Low-Temperature ALD
What's Limiting?

Stephen E. Potts

Outline

General ALD Considerations

- What is atomic layer deposition (ALD)?
- The ALD temperature window
- Growth rate: nm/cycle or atoms/(cycle nm^2)?
- Typical trends in film composition with deposition temperature

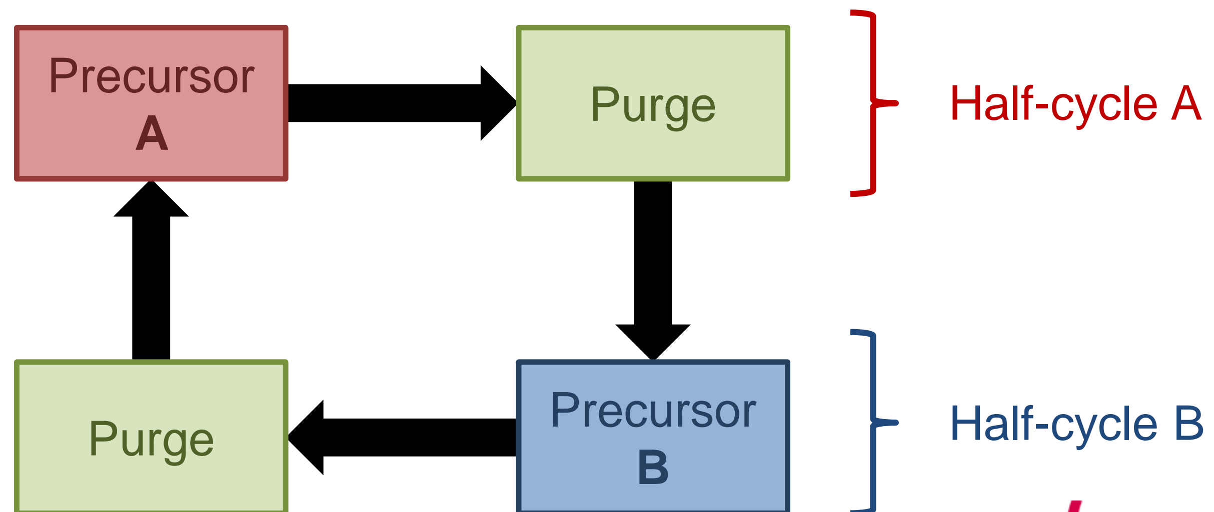
Factors Affecting Low-Temperature ALD

1. The metal precursor
2. The co-reactant
3. The purge times

Knoops *et al.*, *Atomic Layer Deposition* in *Handbook of Crystal Growth 2nd ed.*, Vol. 3B, T. Keuch (ed.), Elsevier (2015). pp. 1101-1134.

What is atomic layer deposition?

- A vapour-phase deposition technique involving two or more precursors
- A layer is built up in stages known as cycles
- Each half-cycle comprises a reaction between the precursor and the surface, followed by a purge
- These reactions are saturating and self-limiting



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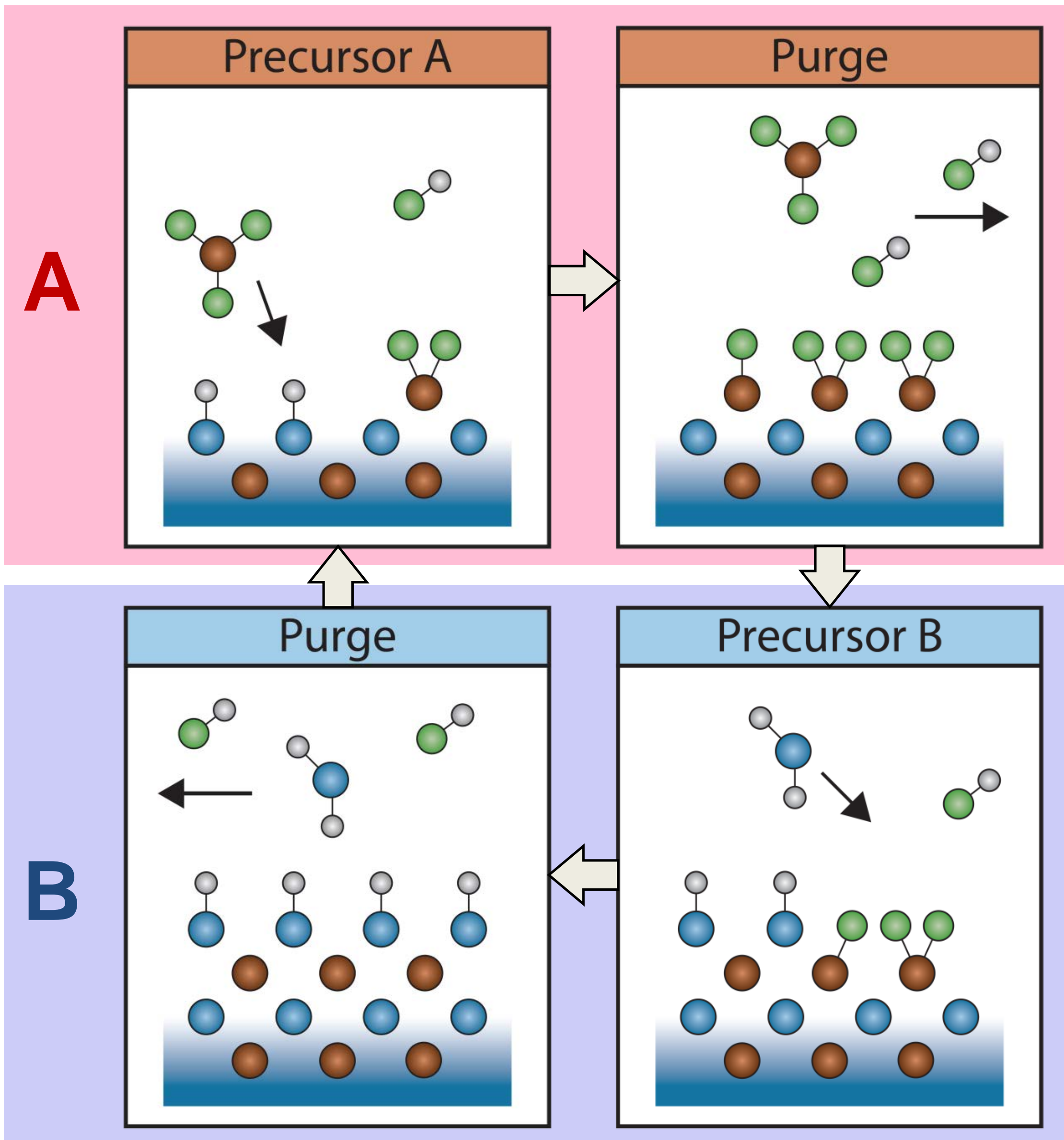
Atomic Layer Deposition (ALD)



- "Digital CVD", two steps A and B, which form a cycle.
- Saturated surface reactions.
- Self-limiting
- One (sub)-monolayer per cycle.

Atomic Layer Deposition (ALD)

A

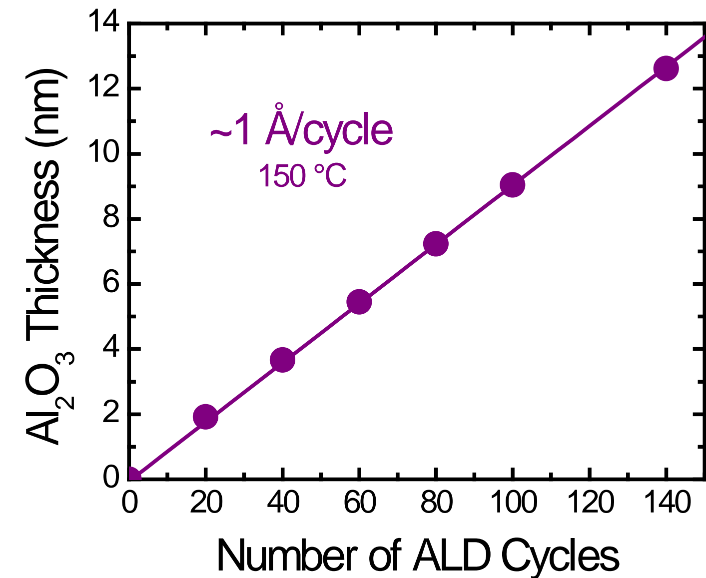
Precursor A

Purge

B

Purge

Precursor B



Film thickness is ruled by the number of cycles chosen:

for Al_2O_3 ~1 Å is obtained per cycle at 150 °C.

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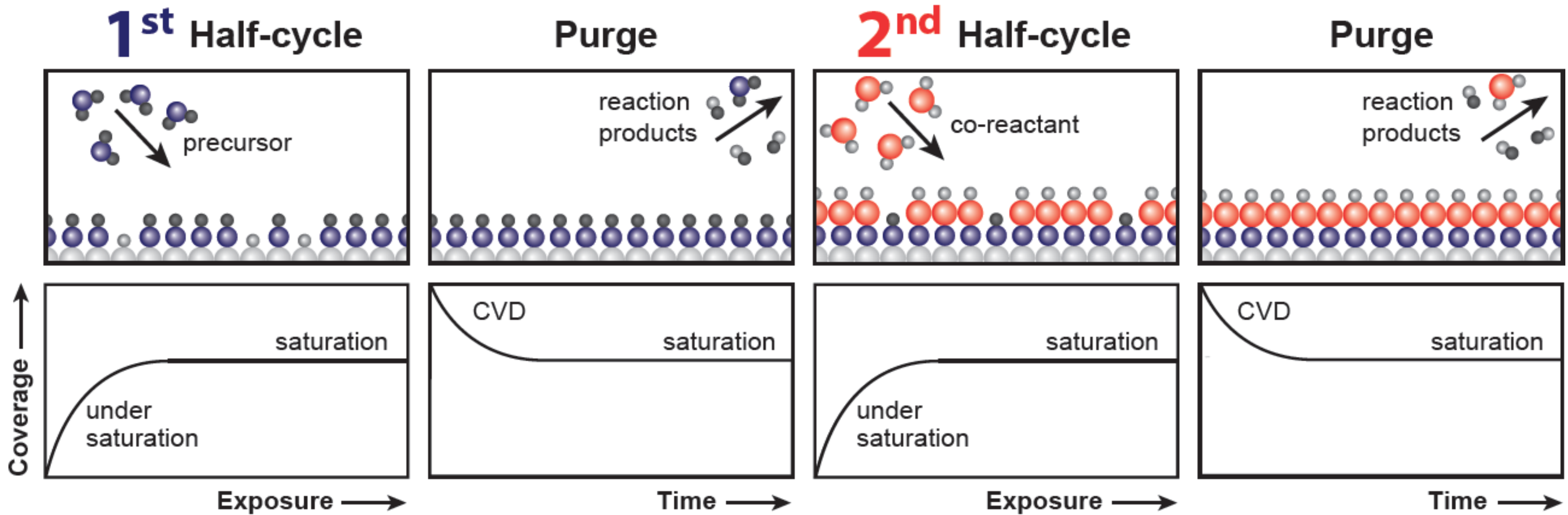
Atomic Layer Deposition (ALD)



- Each step of the half-cycle should be self-limiting

- Typically, less than a monolayer is deposited
  - Size of metal precursor
  - Availability of reactive surface sites

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Knoops *et al.*, *Atomic Layer Deposition* in *Handbook of Crystal Growth 2nd ed.*, Vol. 3B, T. Keuch (ed.), Elsevier (2015). pp. 1101-1134.

