Non-Pyrophoric Al Precursor for the ALD of Al_2O_3 and Al-Doped ZnO

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ALD Conference 2012, Dresden, Germany
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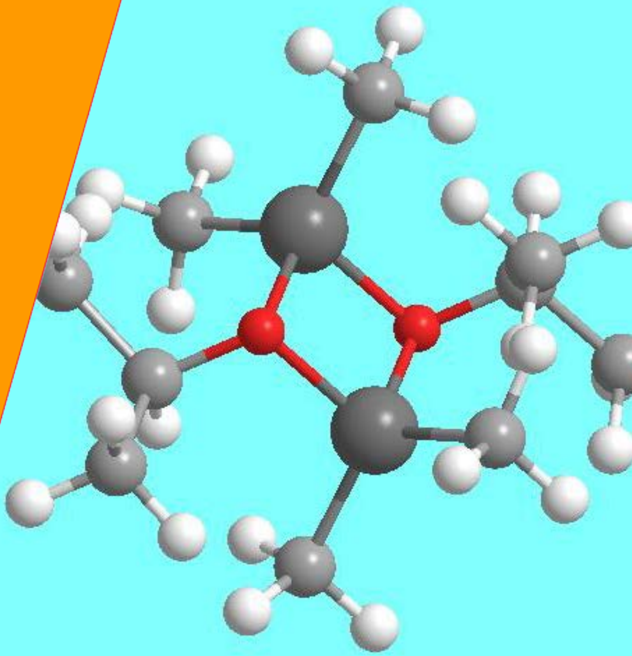

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Where innovation starts

Outline

- **Motivation**

- **Plasma-enhanced and thermal ALD characteristics of DMAI**
    - Experimental: ALD reactor
    - Temperature series study: comparison with TMA

- **Al_2O_3 from DMAI as a surface passivation layer**
    - Experimental: annealing and lifetime measurement
    - Effective lifetime of charge carriers in c-Si

- **DMAI as an Al source for ZnO:Al (AZO)**
    - Experimental: ALD supercycles
    - Resistivity as a function of Al content

