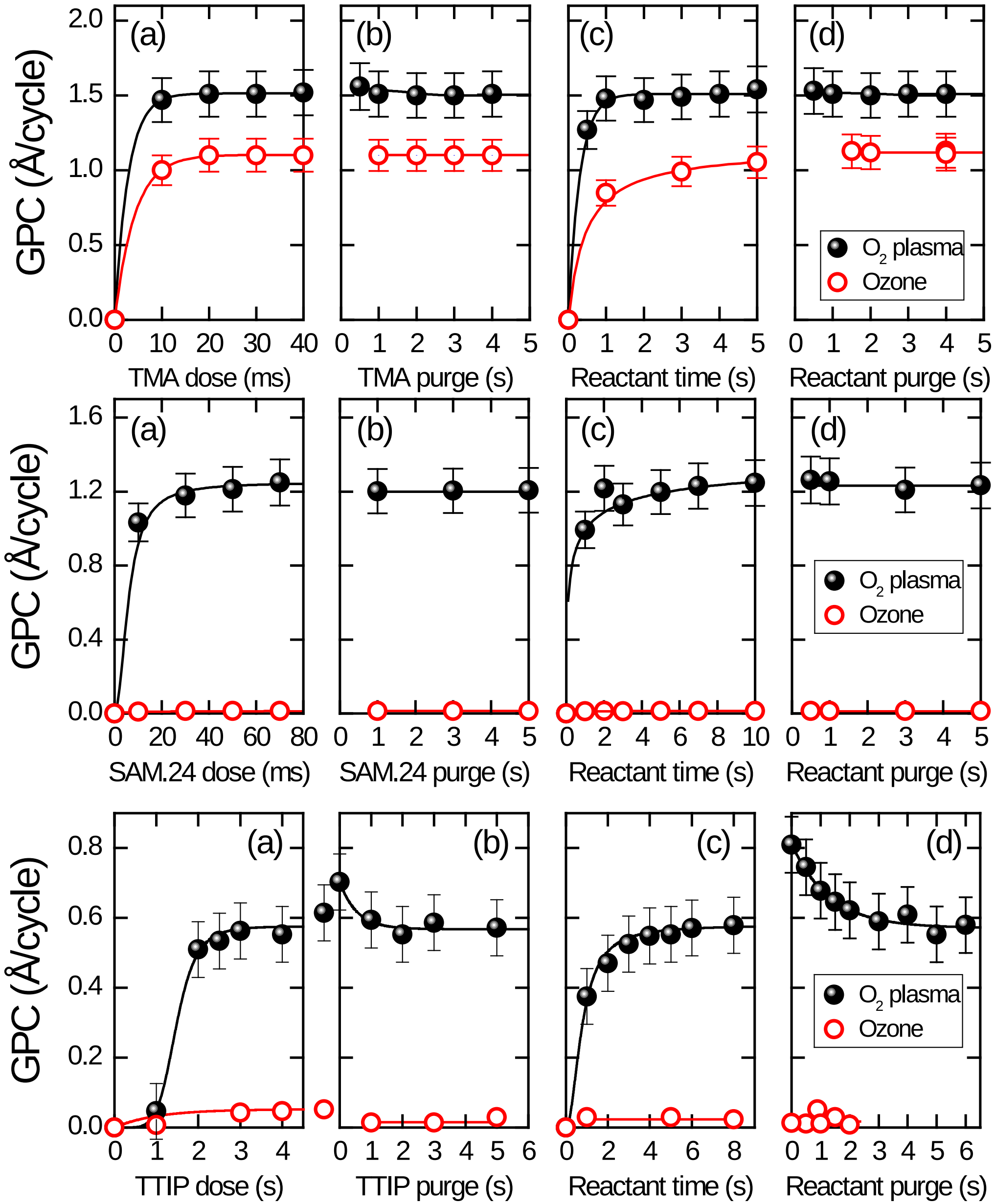


SiO_2



TiO_2





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

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