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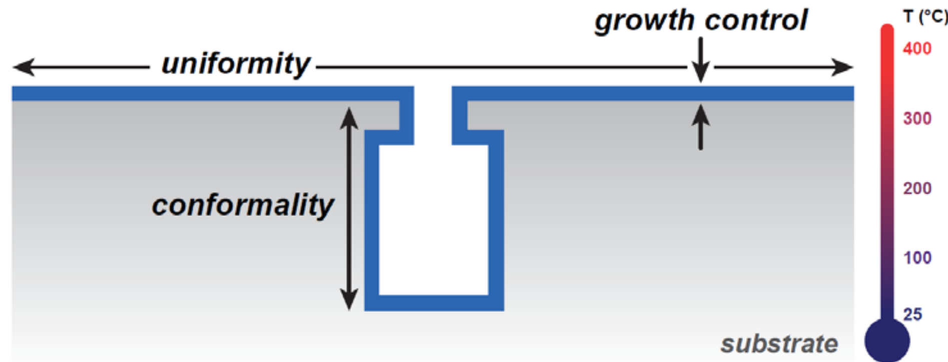
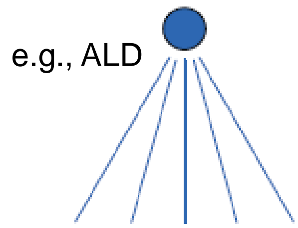
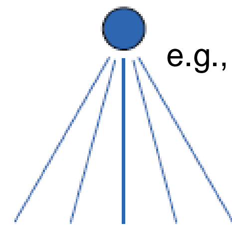
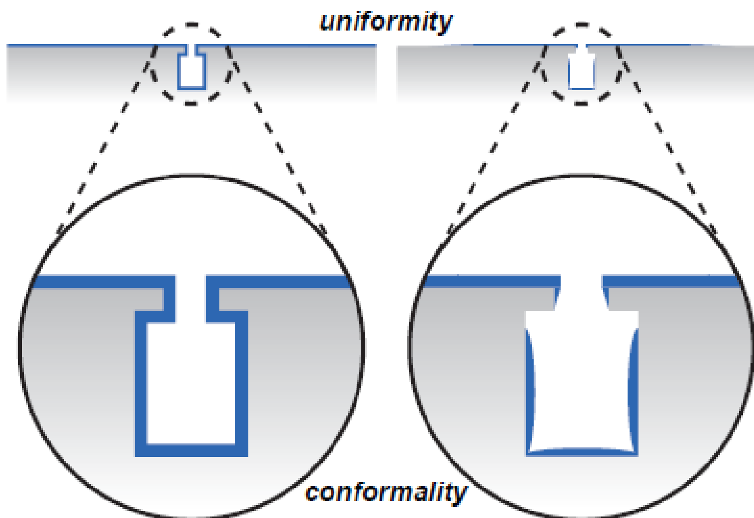
Attributes of ALD









ALD is surface-controlled

- "Digital" growth control (dependent on cycles, not time)
- Uniform across (large) substrates
- Conformal across 3D substrate features
- Low defect density
- Lower temperatures possible (not decomposition-dependent)

Knoops *et al.*, *Atomic Layer Deposition* in *Handbook of Crystal Growth 2nd ed.*, Vol. 3B, T. Keuch (ed.), Elsevier (2015). pp. 1101-1134.

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Factors Affecting Low-Temperature ALD

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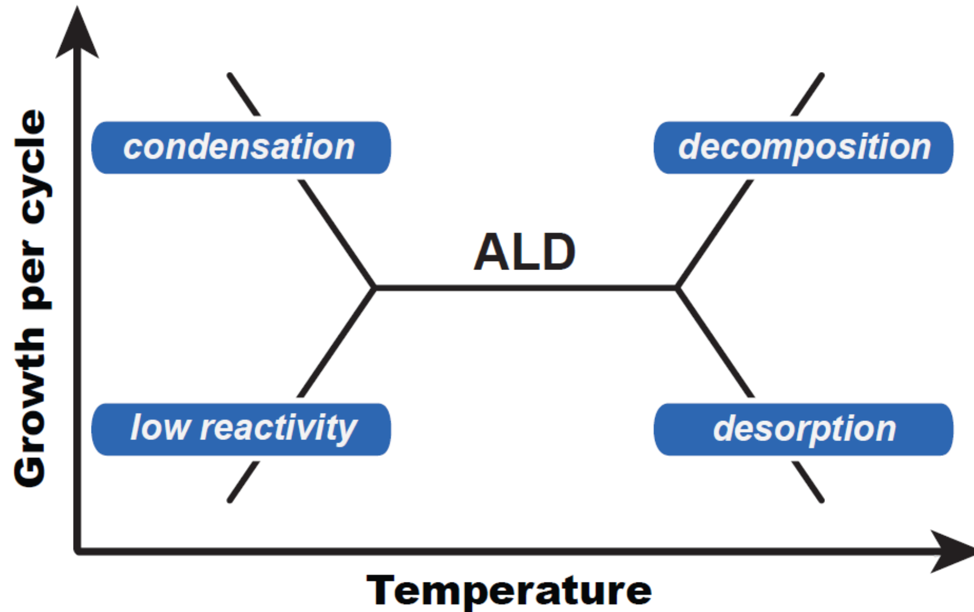
The ALD Temperature Window



- No growth per cycle (GPC) variation, supposedly the only true ALD.
- Typical temperature range:

~150-350 °C

Assumption: a sub-monolayer of material is deposited

Assumption: saturating behaviour is lost outside the temperature window.

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T. Suntola, *Mater. Sci. Rep.*, **4**, 261 (1989).
Figure: Knoops *et al.*, *Atomic Layer Deposition* in *Handbook of Crystal Growth 2nd ed.*, Vol. 3B, T. Keuch (ed.), Elsevier (2015). pp. 1101-1134.

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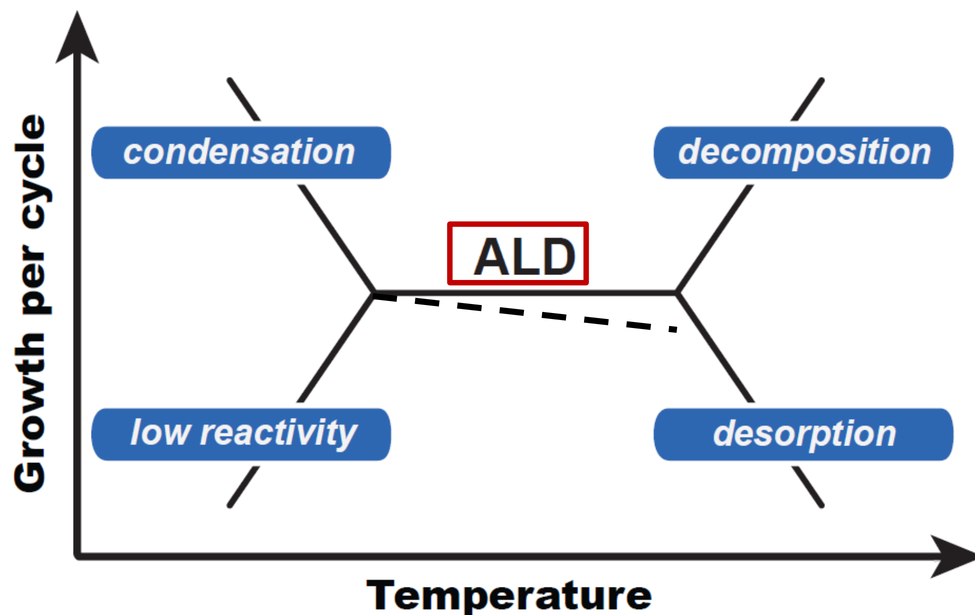
The ALD Temperature Window



(a) Typical “expected” ALD growth regime – no GPC variation. Supposedly the only true ALD.

(b) Typical growth regime for metal oxides. Loss of surface groups with T leads to a drop in GPC.

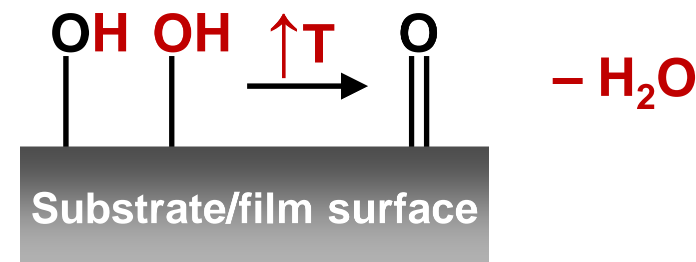


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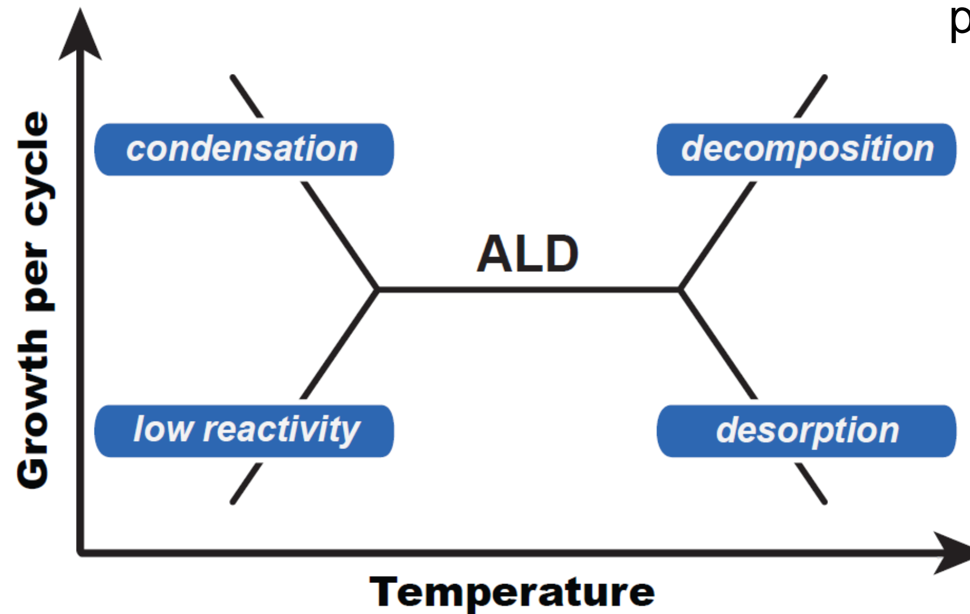
Figure: Knoops *et al.*, *Atomic Layer Deposition* in *Handbook of Crystal Growth 2nd ed.*, Vol. 3B, T. Keuch (ed.), Elsevier (2015). pp. 1101-1134.