- **Conclusions**

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

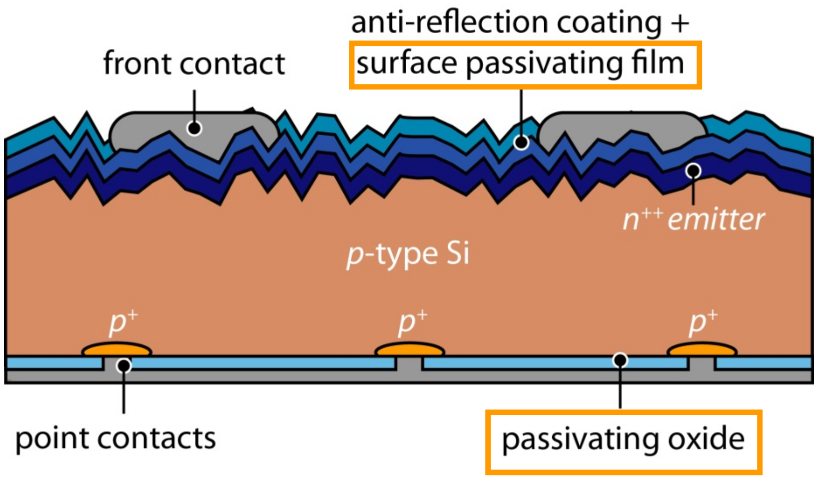
TMA: $[Al(CH_3)_3]_2$

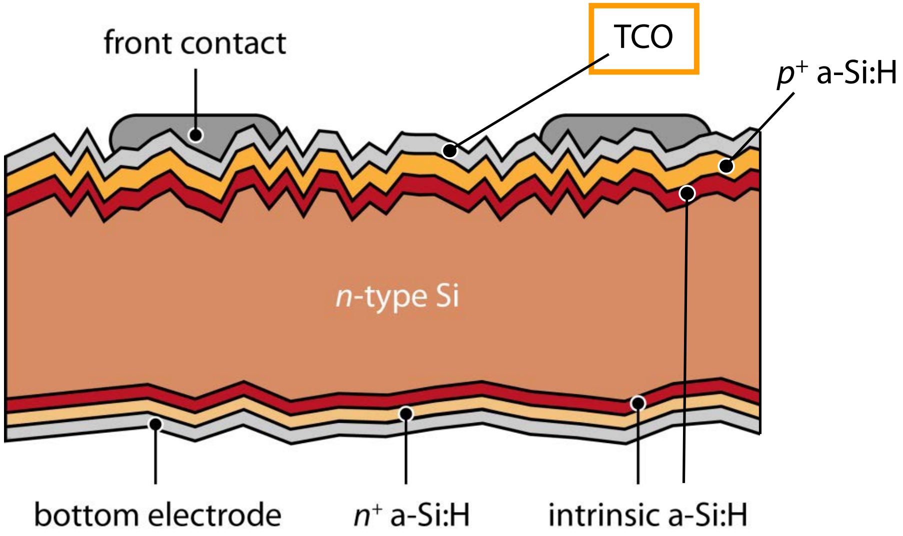
Motivation: Photovoltaics

1. **Surface passivation of polycrystalline Si solar cells**

- Thin films, e.g., Al_2O_3
- Reduces recombination losses of charge carriers

G. Dingemans *et al.*, *J. Vac. Sci. Technol. A*, **30**, in press (2012).





2. **Transparent conducting oxide (TCO) materials for front contacts**

- Low resistivity ($<10^{-3}$ Ω.cm)
- High transmittance (>80%)
- ZnO:Al (AZO) is an ideal candidate

J. A. van Delft *et al.*, *Semicond. Sci. Technol.*, **27**, in press (2012).

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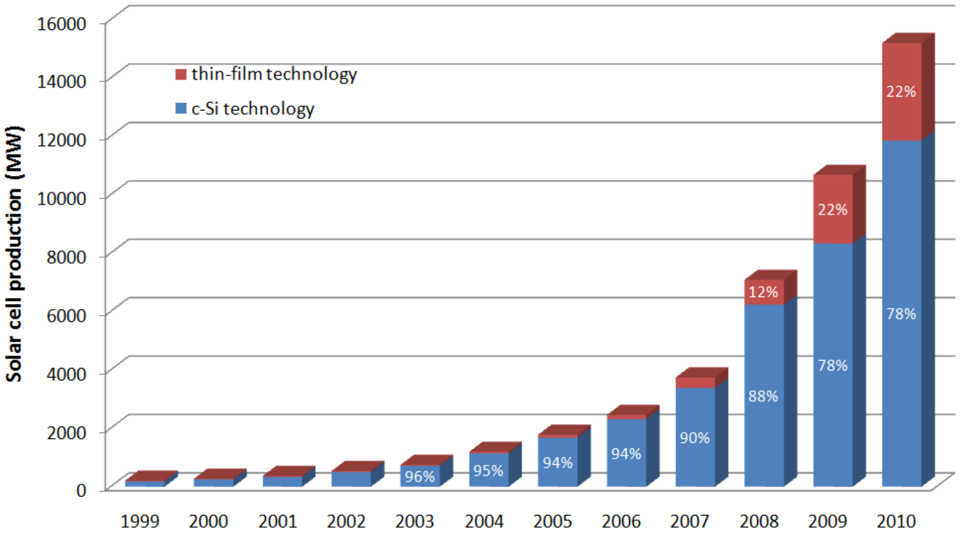
Motivation: DMAI for Photovoltaics?

- Current industrial Al precursors
  - Al_2Cl_6: source of Cl and gives corrosive by-products
  - $[Al(CH_3)_3]_2$ (TMA): 'model' ALD processes, but pyrophoric
- Safer, non-pyrophoric precursors being sought.

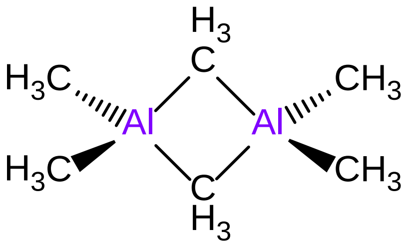
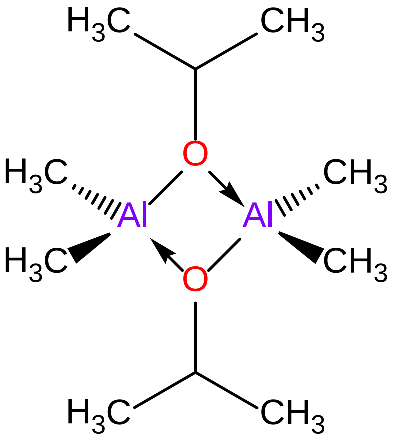


Earth policy institute (Jan. 2011); EPIA (May 2010)

- **Scale-up**
  - Vast amount of precursor required
- **Spatial ALD**
  - Carried out at atmospheric pressure

Can DMAI perform as well as TMA?

