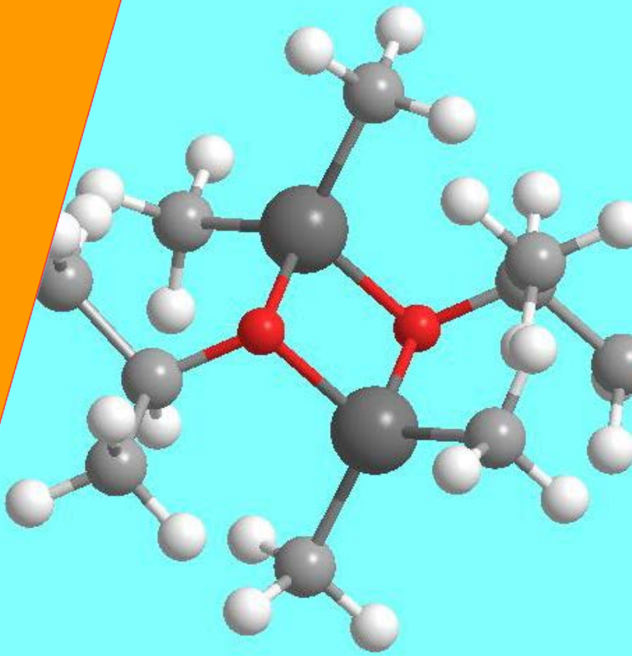
Plasma-Enhanced and Thermal ALD of Al_2O_3 from Dimethylaluminium Isopropoxide, $[Al(CH_3)_2(\mu\text{-}O^iPr)]_2$



Stephen E. Potts and Erwin Kessels
Eindhoven University of Technology, The Netherlands

Christophe Lachaud
Air Liquide Research & Development, France

EuroCVD 18, Cork, Ireland
6th September 2011

Where innovation starts

Outline

DMAI: $[Al(CH_3)_2(\mu\text{-}O^iPr)]_2$

TMA: $[Al(CH_3)_3]_2$

- **Motivation**

- **Experimental Details**

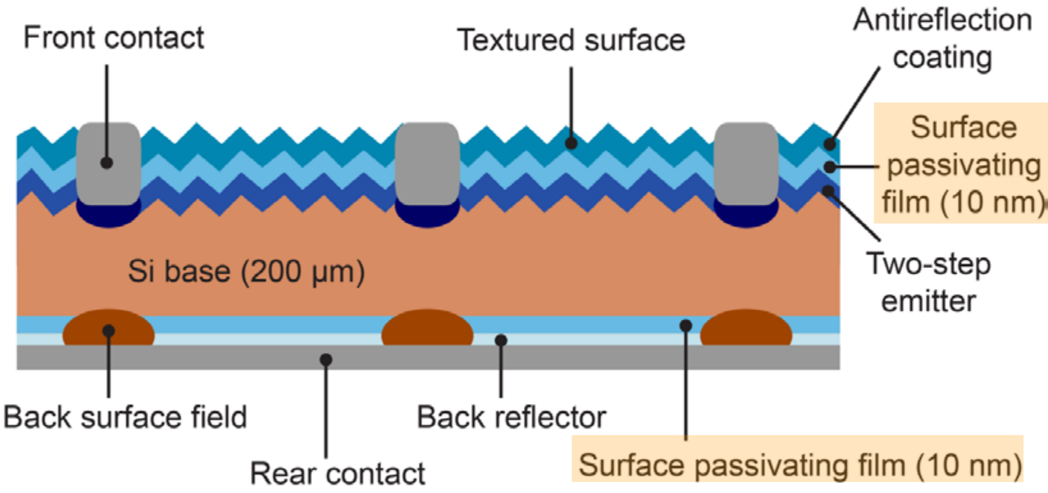
- **Plasma-ehnahced and thermal ALD Characteristics of DMAI**
  - At ‘standard’ ALD temperatures (150 and 200 °C)
  - Temperature series study: **comparison with TMA**
  - Film composition at room temperature (plasma only)

- **Al_2O_3 from DMAI as a Surface Passivation Layer**
  - Effective lifetime of charge carriers in c-Si

- **Conclusions**

Motivation

- Many applications for ALD-synthesised Al_2O_3
  - Microelectronics: medium-*k* dielectric material
  - Protective coatings (e.g. moisture barriers)
  - Passivation layer in solar cells
  - Etc…

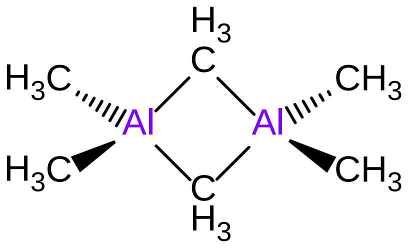
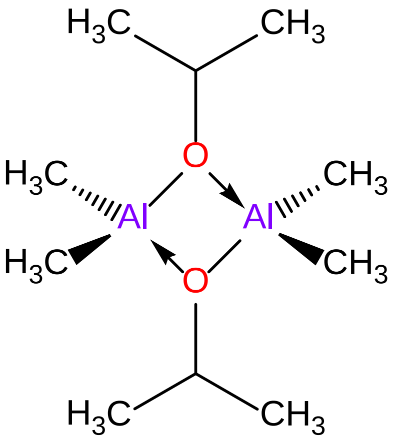


- ALD precursors
  - Al_2Cl_6: source of Cl and gives corrosive by-products
  - $[Al(CH_3)_3]_2$ (TMA): ‘model’ ALD processes, but pyrophoric

- Safer, alternative precursors are being sought

Can DMAI perform as well as TMA?

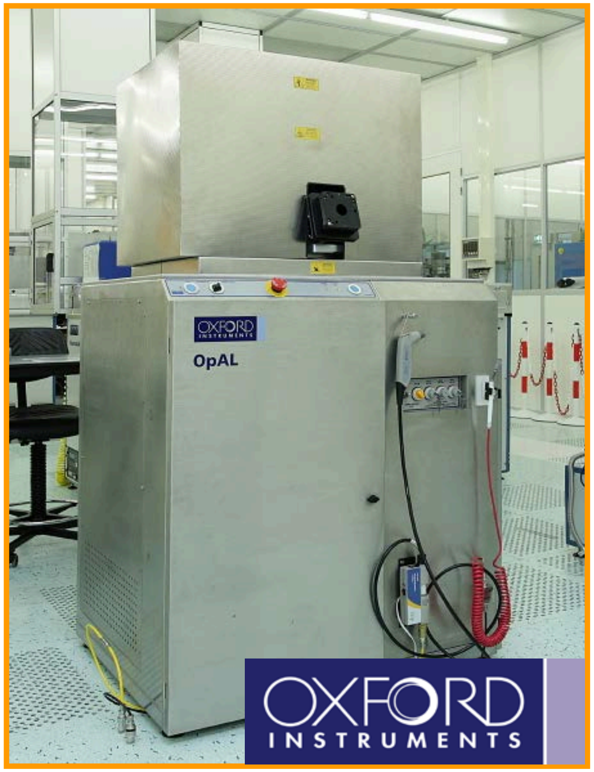
Precursor Properties

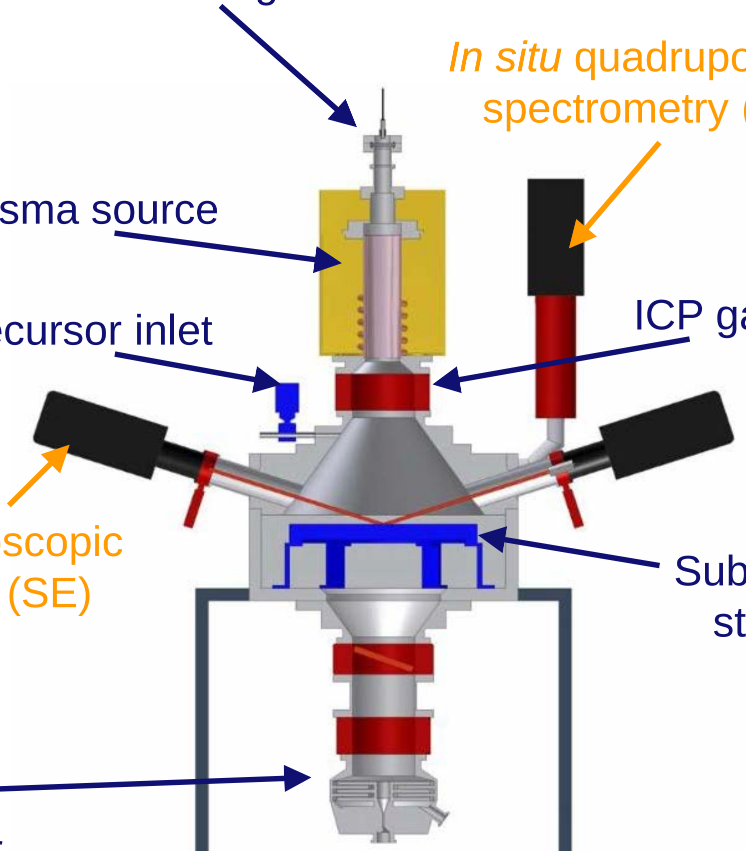
Property	TMA	DMAI
Structure	 Up to ~70 °C	
Physical State (R.T.P.)	Liquid	Liquid
Melting Point	15 °C	< R.T.
Boiling Point	125 °C	186 °C
Vapour Pressure	9 Torr at 16.8 °C	9 Torr at 66.5 °C
Decomposition Temp.	~330 °C	**~370 °C**
Pyrophoricity	High	**Very low**