The ALD Temperature Window

Outside the temperature window: loss of saturating ALD behaviour

Precursor temp. is higher than substrate temp.

Metal precursors are prone to decomposition (typically 200-400 °C)



Insufficient thermal energy for reaction

Film or precursor desorption, etching

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T. Suntola, *Mater. Sci. Rep.*, **4**, 261 (1989).
Figure: Knoops *et al.*, *Atomic Layer Deposition* in *Handbook of Crystal Growth 2nd ed.*, Vol. 3B, T. Keuch (ed.), Elsevier (2015). pp. 1101-1134.

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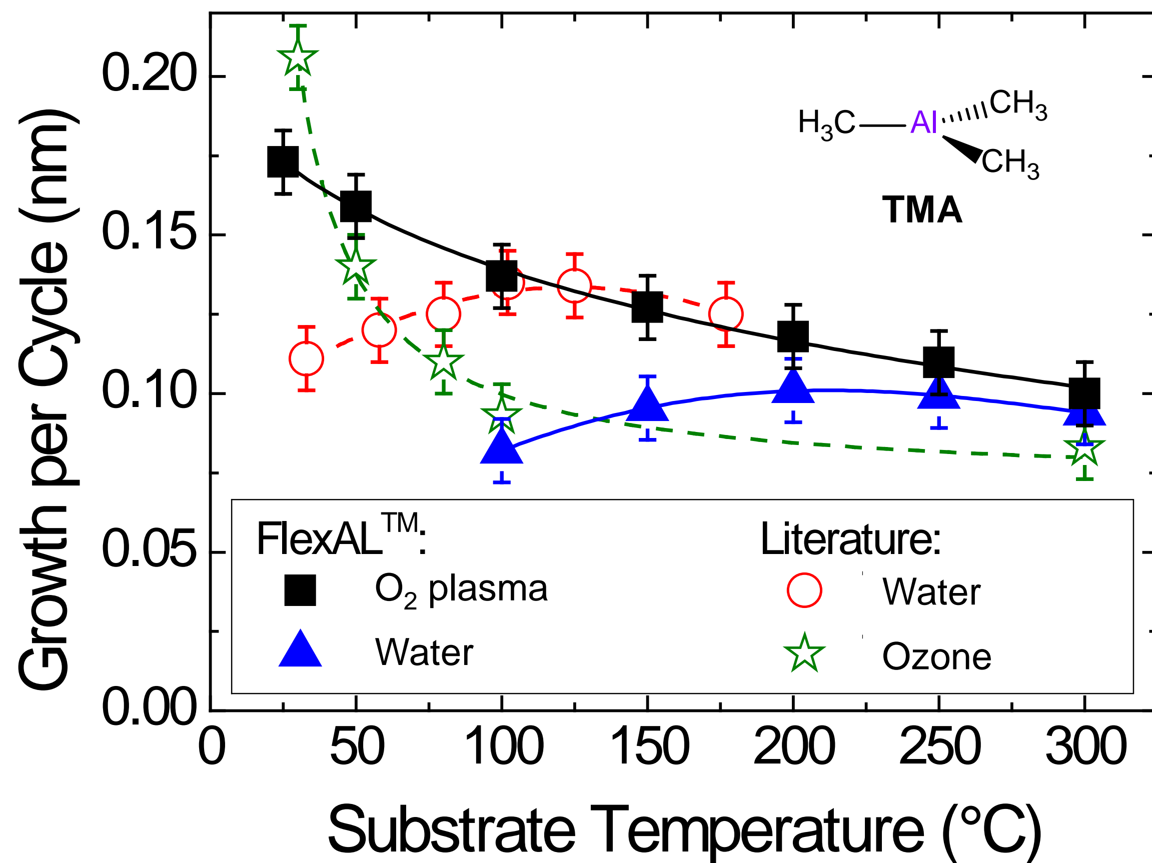
Al_2O_3: Growth per Cycle



Higher temperatures

- Reduction in GPC → dehydroxylation.

Lower temperatures

- Water processes: lower GPC
- Ozone and plasma processes: many extra surface groups at T_s < 100 °C.

Where is the temperature window?

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

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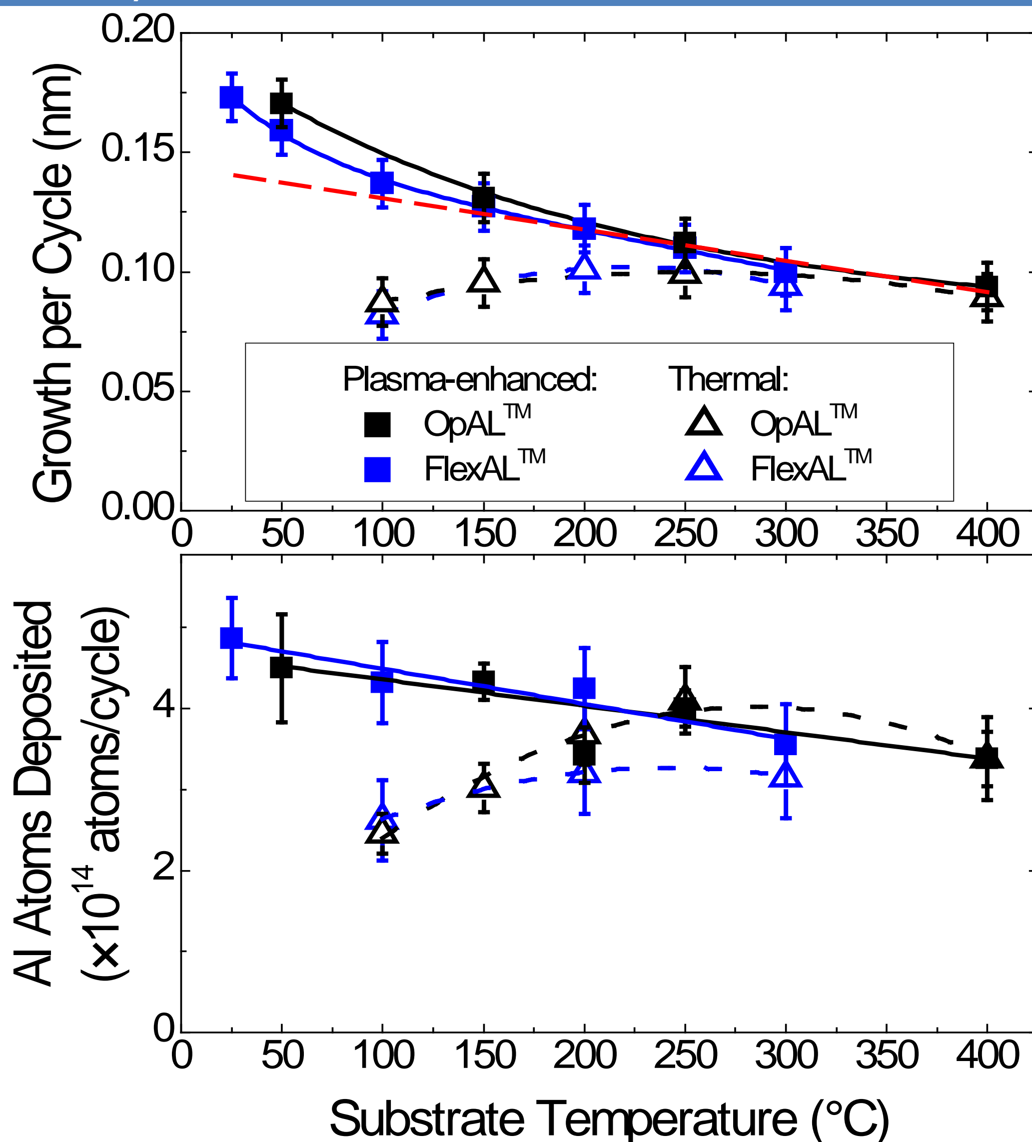
Growth per Cycle
nm/cycle vs. atoms/(cycle.nm^2)

- 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.



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

Outline

General ALD Considerations

- What is atomic layer deposition (ALD)?
- The ALD temperature window
- Growth rate: nm/cycle or atoms/(cycle nm^2)?
- Typical trends in film composition with deposition temperature
  - Al_2O_3
  - TiO_2

Factors Affecting Low-Temperature ALD

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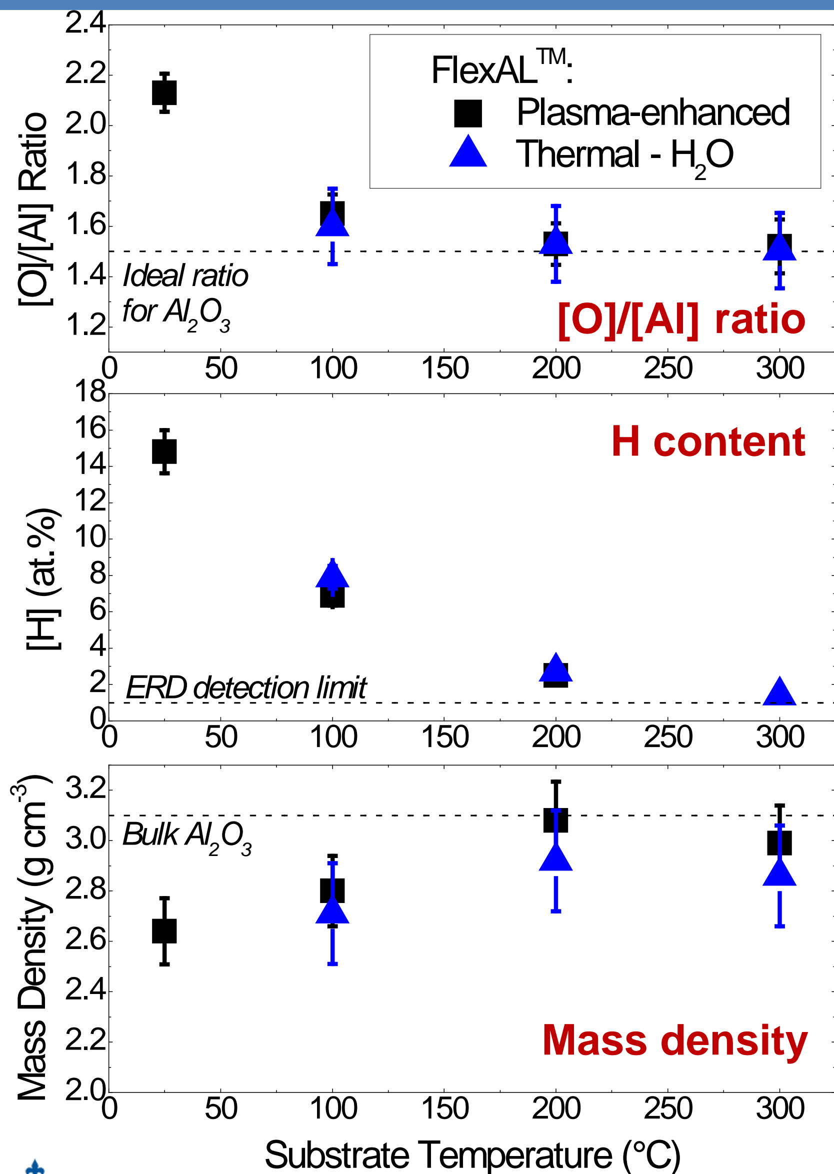
3. The purge times