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

Purge Times

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

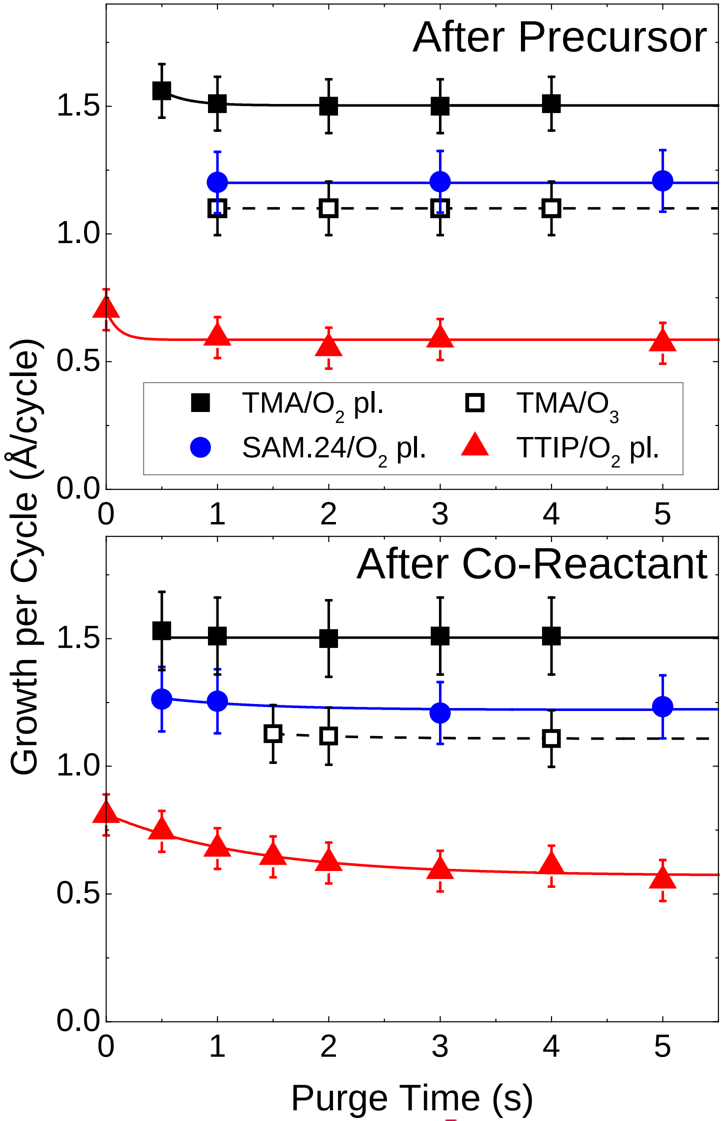
- **Water condenses easily, purging an issue.**