Data from Air Liquide

Experimental: Reactor and Diagnostics

Oxford Instruments OpAL reactor





Process gases

In situ quadrupole mass spectrometry (QMS)

Remote IC plasma source

ICP gate valve

Precursor inlet

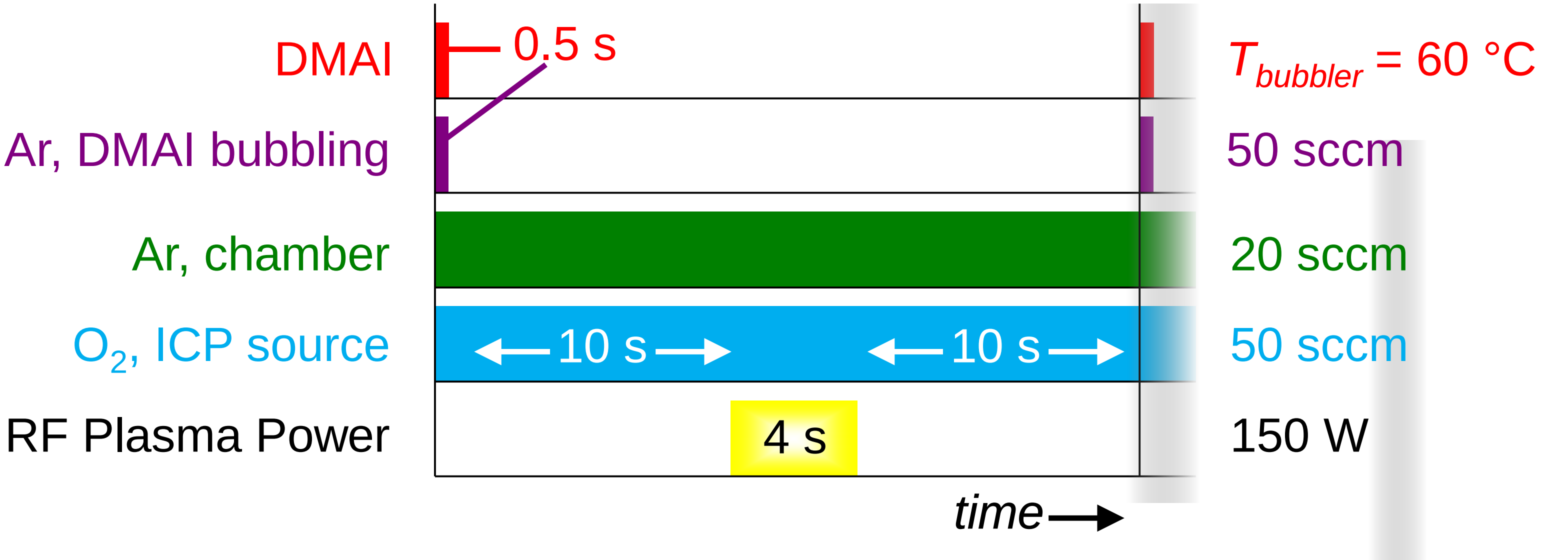
In situ spectroscopic ellipsometry (SE)