Al_2O_3: Film Composition with Temperature



- [O] and [H] increase with decreasing temperature
- –OH is prominent at lower temperatures.
- Leads to lower mass density at lower deposition temperatures.
- Lower mass density can lead to an increase in GPC

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

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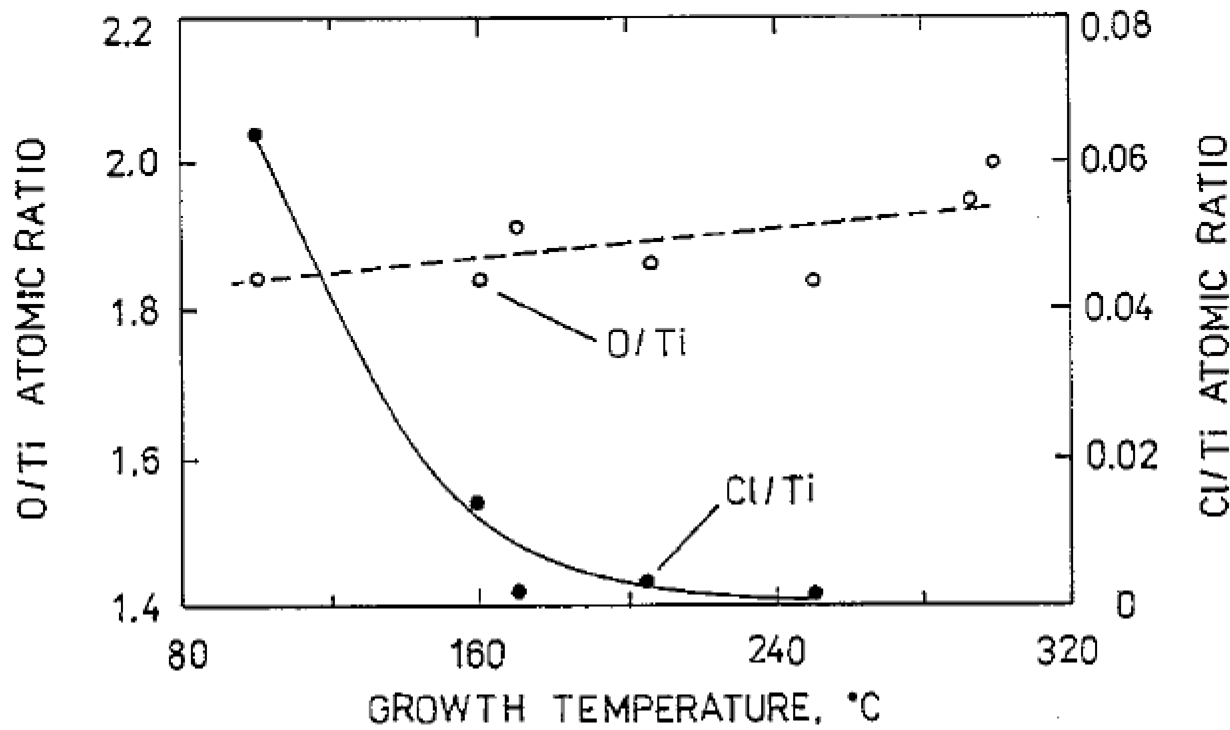
TiO_2: Film Composition with Temperature

$TiCl_4$ and H_2O precursors

An increase in chlorine incorporated at lower deposition temperatures.



J. Aarik *et al.*, *Thin Solid Films*, **305**, 270 (1997).

ALD Films at Lower Temperatures

- Energy-enhanced ALD (e.g., plasma or ozone ALD)
  - An increase in GPC
- Thermal ALD (more on Al_2O_3 later)
  - A decrease in GPC

- Increased inclusion of ligand material from precursors or elements from co-reactants
  - hydrogen, carbon, chlorine, excess oxygen, etc.
  - This is a very general observation – the extent of inclusion of additional atoms is process-dependent

- Lower mass density
  - can lead to a perceived increase in GPC
  - should not change the atoms deposited per cycle

Outline

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What is low-temperature ALD?

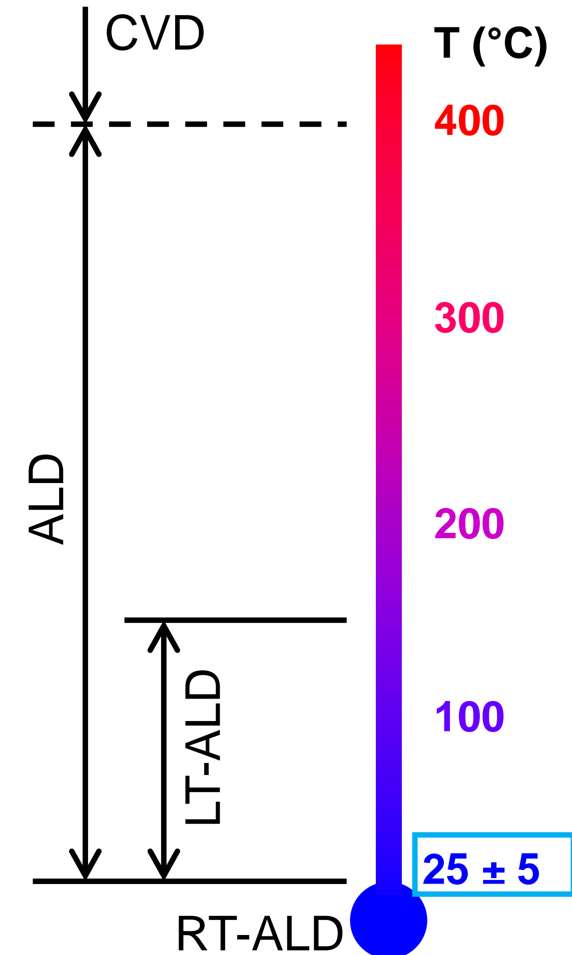
Reminder:

Typical ALD range = ~150-350 °C

Upper limit: (metal) precursor decomposition
film/precursor evaporation

Lower limit: (metal) precursor condensation
lack of thermal energy

Low-temperature ALD: < 150 °C



What can be done to extend the temperature window to lower temperatures?

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

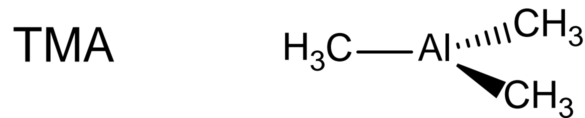
Room-Temperature ALD in the Literature

Material	Precursor	Co-Reactant	Reference
Al_2O_3	$Al(CH_3)_3$	H_2O	Groner, Nam
	$Al(CH_3)_3$	**O_3**	Kim, **Potts**
	$Al(CH_3)_3$	**O_2 plasma**	Kessels, Niskanen, Tang, **Potts**
	$[Al(CH_3)_2(O^iPr)]_2$	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 catalyst**	**Ferguson**
	$Si(NCO)_4$	**H_2O**	**Gasser**
	$SiH_2(NEt_2)_2$	**O_2 plasma**	**Potts**
TiO_2	**$Ti(O^iPr)_4$**	**O_2 plasma**	Potts
	$Ti(NMe_2)_4$	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**

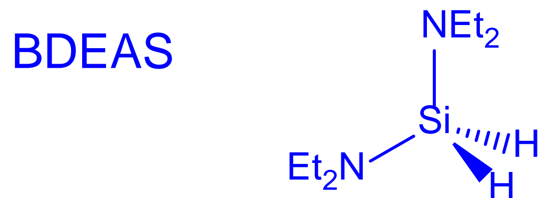
For full reference list, see
S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).