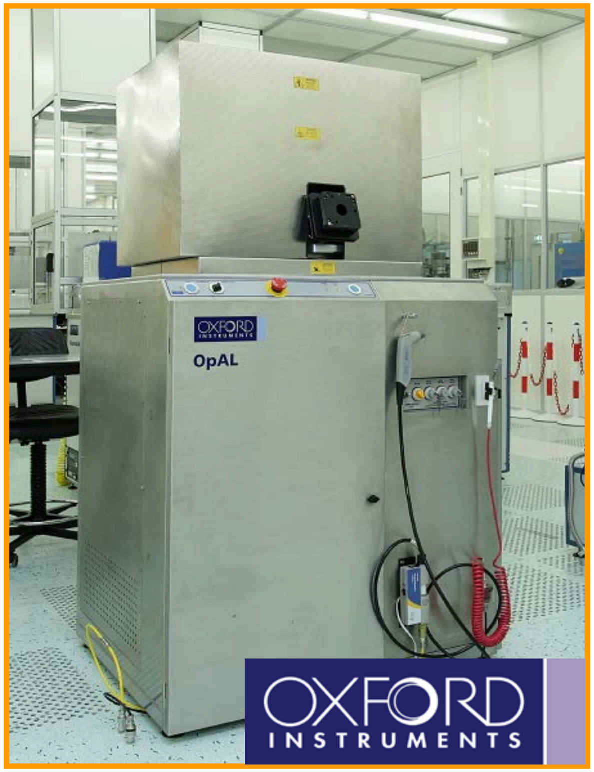
Precursor Properties

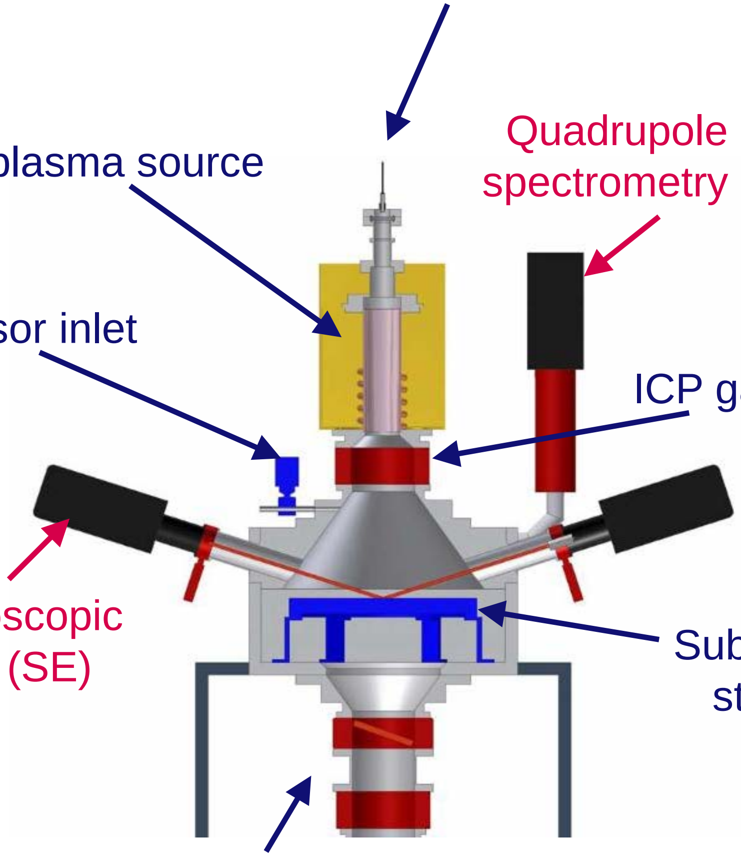
Property	**TMA**	**DMAI**
Structure	 Up to ~70 °C	
Physical State (R.T.P.)	Liquid	Liquid
Melting Point	15 °C	< R.T.
Boiling Point	125 °C	186 °C
Vapour Pressure	9 Torr at 16.8 °C	9 Torr at 66.5 °C
Decomposition Temp.	~330 °C	**~370 °C**
Pyrophoric?	Yes	**No**