Substrate stage

Rotary vane pump
Base pressure <1 mTorr
Operating pressure 100-300 mTorr

Experimental: ALD Cycles on OpAL

Plasma-enhanced ALD



DMAI — 0.5 s — $T_{bubbler}$ = 60 °C

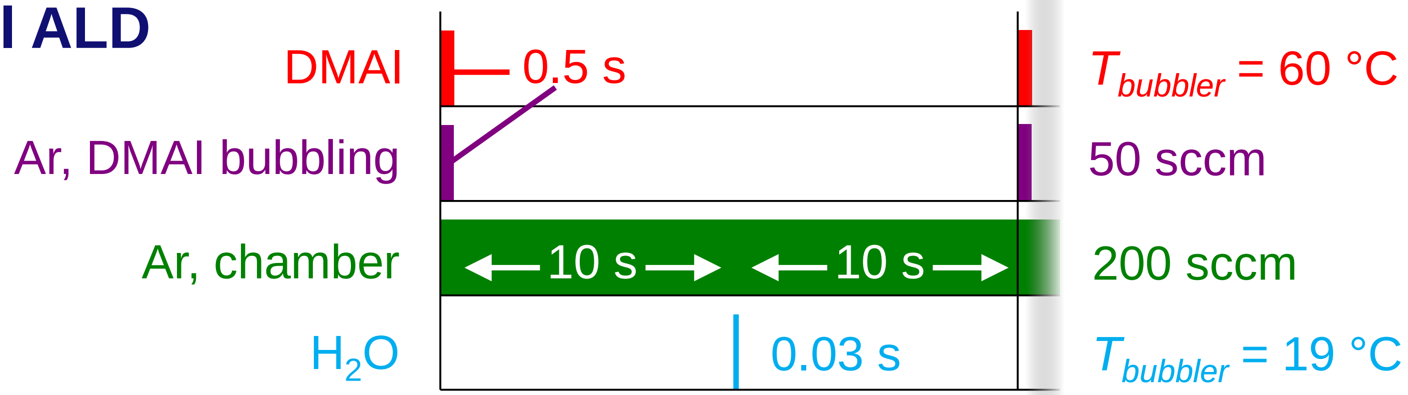
Ar, DMAI bubbling — 50 sccm

Ar, chamber — 20 sccm

O_2, ICP source — ←10 s→ ←10 s→ — 50 sccm

RF Plasma Power — 4 s — 150 W

Thermal ALD



DMAI — 0.5 s — $T_{bubbler}$ = 60 °C

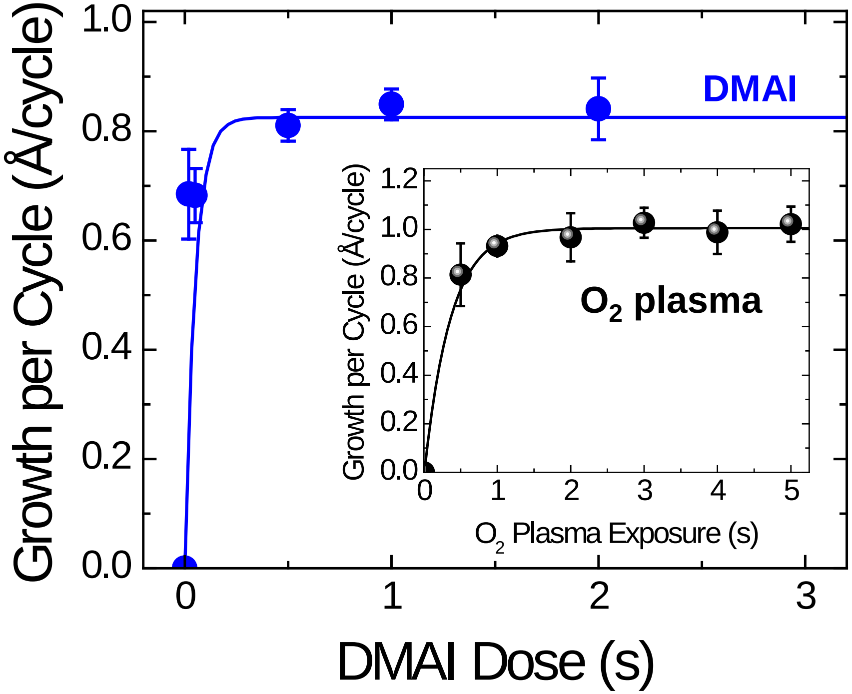
Ar, DMAI bubbling — 50 sccm

Ar, chamber — ←10 s→ ←10 s→ — 200 sccm

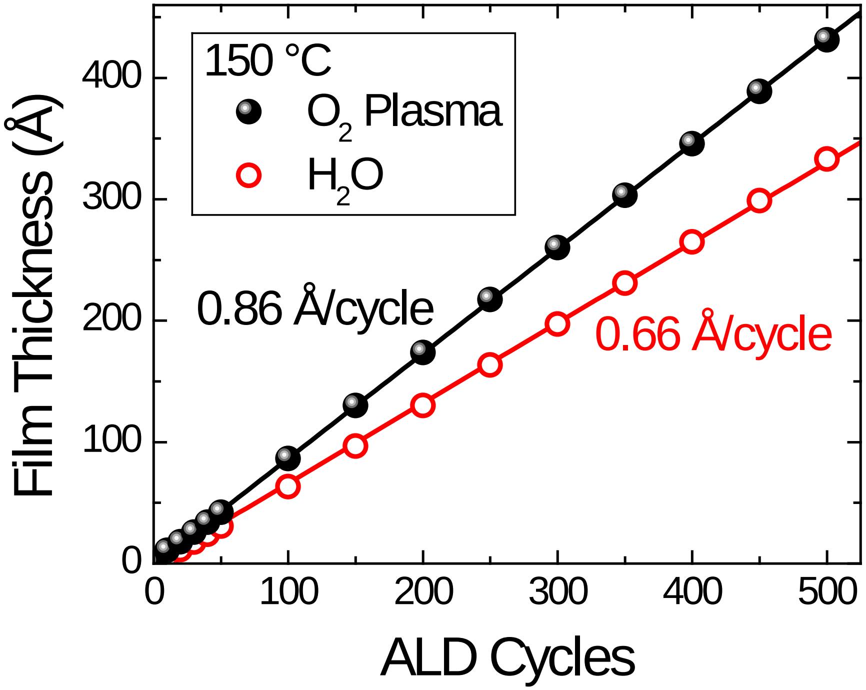
H_2O — 0.03 s — $T_{bubbler}$ = 19 °C

Technische Universiteit Eindhoven University of Technology

ALD Characteristics



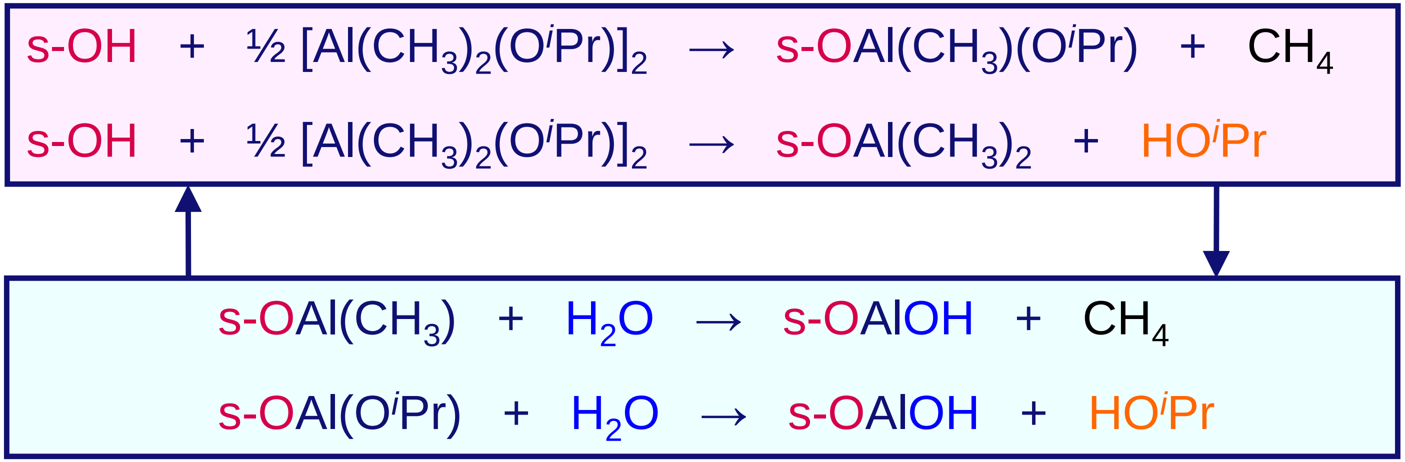
Saturation



Growth

- DMAI saturates within 0.5 s (TMA ~0.02 s)
- DMAI shows linear increase with number of cycles
- No nucleation delay on Si/SiO_2

In Situ QMS: Thermal ALD



DMAI pulse

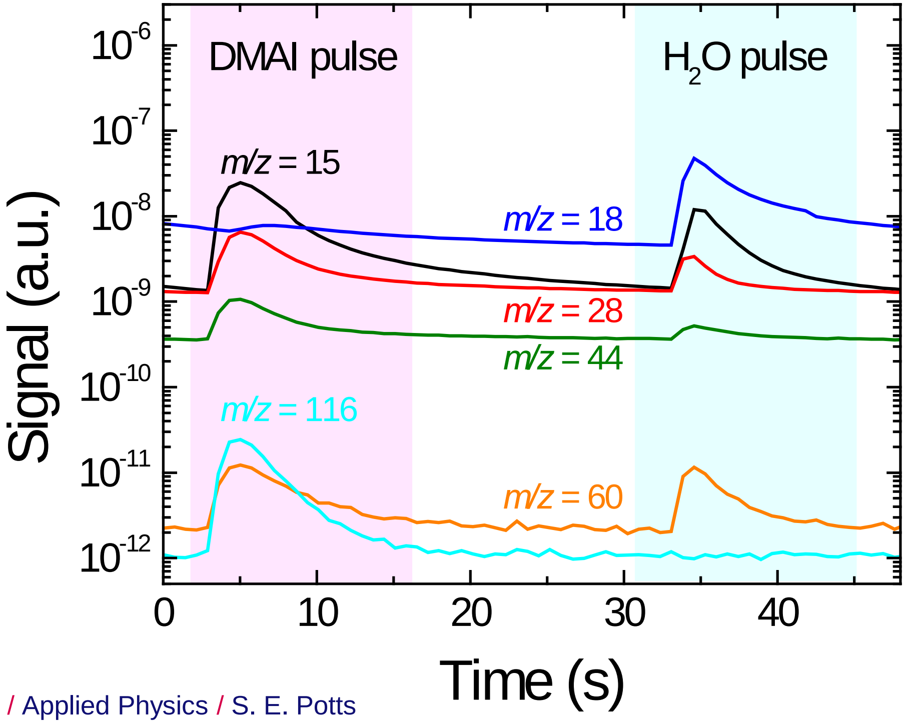
$\text{s-OH} + \tfrac{1}{2}\,[\text{Al(CH}_3)_2(\text{O}^i\text{Pr})]_2 \rightarrow \text{s-OAl(CH}_3)(\text{O}^i\text{Pr}) + \text{CH}_4$

$\text{s-OH} + \tfrac{1}{2}\,[\text{Al(CH}_3)_2(\text{O}^i\text{Pr})]_2 \rightarrow \text{s-OAl(CH}_3)_2 + \text{HO}^i\text{Pr}$

H_2O pulse

$\text{s-OAl(CH}_3) + \text{H}_2\text{O} \rightarrow \text{s-OAlOH} + \text{CH}_4$

$\text{s-OAl(O}^i\text{Pr}) + \text{H}_2\text{O} \rightarrow \text{s-OAlOH} + \text{HO}^i\text{Pr}$



- CH_4 and HO^iPr are expected Brønsted acid/base products
- *m/z* = 28 and 44 are cracking products of HO^iPr and DMAI

K.-S. An, *et al.*, *Bull. Korean Chem. Soc.*, **24**, 1659 (2003).
S. B. S. Heil *et al.*, *J. Appl. Phys.*, **103**, 103302 (2008).