  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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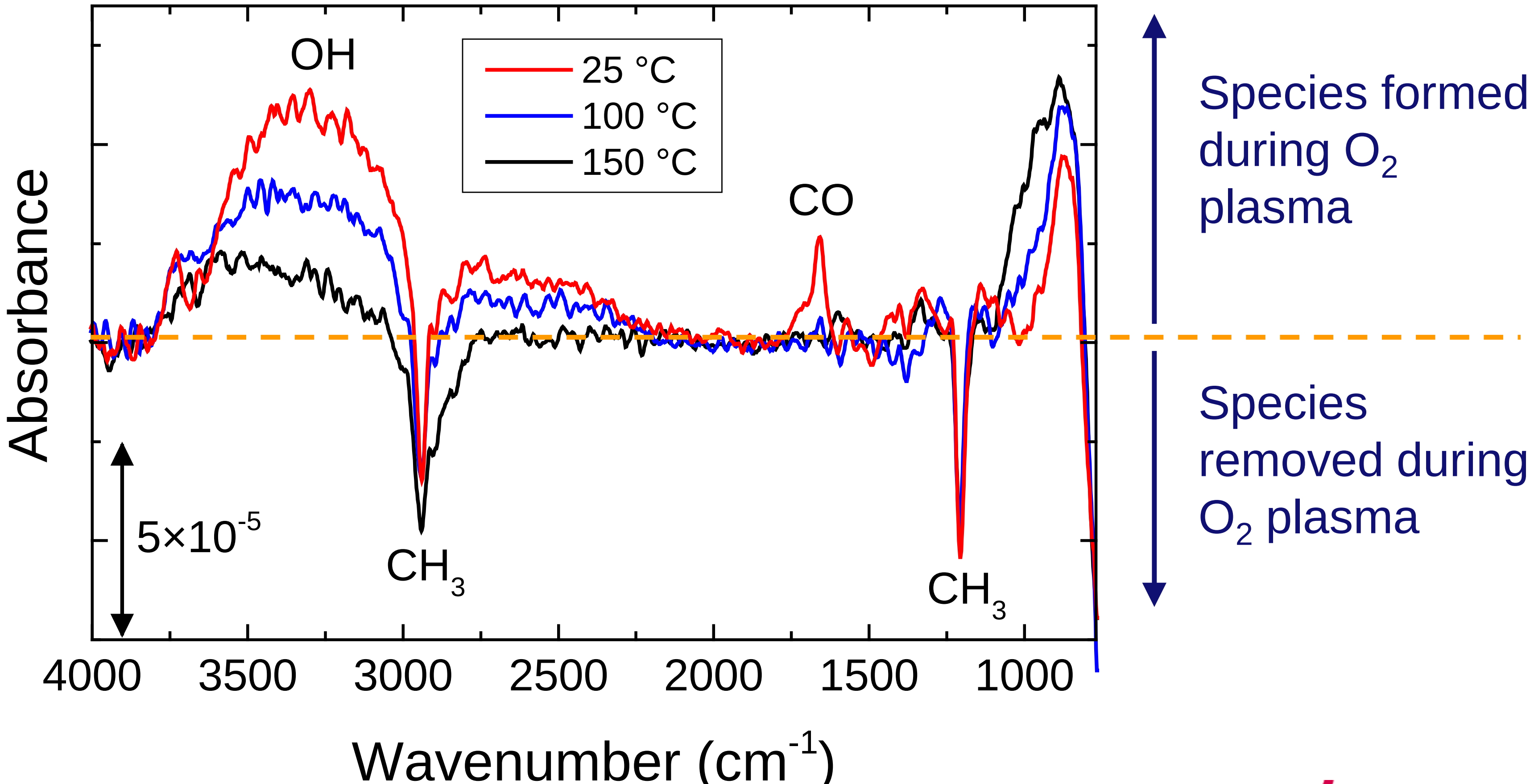
Surface OH During Plasma-Enhanced ALD