Room-Temperature ALD Growth of Metal Oxides

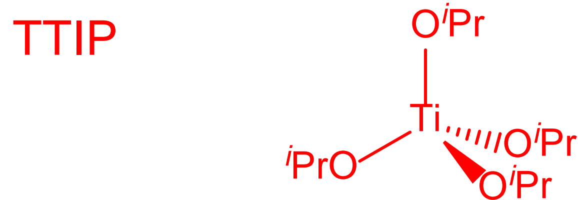
TMA

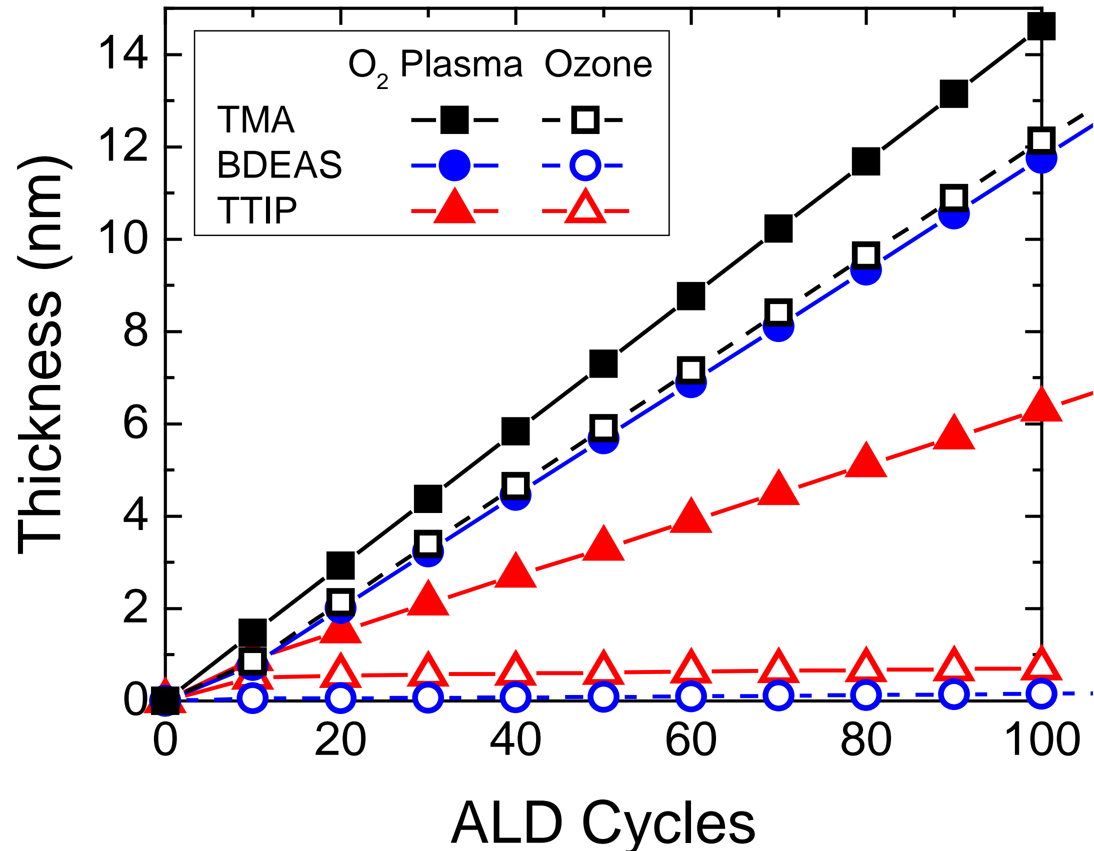


BDEAS



TTIP

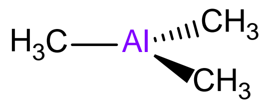


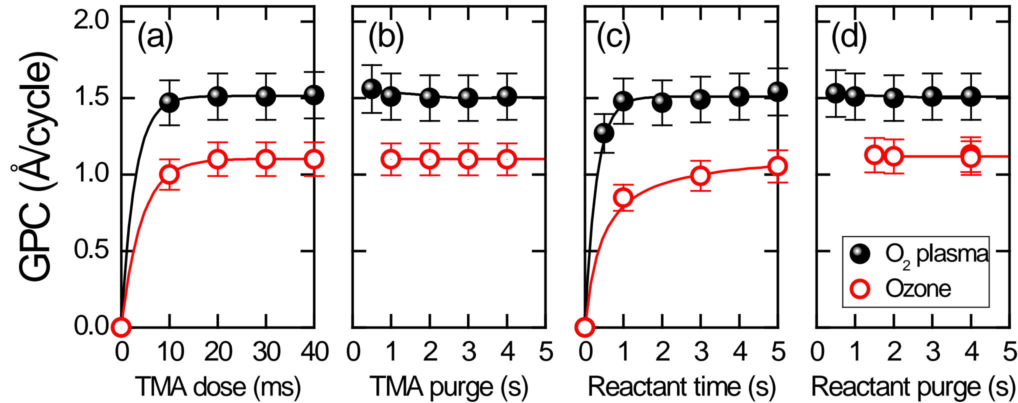


- Linear growth at room temperature.
- Suggests neither a significant CVD component nor condensation.

Room-Temperature ALD Saturation

Al_2O_3

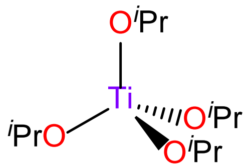


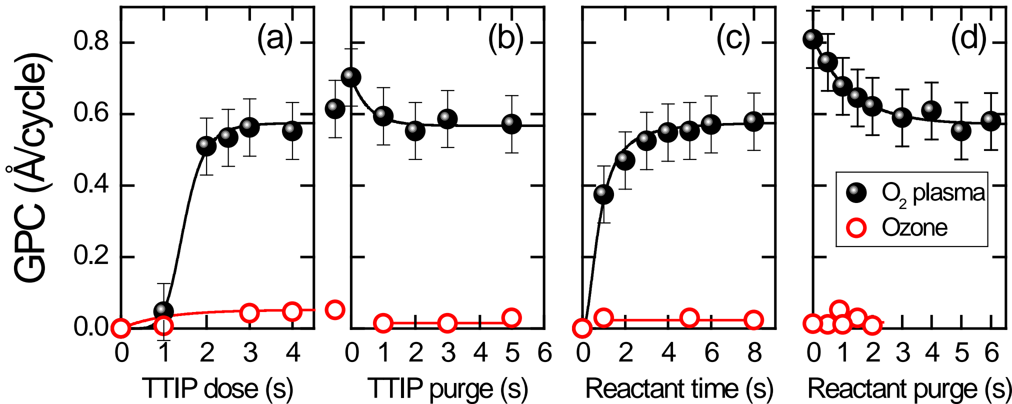


O_2 plasma ✓

Ozone ✓

TiO_2

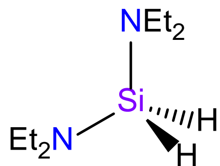


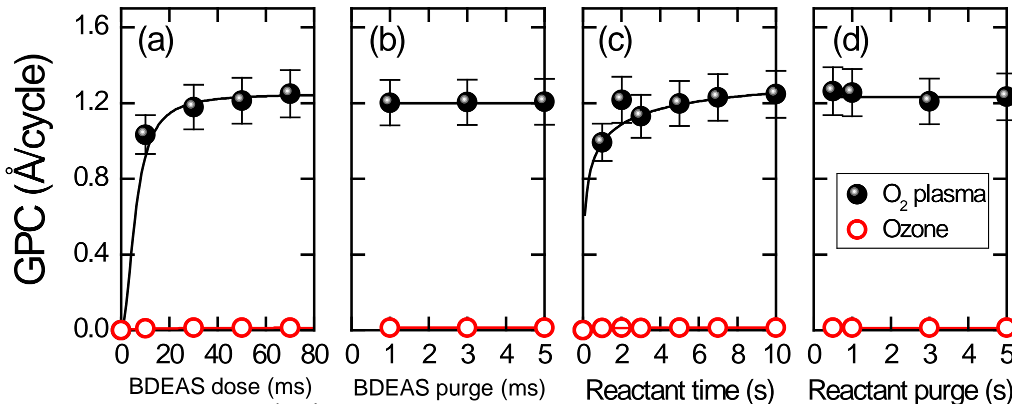


O_2 plasma ✓

Ozone ×

SiO_2





O_2 plasma ✓

Ozone ×

Outline

Factors Affecting Low-Temperature ALD

1. The metal precursor
2. The co-reactant
3. The purge times

1. The Metal Precursor: Requirements

Metal precursors are metalorganic coordination complexes.

Essential! Precursors should:

- React with surface groups (at low temperatures)
- Leave surface groups that react with co-reactant(s)

The above reactions should be self-limiting, *i.e.*, they saturate.

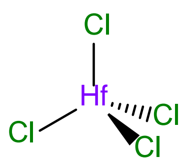
Desirable. A precursor should ideally have:

- A high-vapour pressure, ideally $\sim 5 < p_{vap} < 50$ Torr at 25 °C
- A long shelf-life
- An easy synthesis
- Low toxicity

1. The Metal Precursor

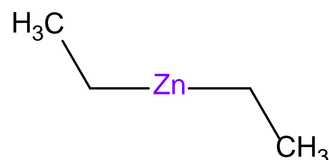
Examples of ALD precursors

Halide



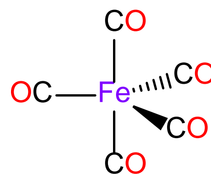
Tetrachlorohafnium(IV)

Alkyl



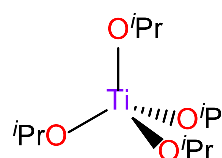
Diethylzinc
DEZ

Carbonyl



Pentacarbonyliron(0)

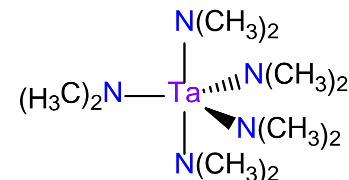
Alkoxide



Tetraisopropoxytitanium(IV)
TTIP

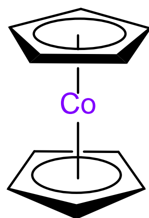
^{i}Pr = $CH(CH_3)_2$

Alkylamide



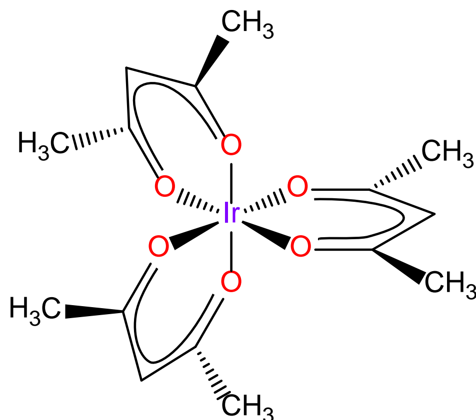
Pentakis(dimethylamino)tantalum(V)
PDMAT

Cyclopentadienyl



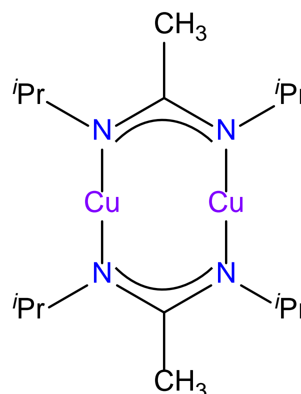
Bis(cyclopentadienyl)cobalt(II)
Cobaltocene

β-Diketonate



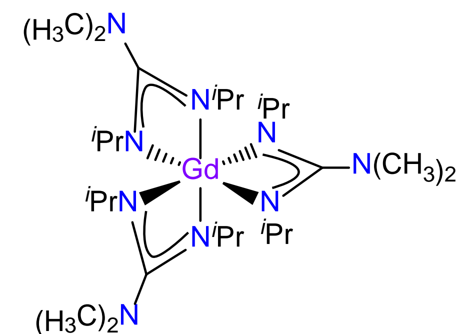
*Tris*acetylacetonatoiridium(III)

Amidinate



Bis(*N*,*N'*-diisopropylacetamidinato)dicopper(I)

Guanidinate



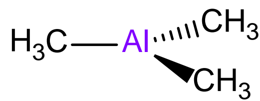
Tris(1,3-diisopropyl-2-dimethylaminoguanidinato)gadolinium(III)

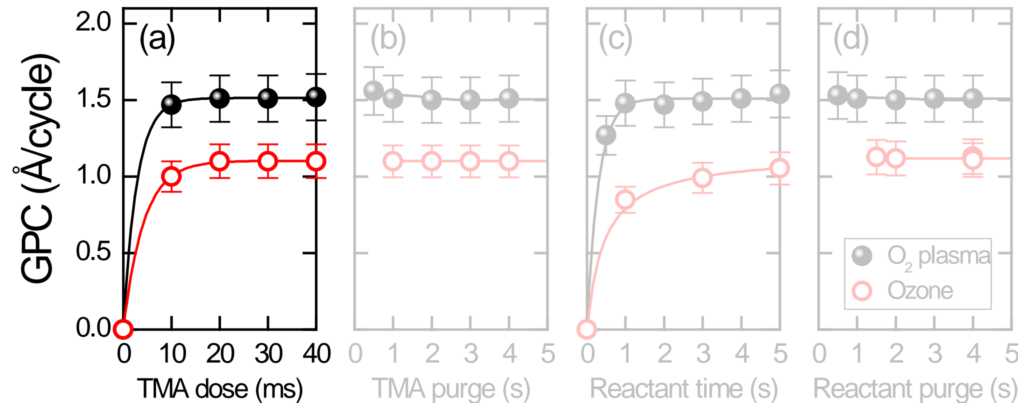
Knoops *et al.*, *Atomic Layer Deposition* in *Handbook of Crystal Growth 2nd ed.*, Vol. 3B, T. Keuch (ed.), Elsevier (2015). pp. 1101-1134.