AIR LIQUIDE

TU/e Technische Universiteit Eindhoven University of Technology

In Situ QMS: Plasma-Enhanced ALD

DMAI pulse

$\mathrm{s\text{-}OH} + \tfrac{1}{2}\,[\mathrm{Al(CH_3)_2(O^{\mathit{i}}Pr)}]_2 \rightarrow \mathrm{s\text{-}OAl(CH_3)(O^{\mathit{i}}Pr)} + \mathrm{CH_4}$

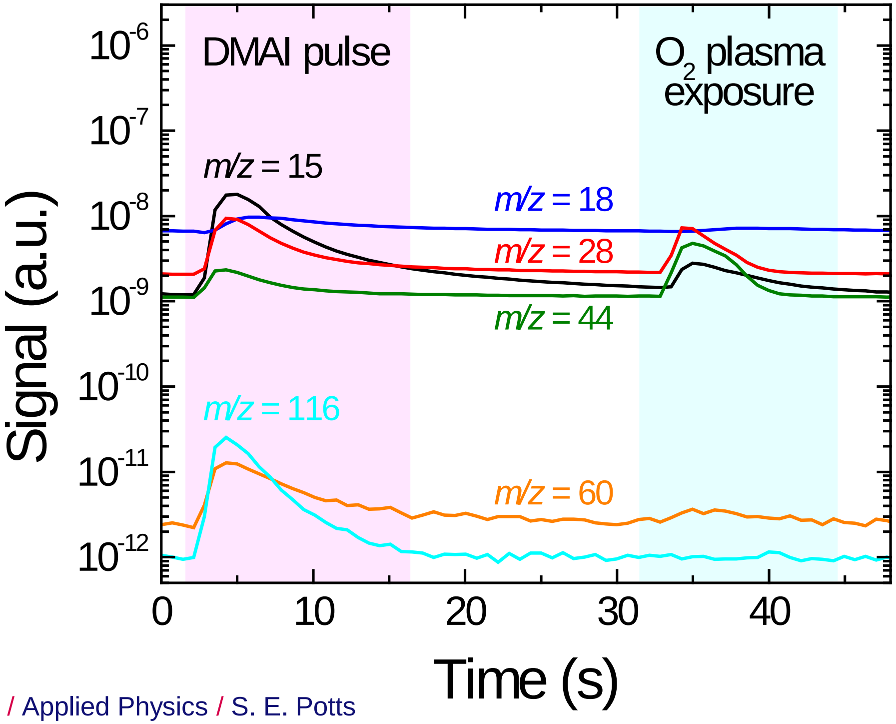
$\mathrm{s\text{-}OH} + \tfrac{1}{2}\,[\mathrm{Al(CH_3)_2(O^{\mathit{i}}Pr)}]_2 \rightarrow \mathrm{s\text{-}OAl(CH_3)_2} + \mathrm{HO^{\mathit{i}}Pr}$

Assuming complete combustion:

O_2 plasma exposure

$\mathrm{s\text{-}OAl(CH_3)} + 4\,\{\mathrm{O}\} \rightarrow \mathrm{s\text{-}OAlOH} + \mathrm{CO_2} + \mathrm{H_2O}$

$\mathrm{s\text{-}OAl(O^{\mathit{i}}Pr)} + 9\,\{\mathrm{O}\} \rightarrow \mathrm{s\text{-}OAlOH} + 3\,\mathrm{CO_2} + 3\,\mathrm{H_2O}$



- The DMAI step the same as thermal ALD, releasing CH_4 and $HO^{i}Pr$.

- *m/z* = 28 and 44 suggest combustion-like products (CO^+, CO_2^+) during the plasma step.

S. B. S. Heil *et al.*, *J. Appl. Phys.*, **103**, 103302 (2008).

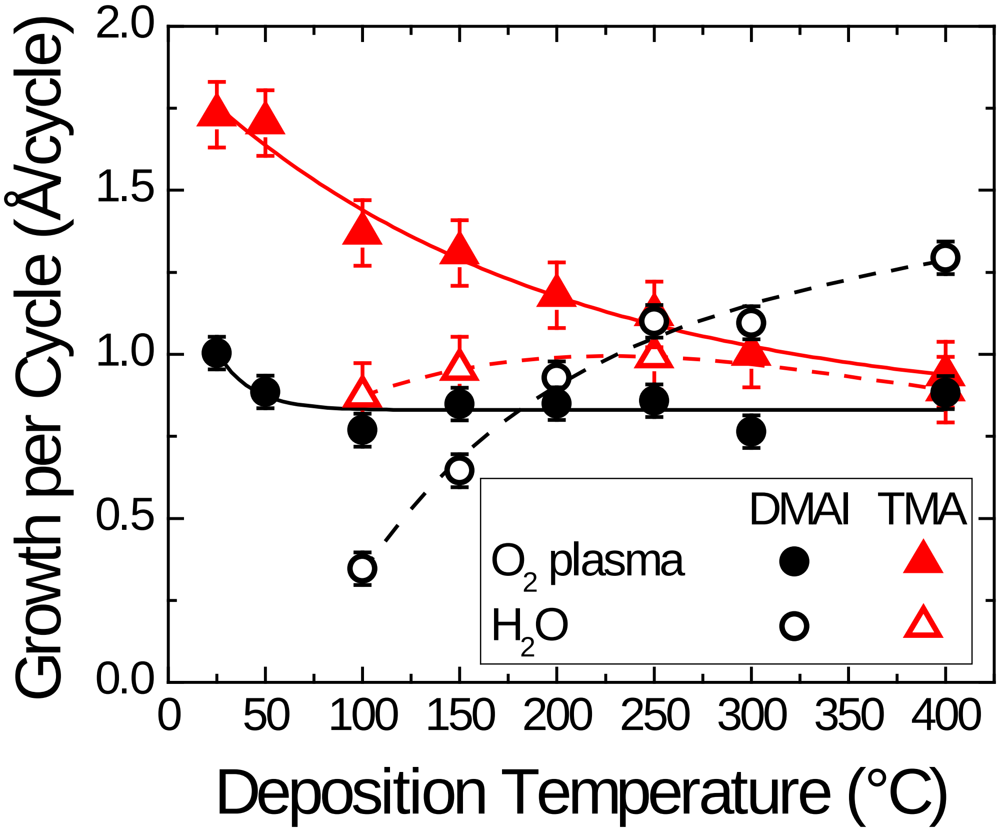
Growth per Cycle (GPC)

Plasma-enhanced

- Lower GPC for DMAI
- Drop for TMA GPC caused by dehydroxylation
- DMAI less affected by this

Thermal

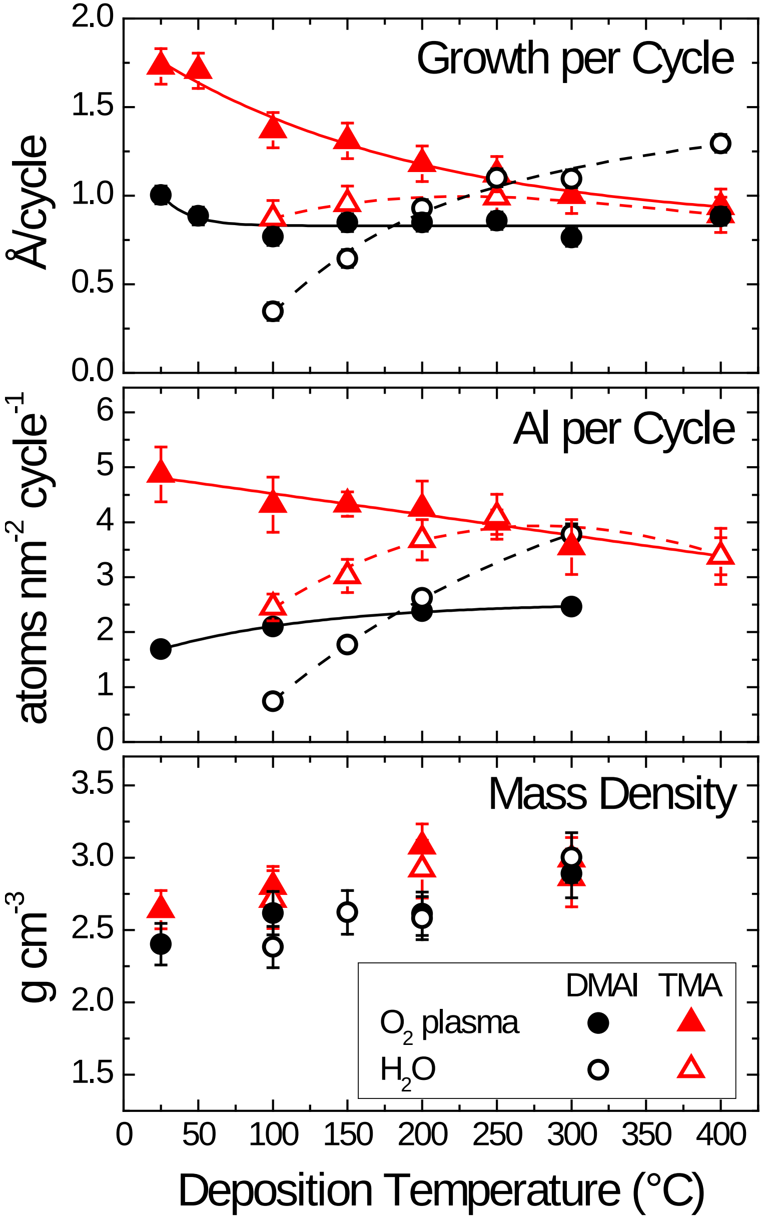
- More thermal activation required for DMAI
- Insufficient thermal energy at lower temperatures
- O^{i}Pr groups may start decomposing at higher temperatures