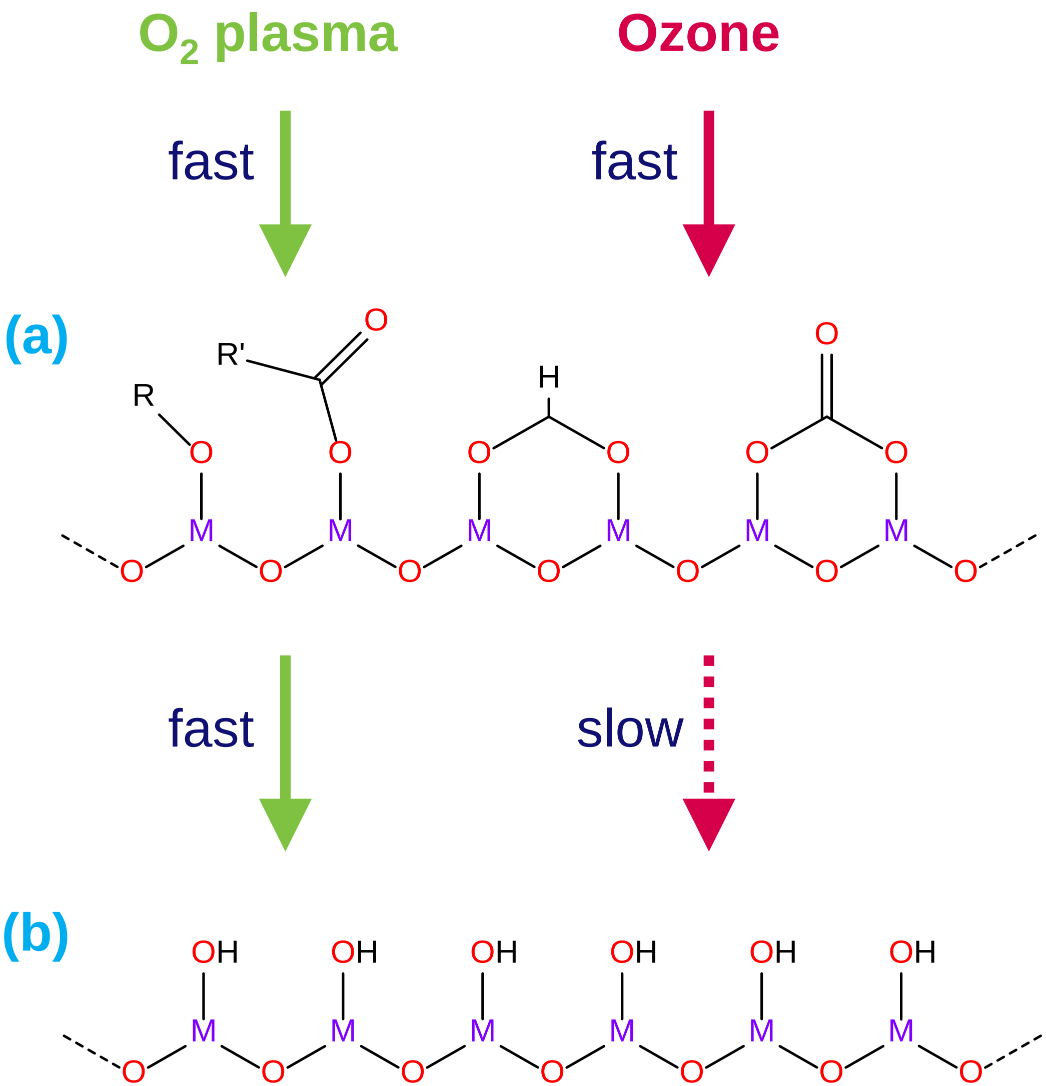
TMA
+
2 s O_2 plasma

- 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
After the Co-Reactant Pulse



(a) Carbonaceous Species

- More transient in O_2 plasma.
- Reactive with low-bond-energy ligands
  - e.g. Al–CH_3.
- No or negligible reactivity with higher-bond-energy ligands
  - e.g. Si–NEt_2, Si–H, Ti–OR.

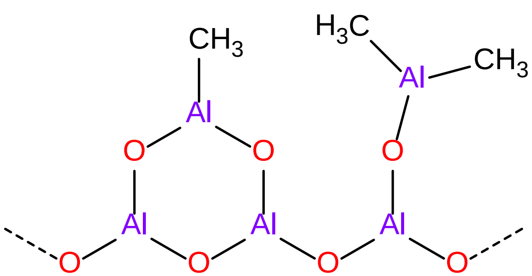
(b) Hydroxyls

- High reactivity towards all incoming precursor ligands.

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

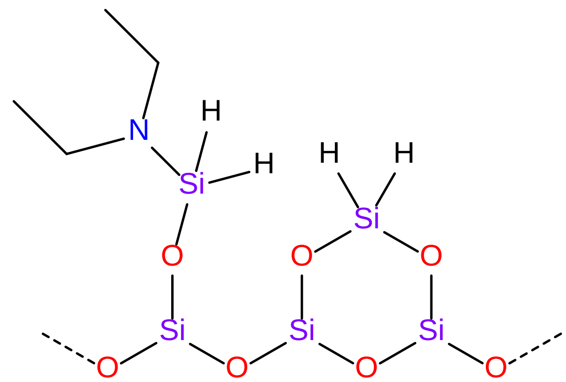
Surface Groups during RT-ALD
After the Metal Precursor Pulse

TMA, Al$(CH_3)_3$



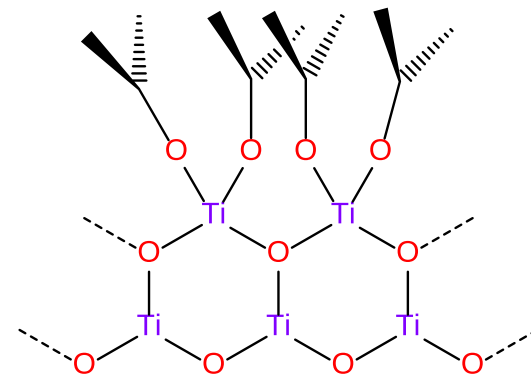
- Highly reactive Al–C bonds.
- Easily removed by O_2 plasma and ozone.