Room-Temperature ALD Saturation

Metal Precursor

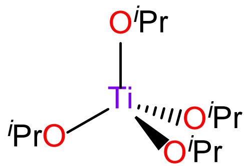
Al_2O_3

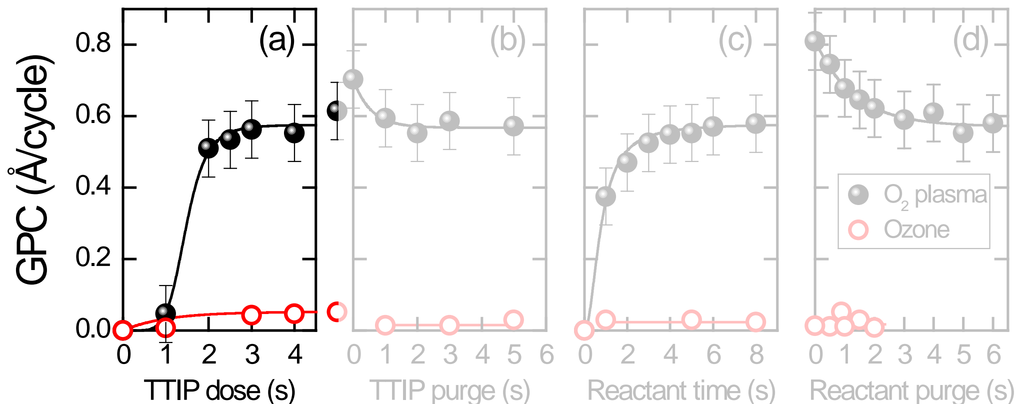




- High vapour pressure
- Reactive ligands
- Fast saturation

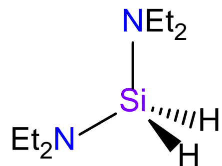
TiO_2

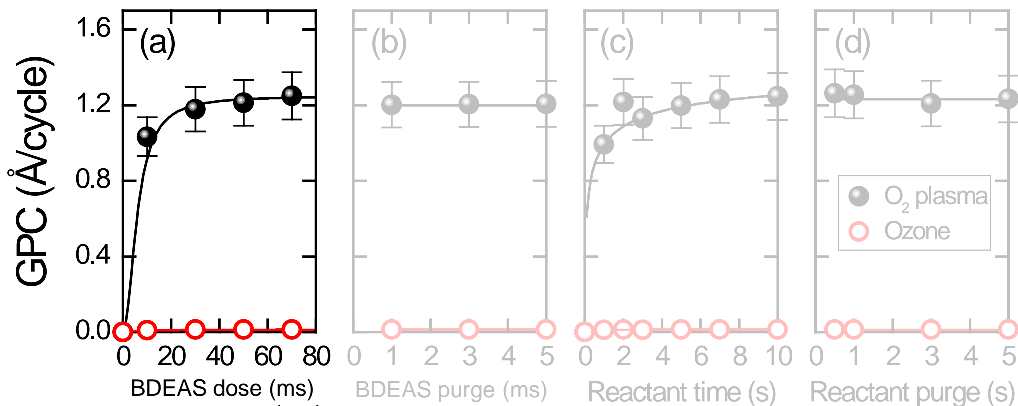




- Moderate vapour pressure
- Reasonably reactive ligands
- By-products have high sticking coefficients.

SiO_2





- High vapour pressure
- Reasonably reactive ligands
- Fast saturation

1. The Metal Precursor: Low Temperatures

Key requirements for suitable low-temperature ALD:

Reactivity

- Alkyl precursors — e.g., $[Al(CH_3)_3]_2$
- Halide precursors — e.g., $TiCl_4$
- Alkoxide precursors — e.g., $[Ti(O^iPr)_4]$
- Alkylamide precursors — e.g., $[Zr(NMe_2)_4]$

High vapour pressure

- Ideally >5 Torr at 25 °C
- If lower, the vapour pressure can be "enhanced" by bubbling an inert gas through the precursor

$Me = CH_3$, $^iPr = CH(CH_3)_2$

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2. The co-reactant
3. The purge times

2. The Co-Reactant

- The co-reactant (non-metal source) defines the category or type of ALD taking place
- Typically, ALD processes are either categorised as thermal or plasma ALD
- There are some “thermal” ALD processes that exhibit different properties to standard thermal ALD
  - e.g., Al_2O_3 from TMA and ozone

2. The Reactivity of the Co-Reactant (1/2)

(a) Substrate heating only

Thermal ALD

"Standard" reactivity

H_2O
NH_3
H_2S
H_2
O_2
etc.

Higher reactivity

H_2O_2
N_2H_4
N_2R_4
N_xO_y (as supplied)
etc.

Chemically-catalysed ALD

Additive molecules that accelerate the reaction without formally participating

NH_3 catalyst
NR_3 catalysts
$[Al(CH_3)_3]_2$ catalyst
Etc.

S. E. Potts & W. M. M. Kessels, *Coord. Chem. Rev.*, **257**, 3254 (2013).

2. The Reactivity of the Co-Reactant (2/2)

(b) Additional energy to convert gaseous species (away from substrate)

Energy-Enhanced ALD

Electrical Discharge

Plasmas

Radicals

Ions

Electrons

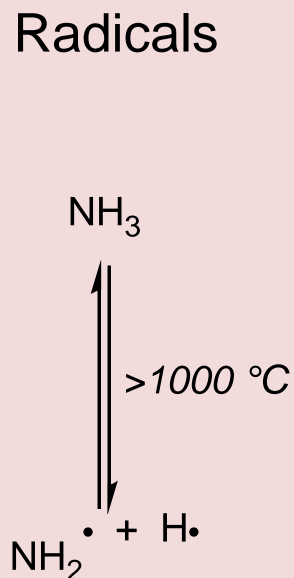
(UV) Photons

Ozone

N_xO_y

Thermal Cracking

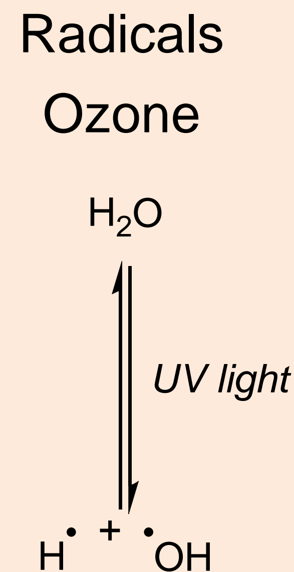
Radicals



Photodissociation

Radicals

Ozone



S. E. Potts & W. M. M. Kessels, *Coord. Chem. Rev.*, **257**, 3254 (2013).

Energy-Enhanced ALD in Practice

Reactive species with a short lifetime made *in situ*, away from the substrate.

Electrical Discharge

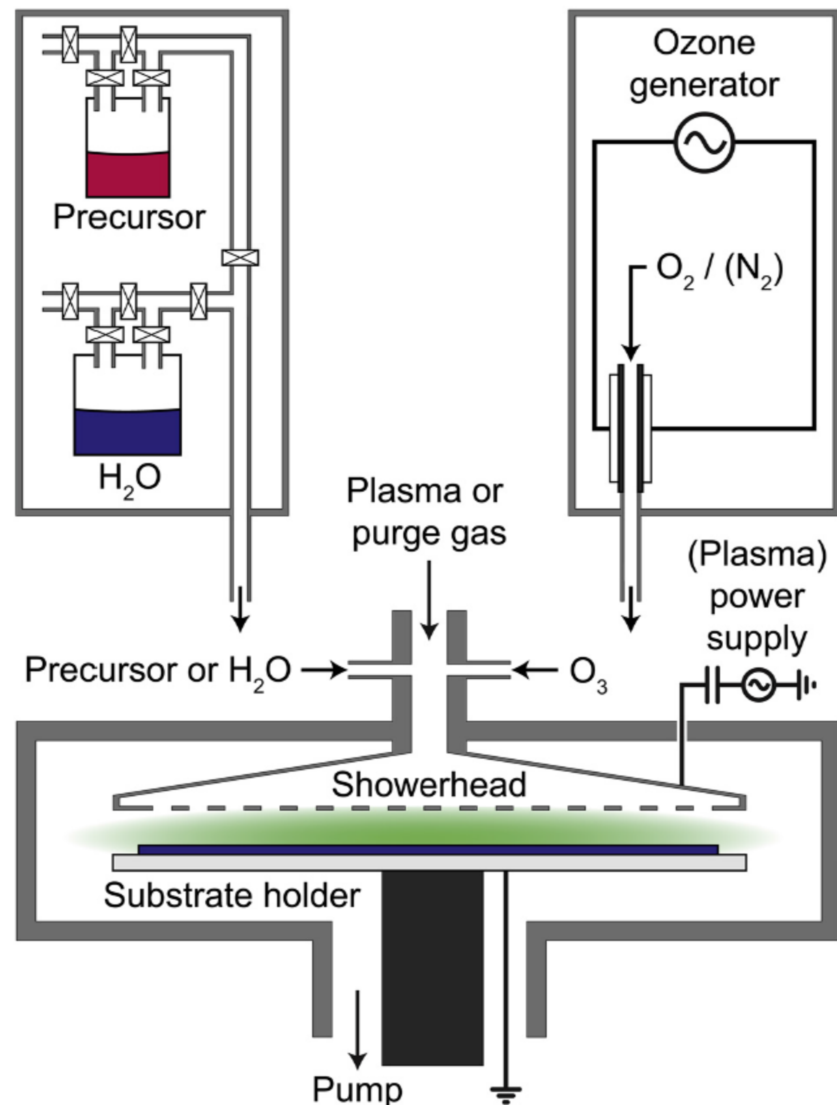
- Plasma ALD
- Ozone ALD
- Radical-enhanced ALD