Thermal energy input required:

s-OH + Al–**O^{i}Pr** **>** s-OH + Al–**CH$_3$**

Film Composition

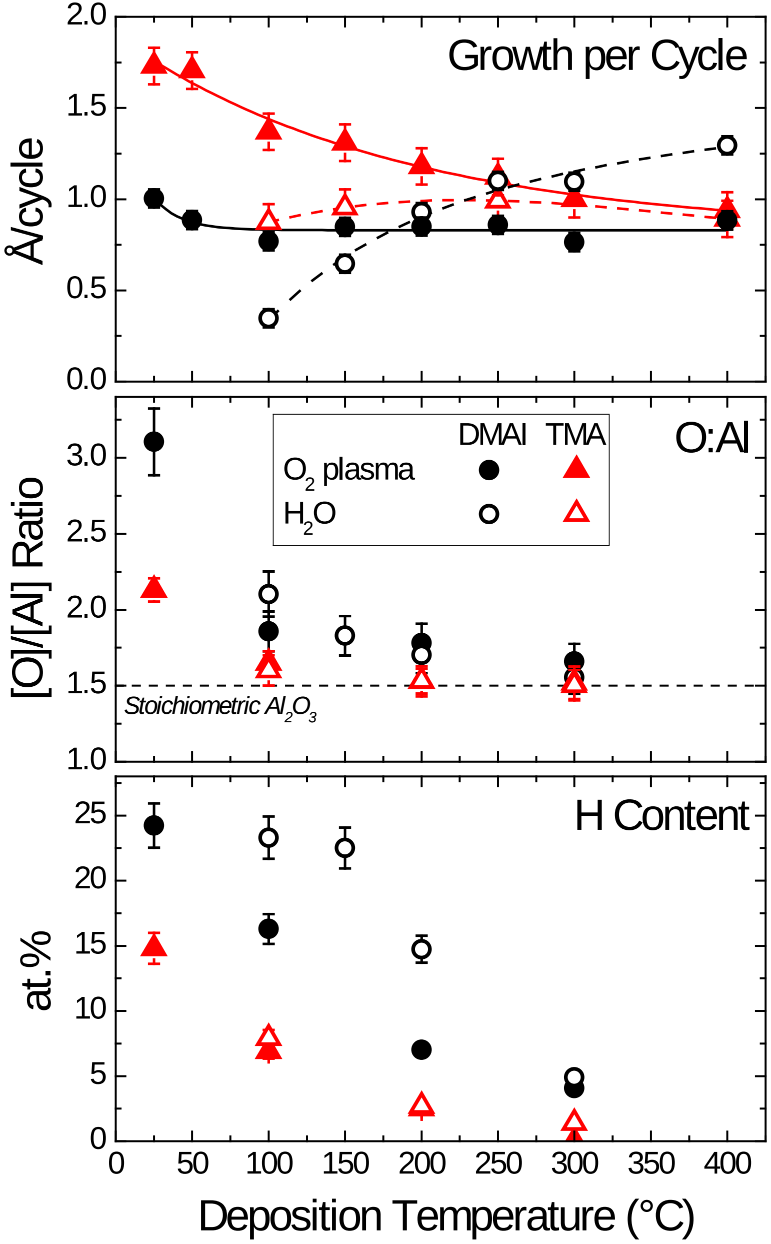


- Obtained using Rutherford backscattering spectrometry and elastic recoil detection
- GPC is affected by film density
- DMAI affords fewer Al atoms per cycle
  - Plasma ALD almost half
  - Increase of Al with temperature confirms thermal input
- Density between two precursors does not differ significantly
  - Plasma ALD films slightly denser than thermal
  - DMAI films less dense than TMA

AIR LIQUIDE

TU/e Technische Universiteit Eindhoven University of Technology

Film Composition



- General trend: more H and O at lower temperatures
- Typically due to OH in the films
- Films from DMAI contain more O and H than those from TMA
- At 25 °C,
  - O/Al for DMAI > TMA
  - O/Al > 3 (DMAI), suggests carbonate or formate incorporation
  - Most likely a result of $O^{i}Pr$

AIR LIQUIDE

TU/e Technische Universiteit Eindhoven University of Technology

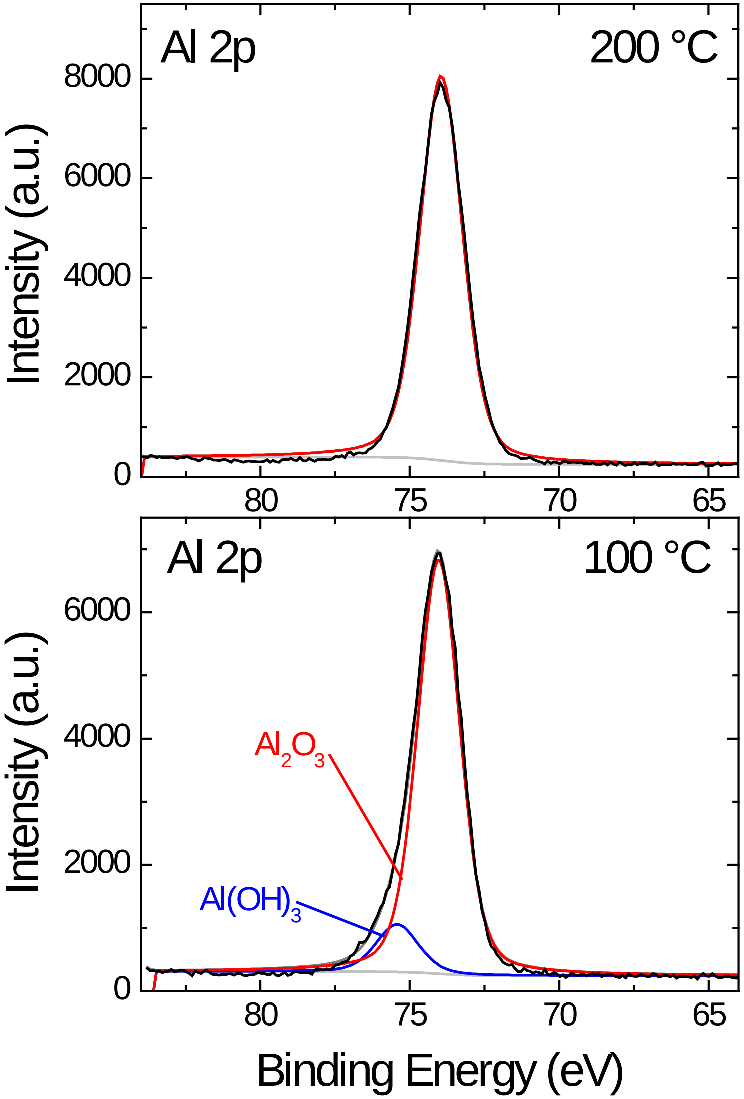
XPS: Thermal ALD

200 °C ‘standard temperature’

- Same for 150 °C and above
- Only Al_2O_3 environment
- C not observed
- Same for films from TMA

100 °C

- Some OH
- No C observed in ‘bulk’
- Similar to films from TMA but higher OH concentration (RBS).