SAM.24, $SiH_2(NEt_2)_2$



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

TTIP, Ti$(O^iPr)_4$

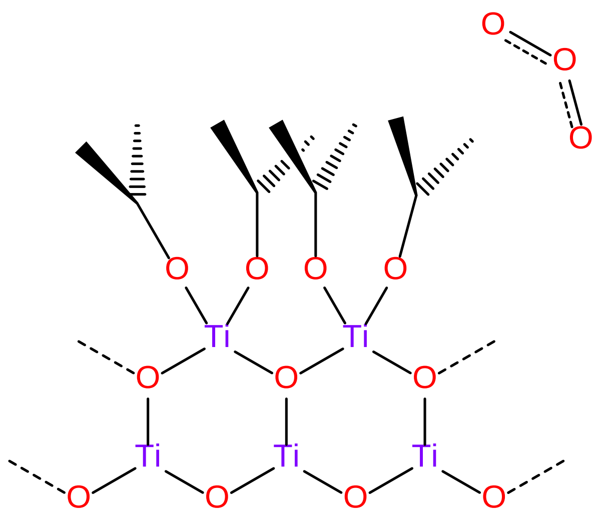


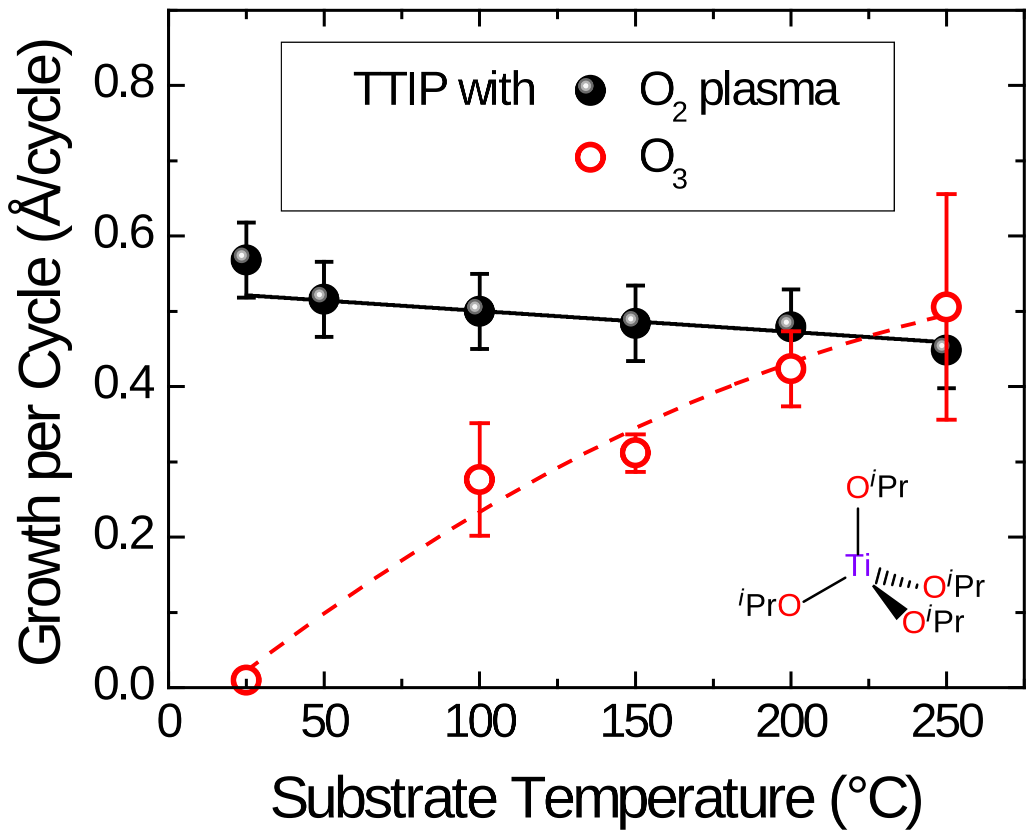
- Ti–O bond already relatively strong.
- Easily removed by O_2 plasma.
- No or negligible reactivity with ozone.

Surface Groups during RT-ALD
TTIP + Ozone

TTIP with Ozone

- ALD process has a thermal activation component.
- Increase in temperature
  → increase in growth.
- TTIP surface groups/ozone simply unreactive at RT.