Data from Air Liquide

Experimental: ALD Reactor and Diagnostics

Oxford Instruments OpAL reactor





Process gases

Remote IC plasma source

Quadrupole mass spectrometry (QMS)

Precursor inlet

ICP gate valve

In situ spectroscopic ellipsometry (SE)

Substrate stage

Rotary vane pump

Base pressure <1 mTorr

Operating pressure 100-300 mTorr

Film composition:

Rutherford backscattering spectroscopy (RBS)

X-ray photoelectron spectroscopy (XPS)

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QMS: Plasma-Enhanced ALD

DMAI pulse

$\text{s-OH} + \tfrac{1}{2}\,[\mathrm{Al(CH_3)_2(O^iPr)}]_2 \rightarrow \text{s-OAl(CH}_3\text{)(O}^i\text{Pr)} + \mathrm{CH_4}$

$\text{s-OH} + \tfrac{1}{2}\,[\mathrm{Al(CH_3)_2(O^iPr)}]_2 \rightarrow \text{s-OAl(CH}_3\text{)}_2 + \mathrm{HO^iPr}$

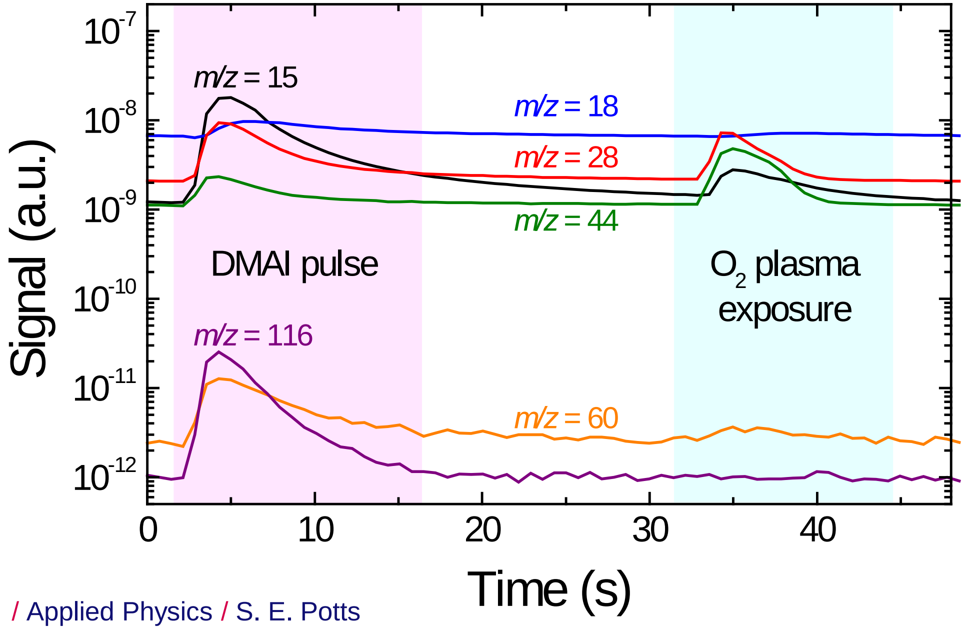
Assuming complete combustion:

O_2 plasma exposure

$\text{s-OAl(CH}_3\text{)} + 4\,\{\mathrm{O}\} \rightarrow \text{s-OAlOH} + \mathrm{CO_2} + \mathrm{H_2O}$