Thermal Cracking

- Hot-wire ALD

Photodissociation

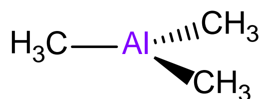
- Ozone ALD
- Radical-enhanced ALD

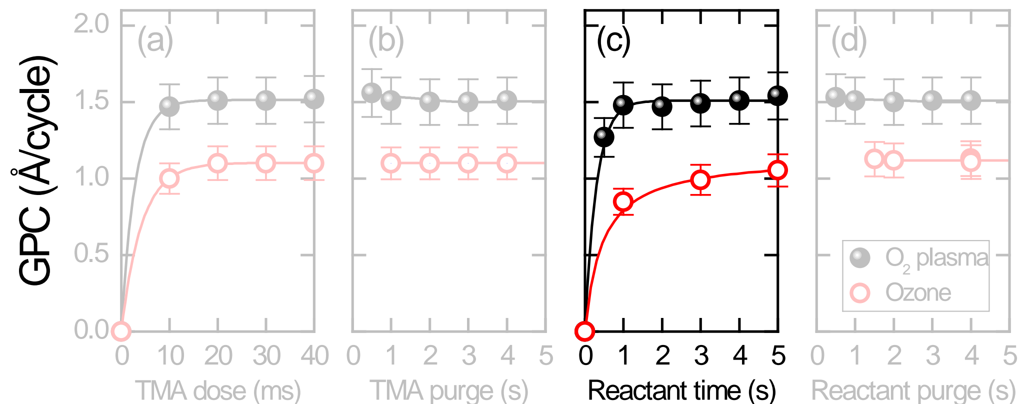


S. E. Potts & W. M. M. Kessels, *Coord. Chem. Rev.*, **257**, 3254 (2013).

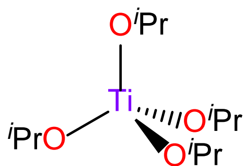
Room-Temperature ALD Saturation
Co-Reactant

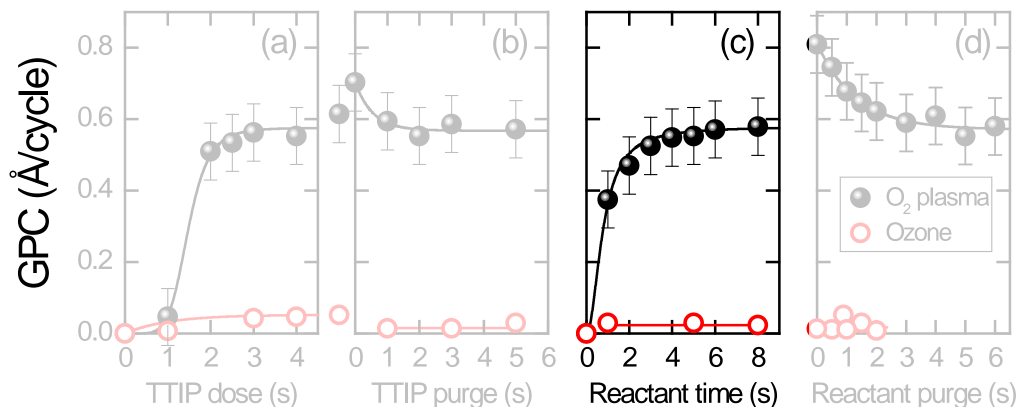
Al_2O_3



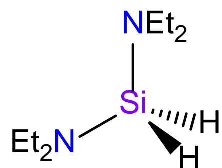


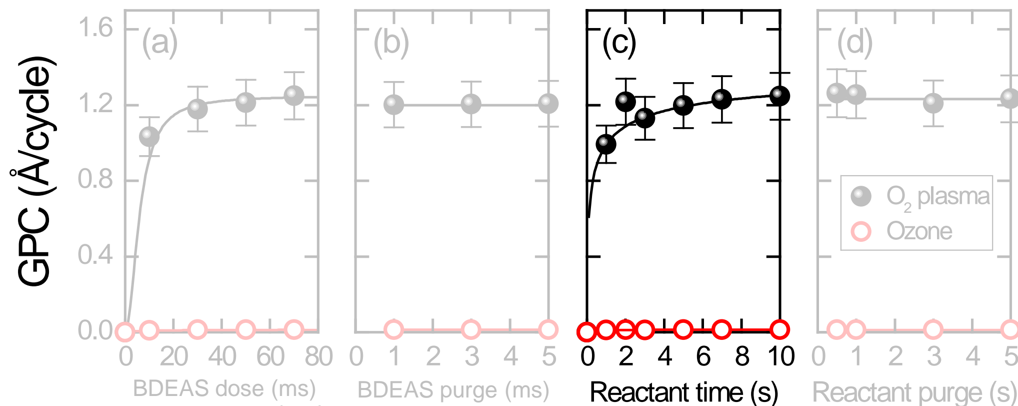
TiO_2





SiO_2





Black lines: O_2 plasma

Red lines: Ozone

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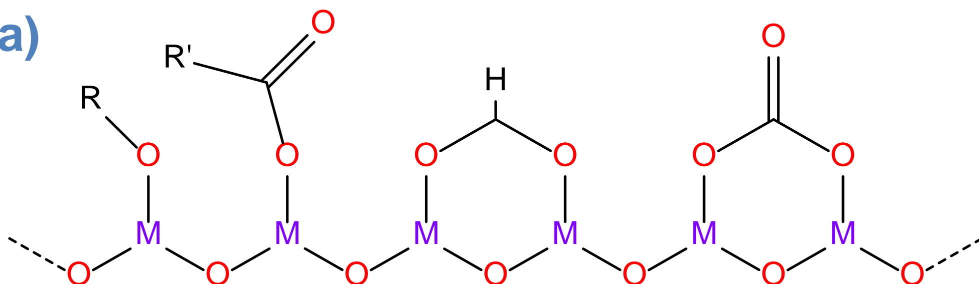
Surface Groups during RT-ALD

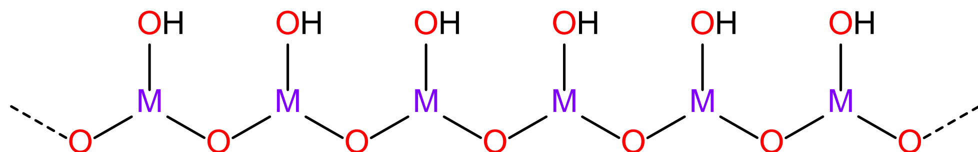
After the Co-Reactant Pulse

O_2 plasma **Ozone**

fast fast



fast slow



(a) Carbonaceous Species

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

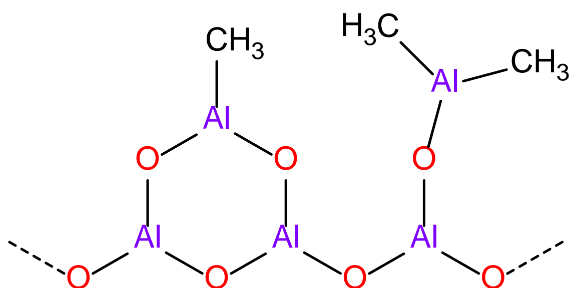
(b) Hydroxyls

- High reactivity towards all incoming precursor ligands.

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

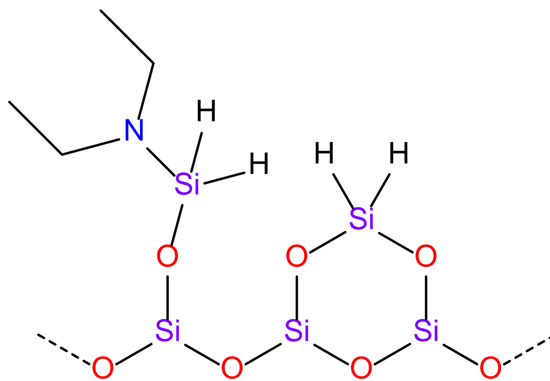
Surface Groups during RT-ALD
After the Metal Precursor Pulse

TMA, $Al(CH_3)_3$



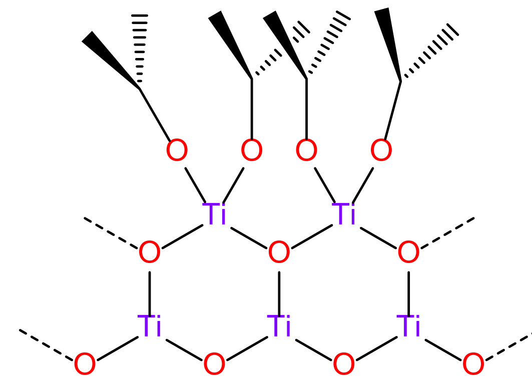
- Highly reactive Al–C bonds.
- Easily removed by O_2 plasma and ozone.

BDEAS, $SiH_2(NEt_2)_2$



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

TTIP, $Ti(O^iPr)_4$

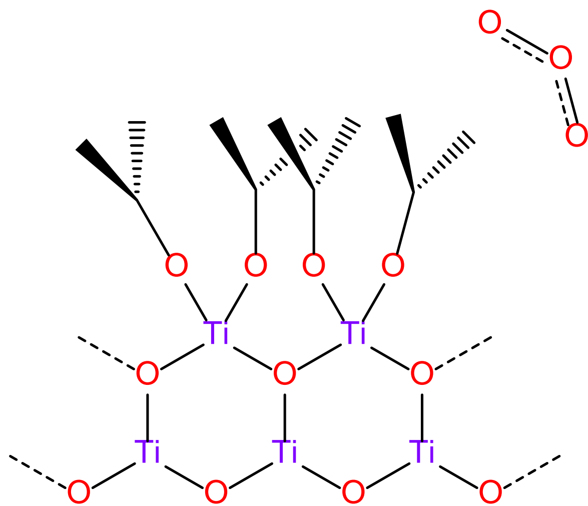


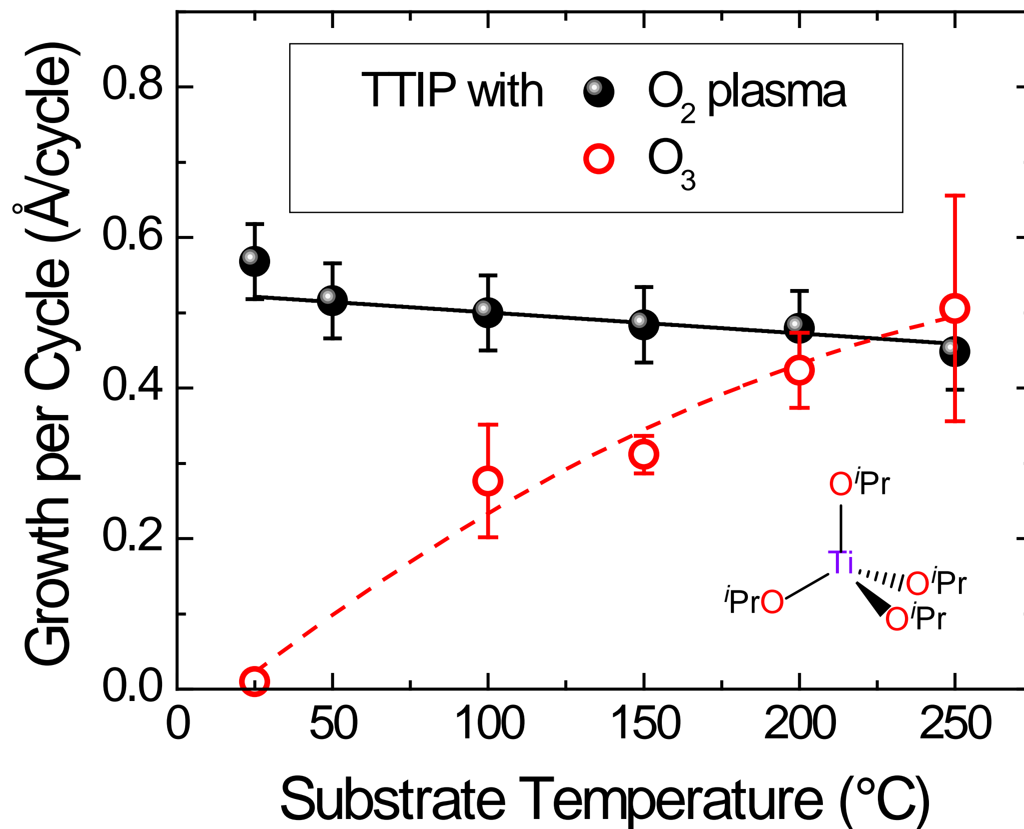
- Ti–O bond already relatively strong.
- Easily removed by O_2 plasma.
- No or negligible reactivity with ozone.