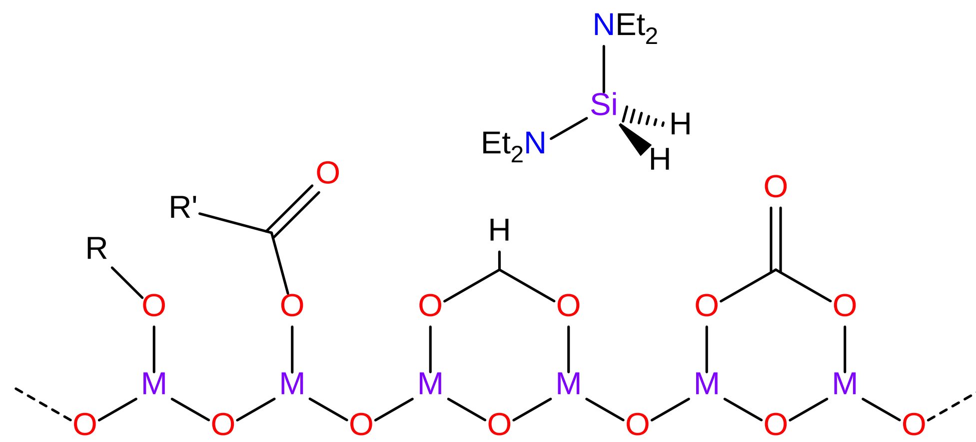
O_2 plasma: S. E. Potts *et al.*, *J. Electrochem.Soc.*, **157**, P66 (2010).
O_3: P. Willaims *et al.* at ALD Conference 2008, Bruges. This work (RT).

Surface Groups during RT-ALD
SAM.24 + Ozone

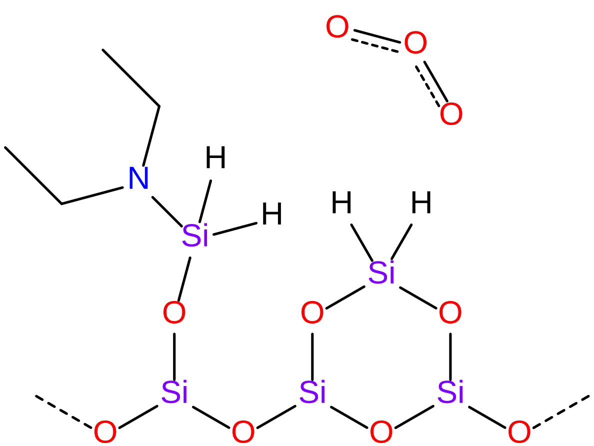
Two Explanations:

1. Thermal activation

- Low reactivity of Si–NEt_2 and Si–H with carbonaceous species at RT.



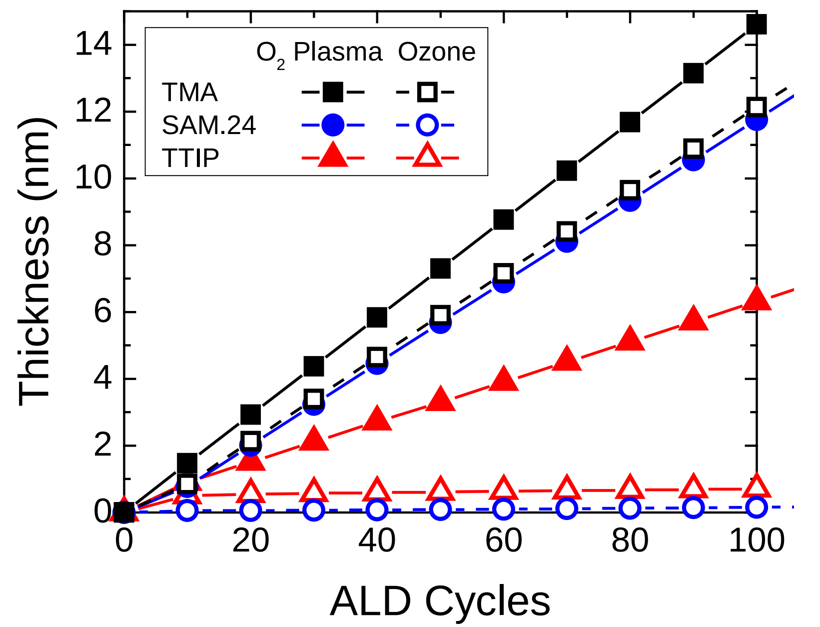
2. Low reactivity of Si–H at room temperature