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

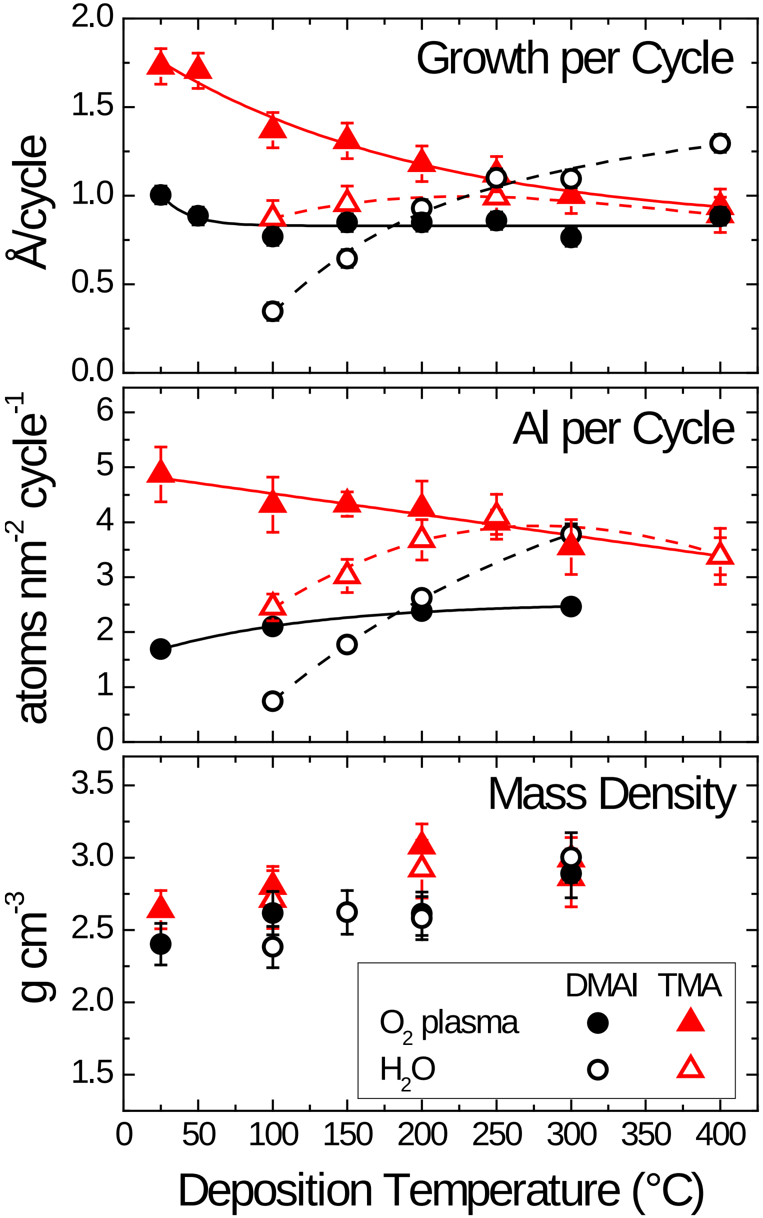
$\mathrm{H_2O} + \text{s-OAlX} \rightarrow \text{s-OAlOH} + \mathrm{HX}$ (X = $\mathrm{CH_3}$, $\mathrm{O^iPr}$)



- Comparable surface reactions to TMA
- $\mathrm{CH_4}$ and $\mathrm{HO^iPr}$ also produced during thermal ALD (not shown)

Plasma-Enhanced and Thermal ALD of Al_2O_3

TMA vs. DMAI



For more details, see:
S. E. Potts *et al.*, *J. Vac. Sci. Technol. A*, **30**, 021505 (2012).

- DMAI affords fewer Al atoms per cycle
  - Plasma ALD almost half
  - Increase of Al with temperature confirms thermal input
  - s-OH + Al–**O^{i}Pr** > s-OH + Al–**CH_3**
- Density between two precursors does not differ significantly
  - Plasma ALD films slightly denser than thermal
  - DMAI films less dense than TMA
    - More C, O, H
- Films equivalent at higher temperatures

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Experimental: Effective Lifetime Procedure

Effective Lifetime (τ_{eff})

- The lifetime of charge carriers (e^- and h^+) in the bulk silicon.
- Higher lifetimes = better passivation.