XPS: Plasma-Enhanced ALD

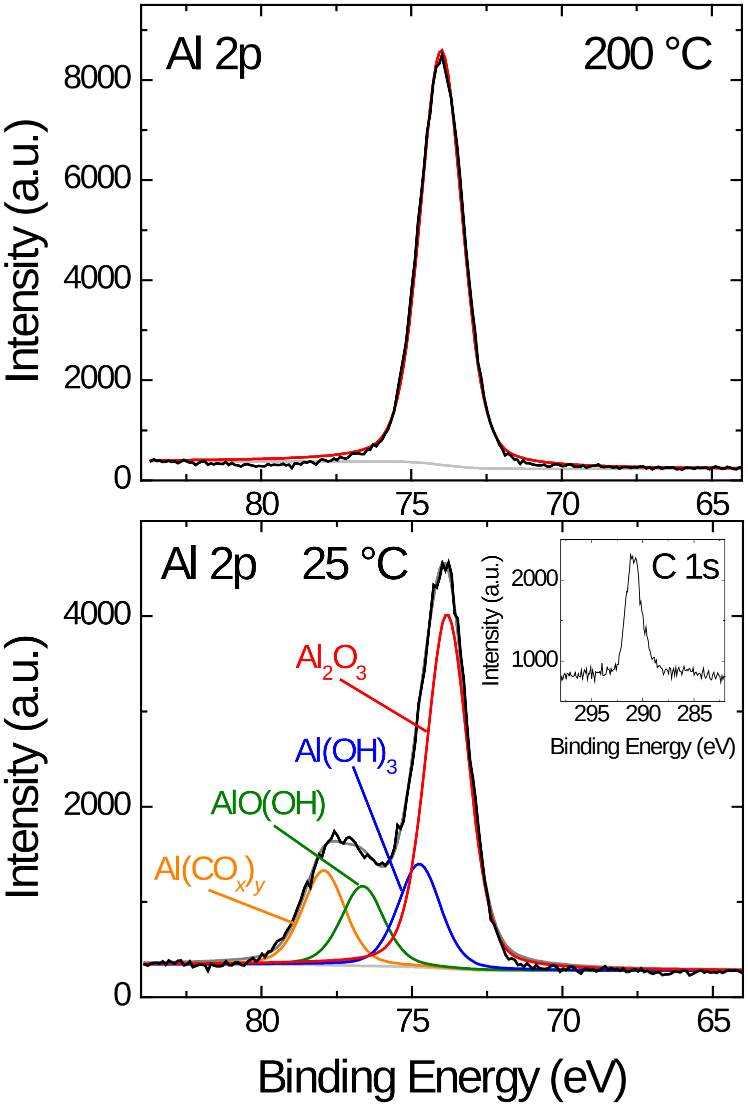
200 °C ‘standard temperature’

- Same for 100 °C and above
- No C observed
- As with thermal ALD, only Al_2O_3

25 °C

- Substantial concentration of
  - Hydroxide
  - Oxyhydroxide
  - Carbonates, confirmed by C
- Consistent throughout the film

- Carbonates generally observed in ozone-based and O_2 plasma ALD



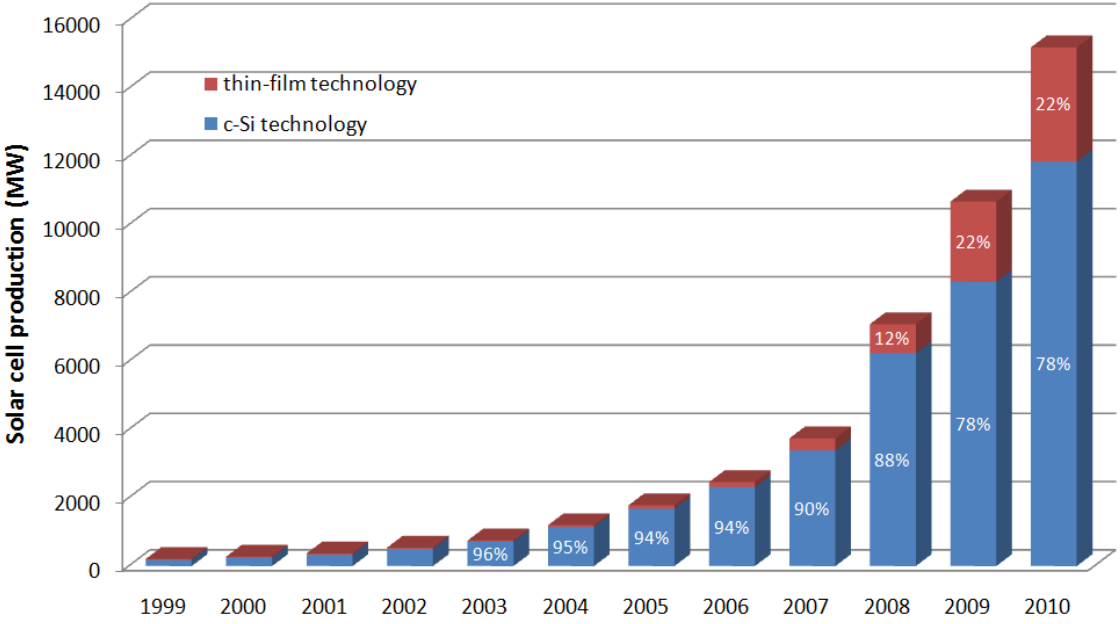
Al assignments: T. Gougousi *et al.*, *Chem. Mater.*, **17**, 5903 (2005).

DMAI as an ALD Precursor

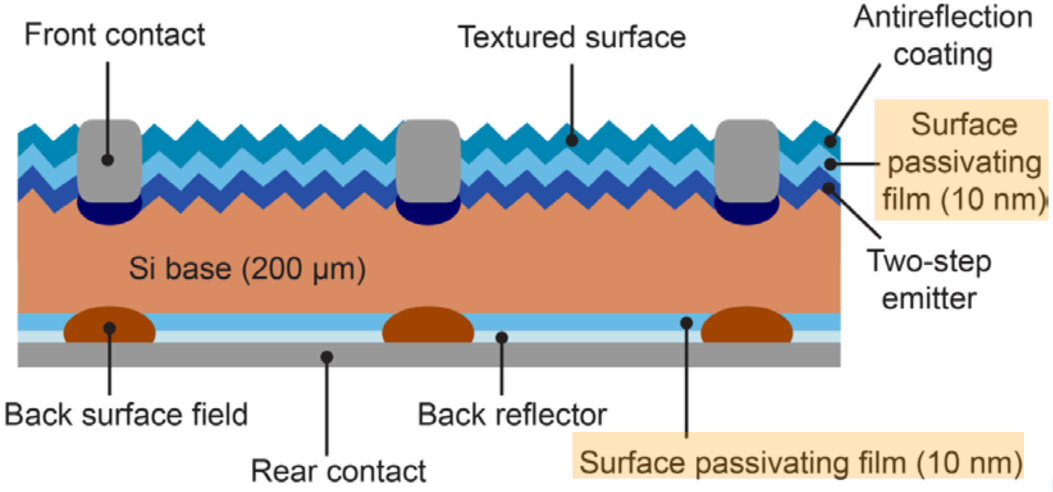
- Al–O^{i}Pr requires more thermal energy for reaction
- Lower growth per cycle than TMA
- ≥150 °C – equivalent to those from TMA
- <150 °C – higher [OH], inclusion of carbonates at 25 °C

- How does it behave as a surface passivation layer for c-Si?