- Reactivity with surface OH: Si–NR_2 >> Si–H.
  B. B. Burton *et al.*, *J. Phys. Chem. C*, **113**, 8249 (2009).
  G. Dingemans *et al.*, *J. Electrochem. Soc.*, **159**, H277 (2012).
- High (initial) surface [OH] → bifunctional binding.
  S. Haukka *et al.*, *Appl. Surf. Sci.*, **82/83**, 548 (1994).
  S. Haukka *et al.*, *Interface Sci.*, **5**, 119 (1997).
- Si–H remains, but is unreactive with ozone.
- Surface NEt_2 reacts and is present at higher temperatures.

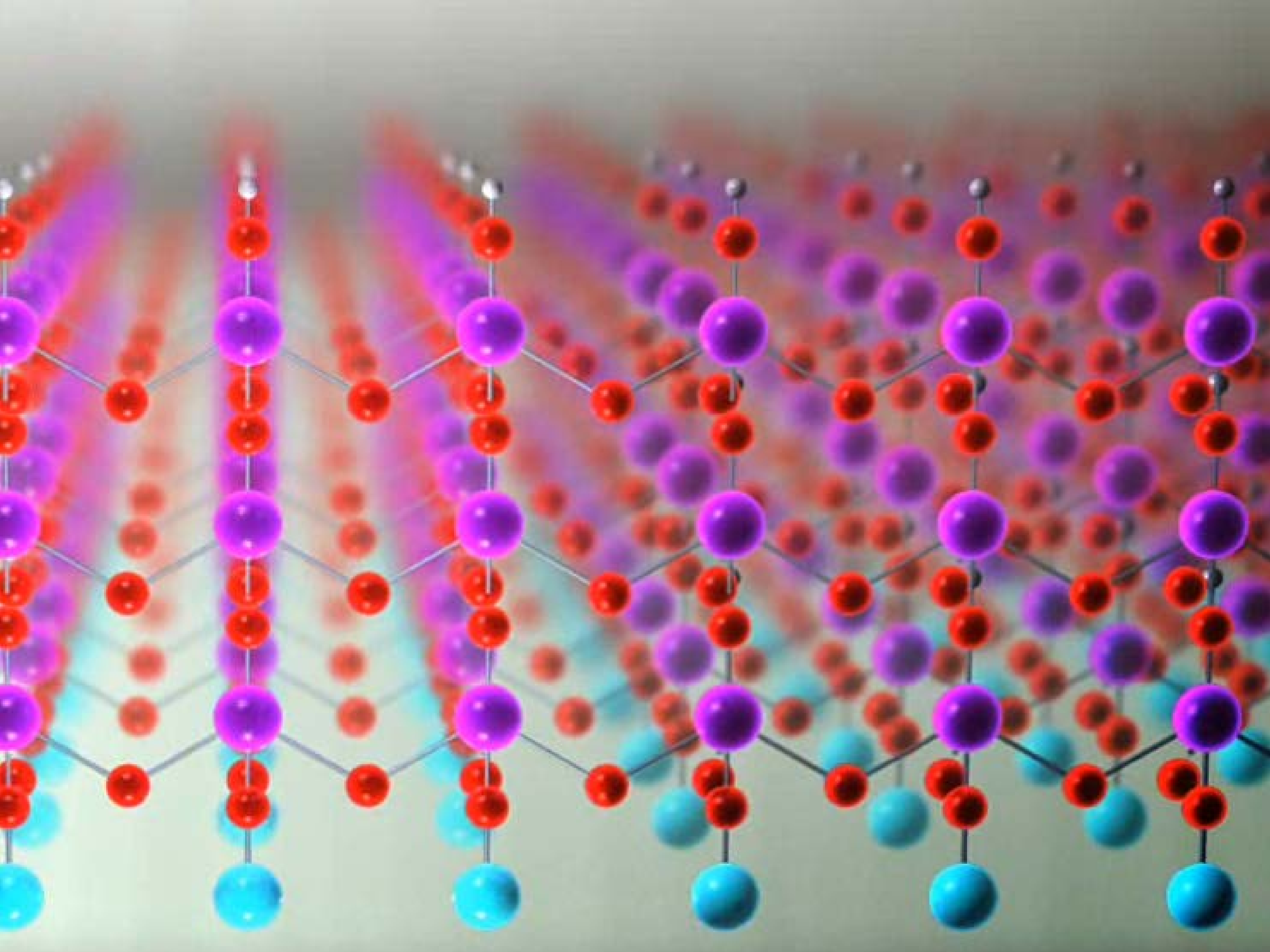
Summary/Conclusions

RT-ALD?	Al_2O_3 TMA	SiO_2 SAM.24	TiO_2 TTIP
O_2 plasma	✓	✓	✓
Ozone	✓	✗	✗



Requirements for RT-ALD

- Desirable: high vapour-pressure precursors (≥ 5 Torr at RT).