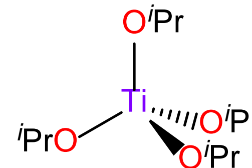
Surface Groups during RT-ALD
TTIP + Ozone

- ALD process has a thermal activation component.
- Increase in temperature

  → increase in growth.
- TTIP surface groups/ozone simply unreactive at RT.



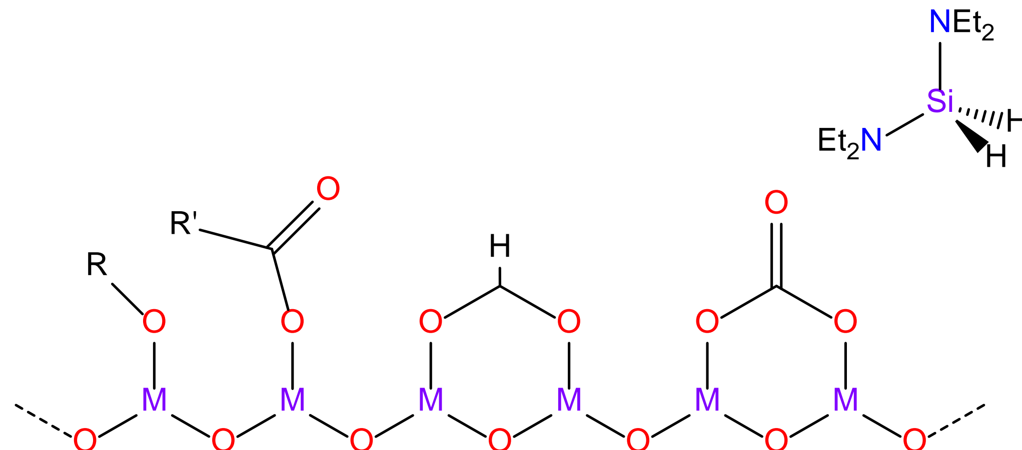




S. E. Potts *et al.*, *Chem. Vap. Deposition*, **19**, 125 (2013).

Surface Groups during RT-ALD
BDEAS + Ozone

Two explanations:

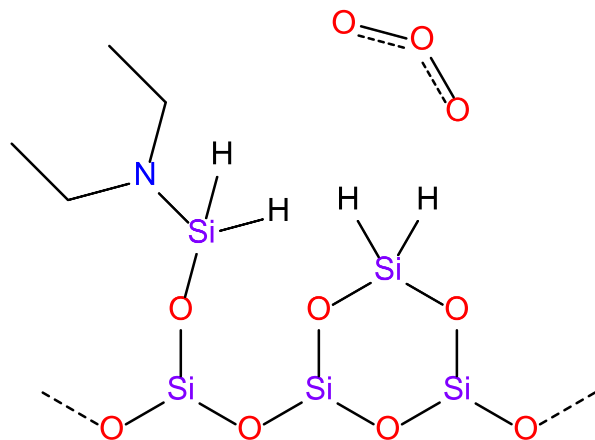


1. Thermal activation

- 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.



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Outline: Low-Temperature ALD

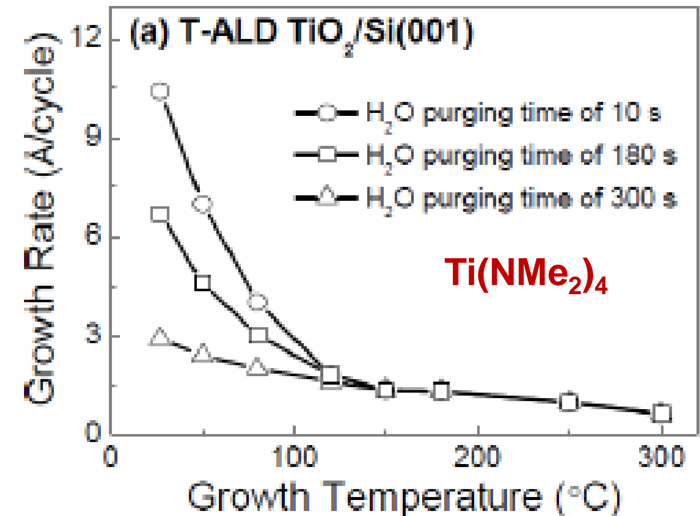
Factors Affecting Low-Temperature ALD

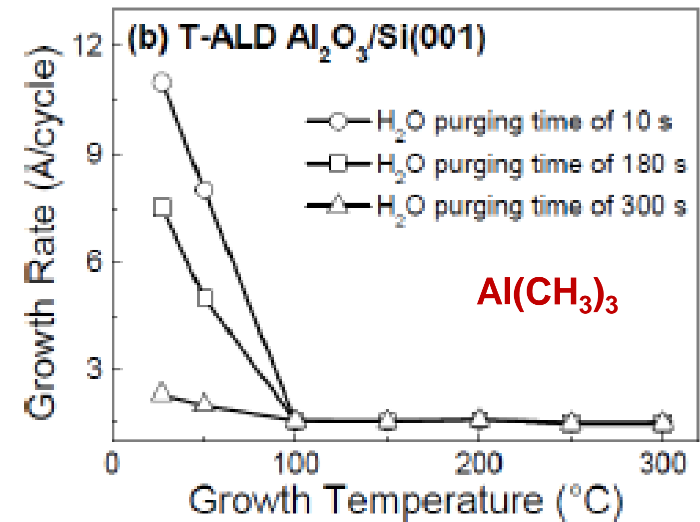
1. The metal precursor
2. The co-reactant
3. The purge times

3. The Purge Times

Thermal ALD

- Below 100 °C, significantly longer co-reactant purges are required
- Incomplete removal of water results in more reactive surface sites
- These lead to lower density films and loss of saturating behaviour





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T. Nam *et al.*, *J. Korean Phys. Soc.*, **59**, 452 (2011).

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3. The Purge Times

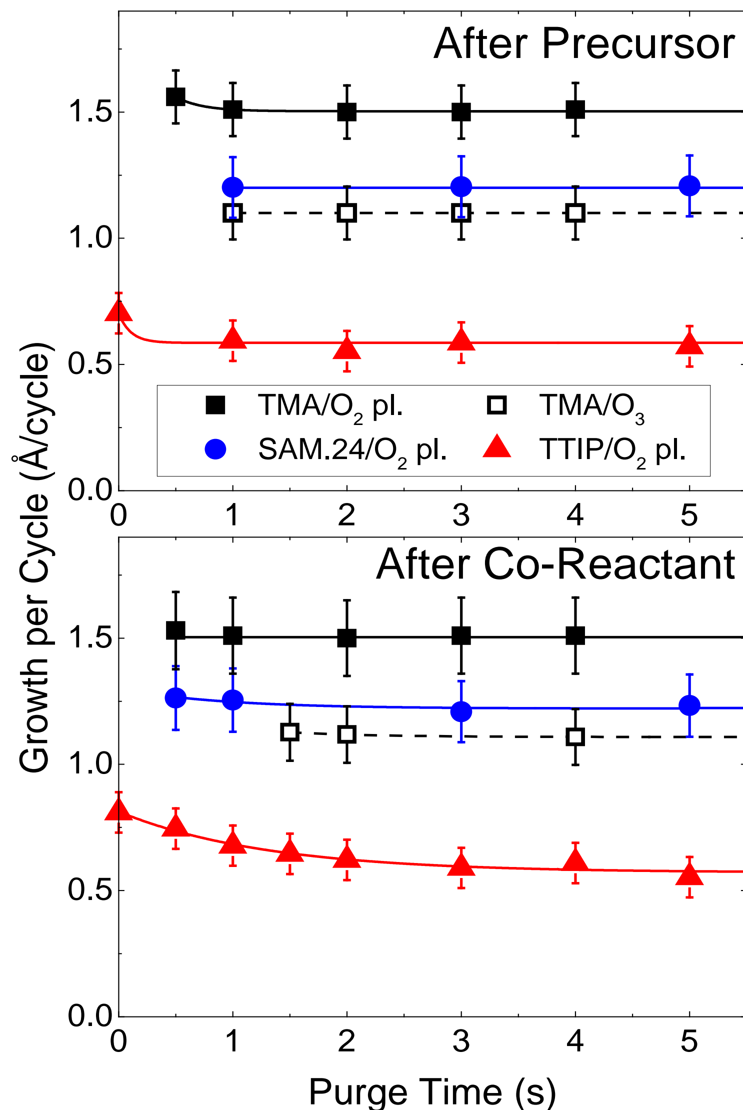
Energy-Enhanced ALD

Quickly pumped from reactor

- Precursors with high vapour pressures.
- Gaseous reaction products.

Reactive species from energy-enhanced ALD can be “turned off”

- Plasma
  - Ions and electrons dissipate almost instantaneously
  - Radicals quickly recombine (surface-dependent)*
- Ozone is quickly pumped away.



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

Summary
Low-temperature ALD: what's limiting?

1. The metal precursor
   - The ligands need to be sufficiently reactive at low temperatures
   - High vapour pressure desirable

2. The co-reactant
   - Should be sufficiently reactive at low temperatures
   - Higher reactivity can improve film quality and reduce purge times
   - Energy-enhanced ALD processes help to overcome potential thermal shortcomings

3. The purge times
   - Thermal ALD requires substantially longer purges than for higher-temperature ALD processes
   - Purge times can be kept short if co-reactants with short lifetimes are used