Surface Passivation of c-Si for Solar Cells



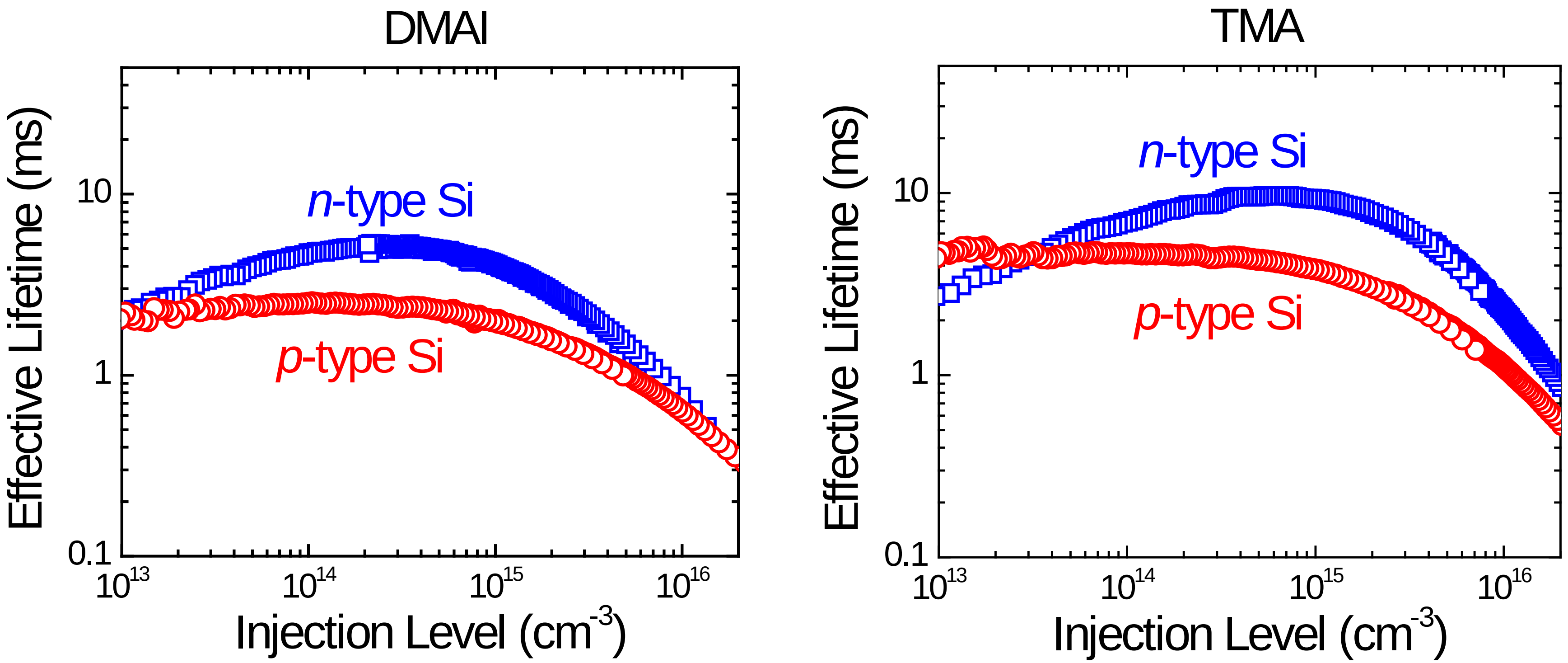
Earth policy institute (Jan. 2011); EPIA (May 2010)



- Solar cells are a huge business!
- Vast amount of TMA required
- An Al_2O_3 layer can passivate the c-Si surface
- Effective lifetime of charge carriers increased → increased efficiency
- Is DMAI a suitable alternative?

Al_2O_3 as a Surface Passivation Layer

- 30 nm Al_2O_3 applied to *n*- and *p*-type Si floatzone wafers at 200 °C
- Annealing step: 10 min, 400 °C under N_2
- Effective lifetimes: 1-5 ms
- **Good surface passivation for c-Si for solar cell applications**



TMA: G. Dingemans *et al.*, *Status Solidi RRL*, **4**, 10 (2010).

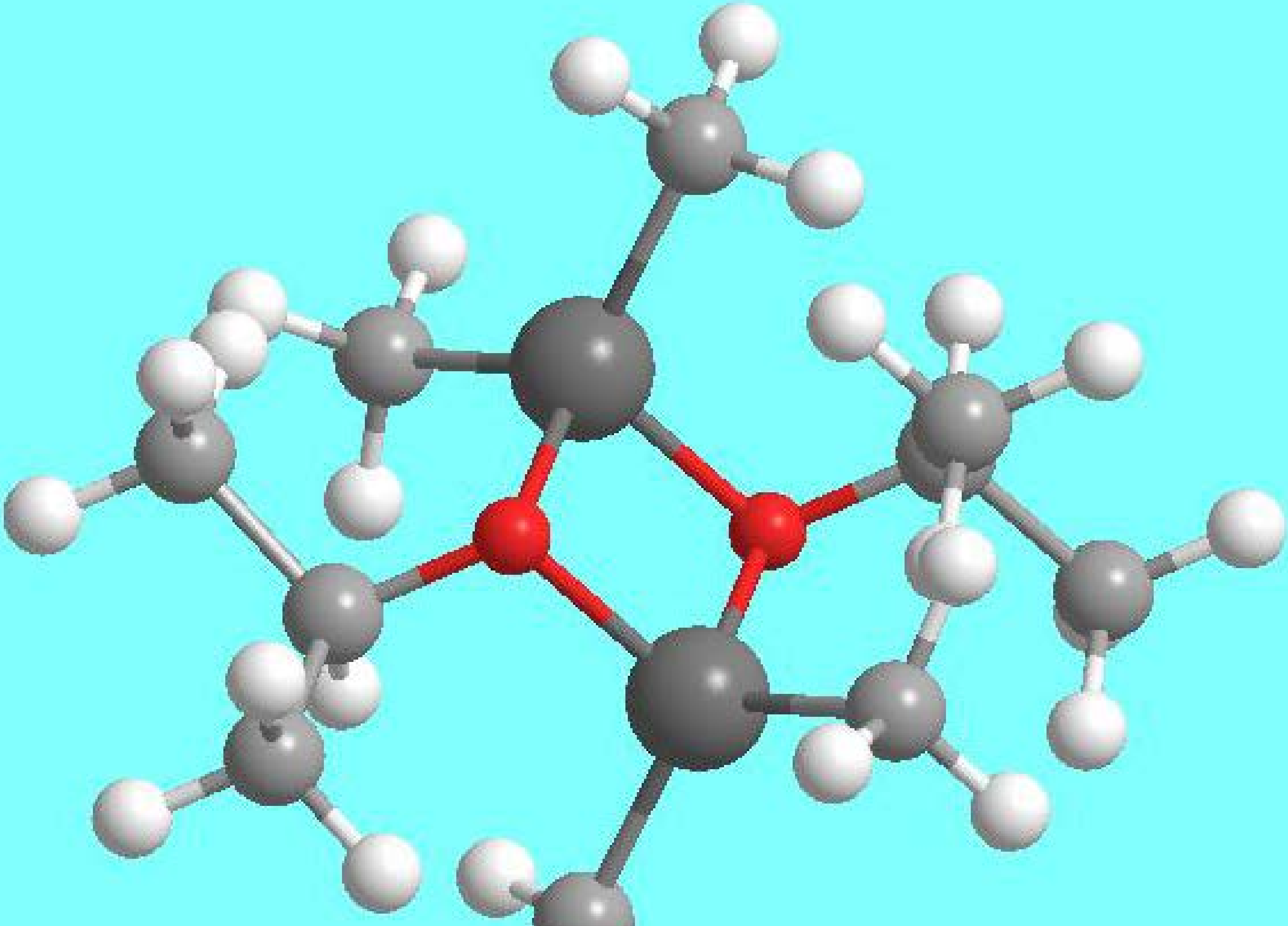
Conclusions

- **Al_2O_3 from ALD using DMAI**
  - Al–O^{i}Pr requires more thermal energy for reaction
  - Lower growth per cycle than TMA
  - ≥150 °C – equivalent to those from TMA
  - <150 °C – higher [OH], inclusion of carbonates at 25 °C

- **Al_2O_3 from DMAI affords good surface passivation of *n*- and *p*-type Si**

- **DMAI is a viable alternative to TMA**

H. B. Profijt, S. E. Potts, M. C. M. van de Sanden and W. M. M. Kessels, **Plasma-Assisted Atomic Layer Deposition: Basics, Opportunities and Challenges**, *J. Vac. Sci. Technol. A*, **29**, 050801 (2011).