- Desirable: short purge times.
- Essential: reactivity with surface groups at room temperature.



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 °C	*1.5*	*< 1*	*2.5*	*3.1*	*3.4*
	Ozone	**RT**	**2.1**	**9.0**	**20.8**	**2.4**	**1.9**
		200 °C	*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 °C	*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 °C	*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!

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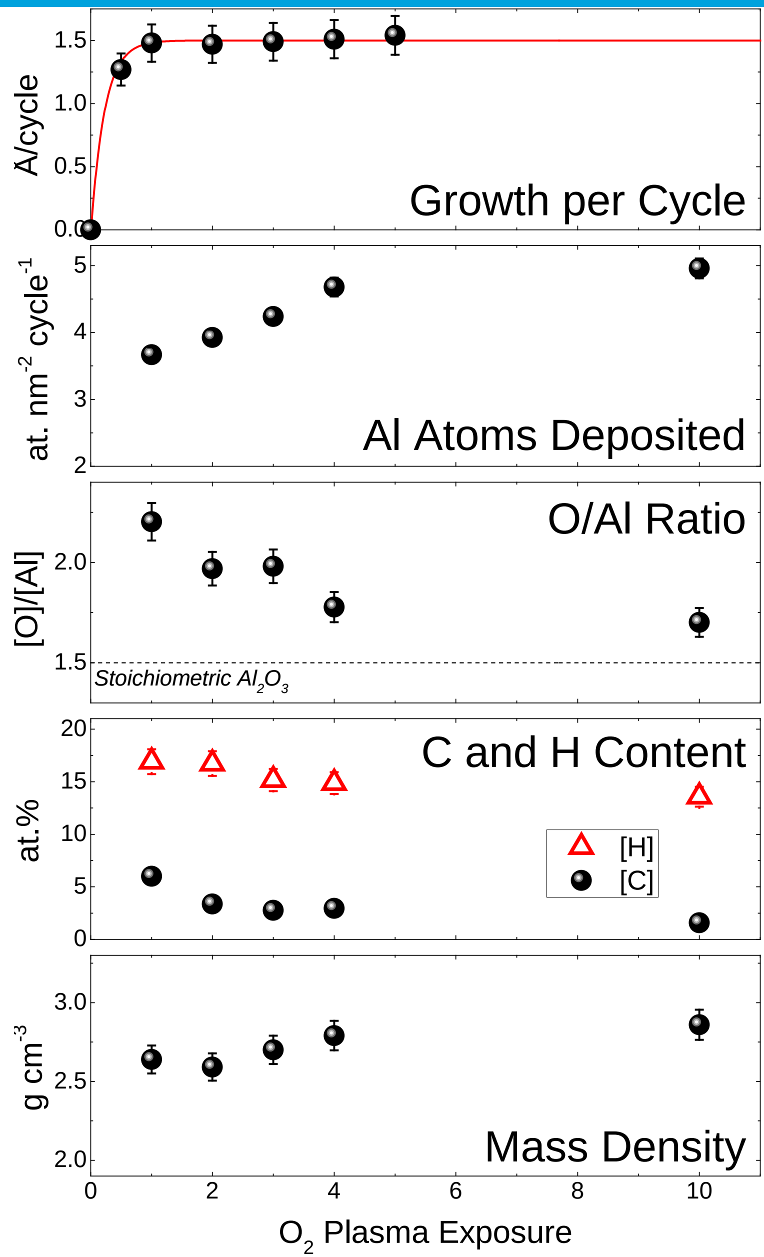
Plasma-Enhanced RT-ALD of Al_2O_3
Variation of Film Composition with Plasma Time



- **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).

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