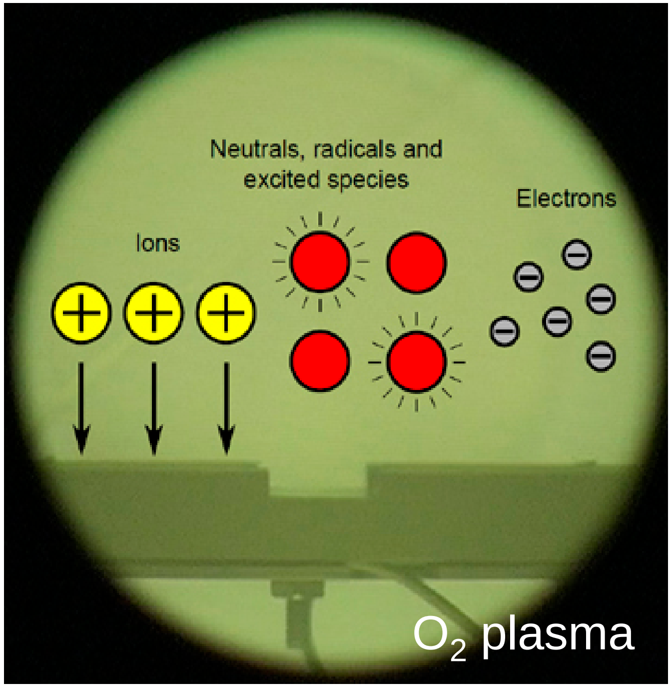


Plasma-Enhanced ALD

Plasma

- Collection of free charged particles and other gas-phase species:
  - Ions
  - Electrons

  } essential for plasma formation
  - Neutral species ("plasma radicals")
- Electrically neutral, on average
- Plasma radicals are the main reacting species with surface groups
- Degree of ionisation is typically very low, ≤0.02%



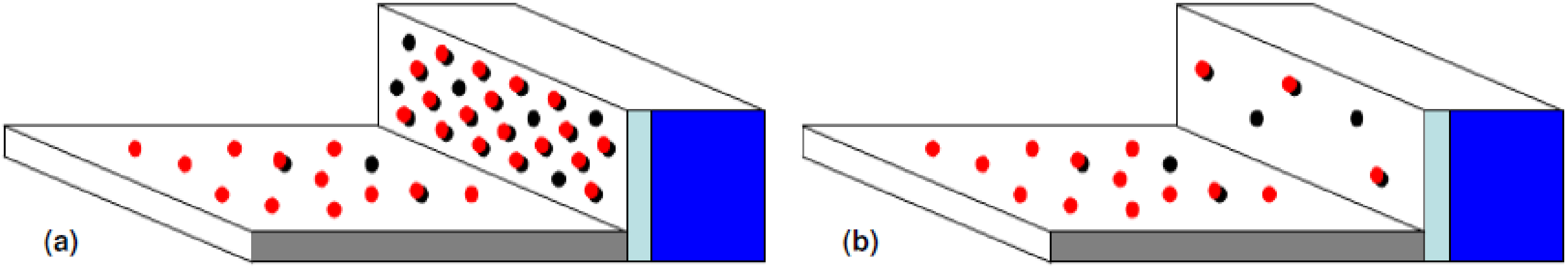
W. M. M. Kessels, H. B. Profijt, S. E. Potts and M. C. M. van de Sanden, **Plasma Atomic Layer Deposition** in *Atomic Layer Deposition of Nanostructured Materials*, editors: M. Knez and N. Pinna, Wiley-VCH, **in press** (2011).

H. B. Profijt, S. E. Potts, M. C. M. van de Sanden and W. M. M. Kessels, **Plasma-Assisted Atomic Layer Deposition: Basics, Opportunities and Challenges**, *J. Vac. Sci. Technol. A*, **29**, 050801 (2011).

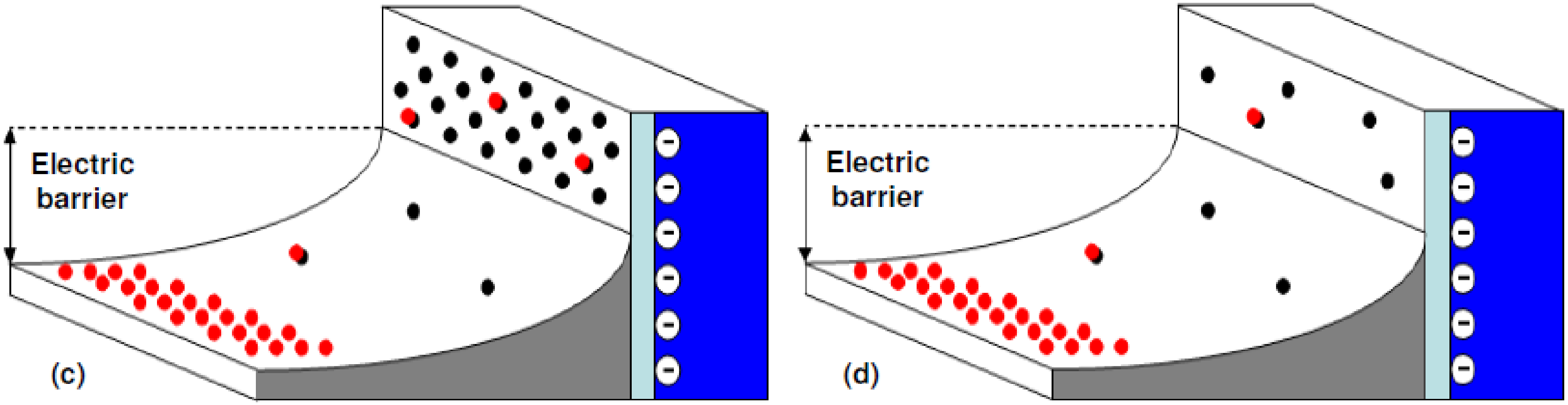
AIR LIQUIDE

TU/e Technische Universiteit Eindhoven University of Technology

c-Si Solar Cell Passivation



No passivation **Chemical passivation**



Field-effect passivation **Combined passivation (Al_2O_3)**

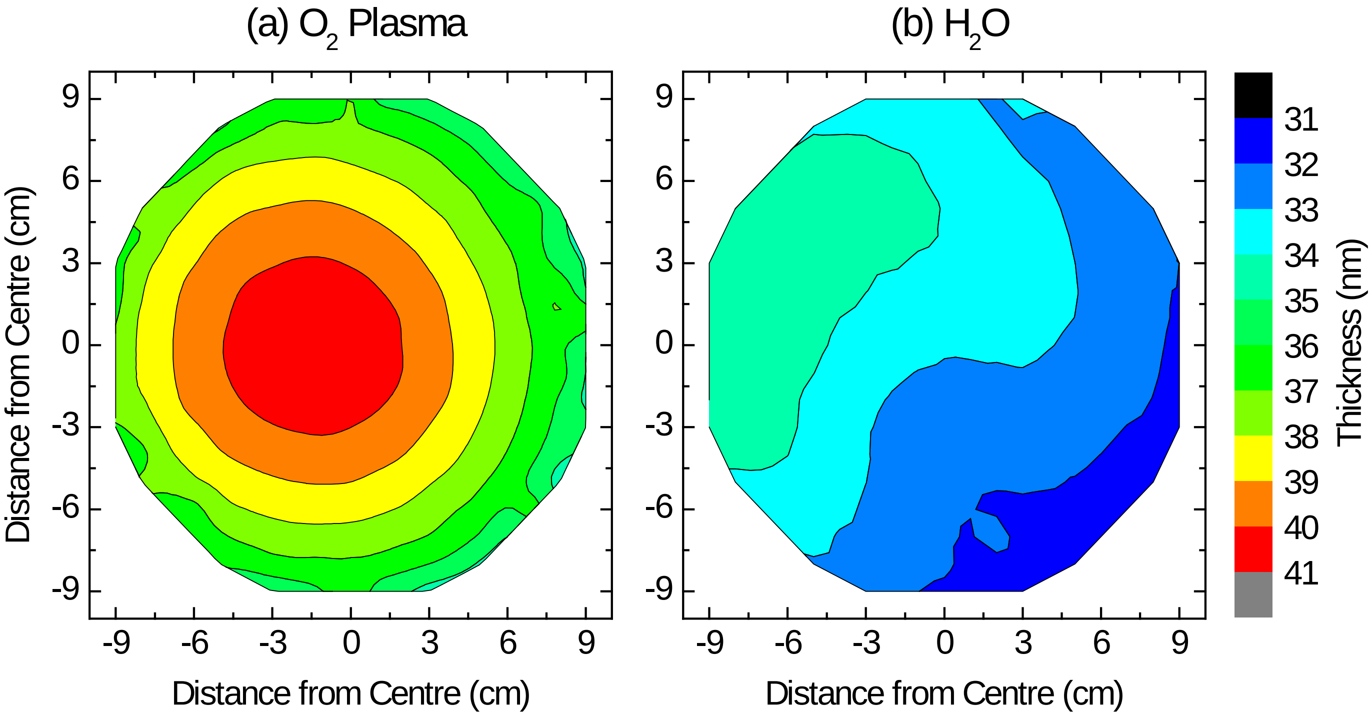
▨ *c*-Si
□ SiO_x
🟦 Al_2O_3

Uniformity (200 mm wafer)

500 cycles at 150 °C

Identical conditions to TMA.

$$Non-Uniformity = \frac{d_{max} - d_{min}}{2d_{average}} \times 100$$



Non-uniformity = 8.1%

C.f. TMA = 4.3%

Non-uniformity = 5.5%

C.f. TMA = 1.6%