OpAL:
30 nm **ALD**
Al_2O_3

200 °C

Measure
τ_{eff}

10 min
anneal
under N_2

400 °C

Measure
τ_{eff}

Substrates

- Double-side-polished floatzone Si
- *n*- and *p*-type
- HF-dip before depositions

Effective Lifetimes

- Sinton WCT-100 Photoconductance tool

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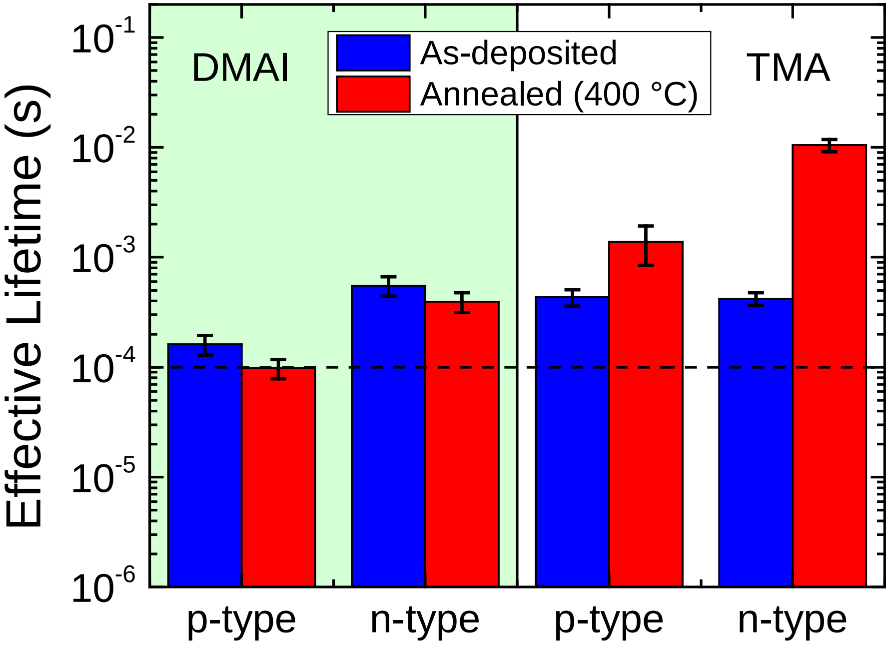
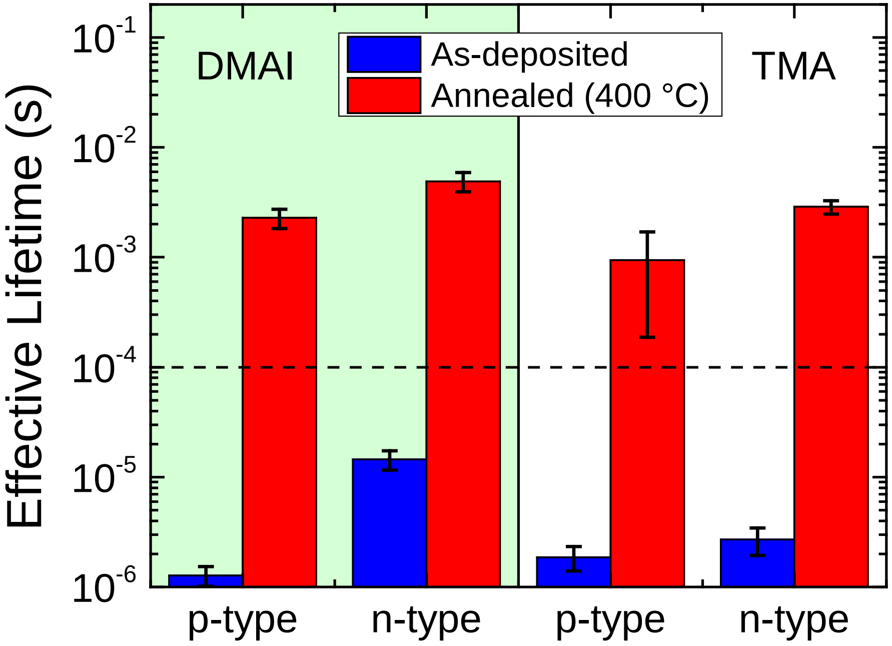
DMAI-Al_2O_3 as a Surface Passivation Layer:
Comparison with TMA

- Effective lifetimes after anneal: 0.1-5 ms with DMAI
- Good surface passivation for c-Si for solar cell applications

Thermal ALD



Plasma-Enhanced ALD

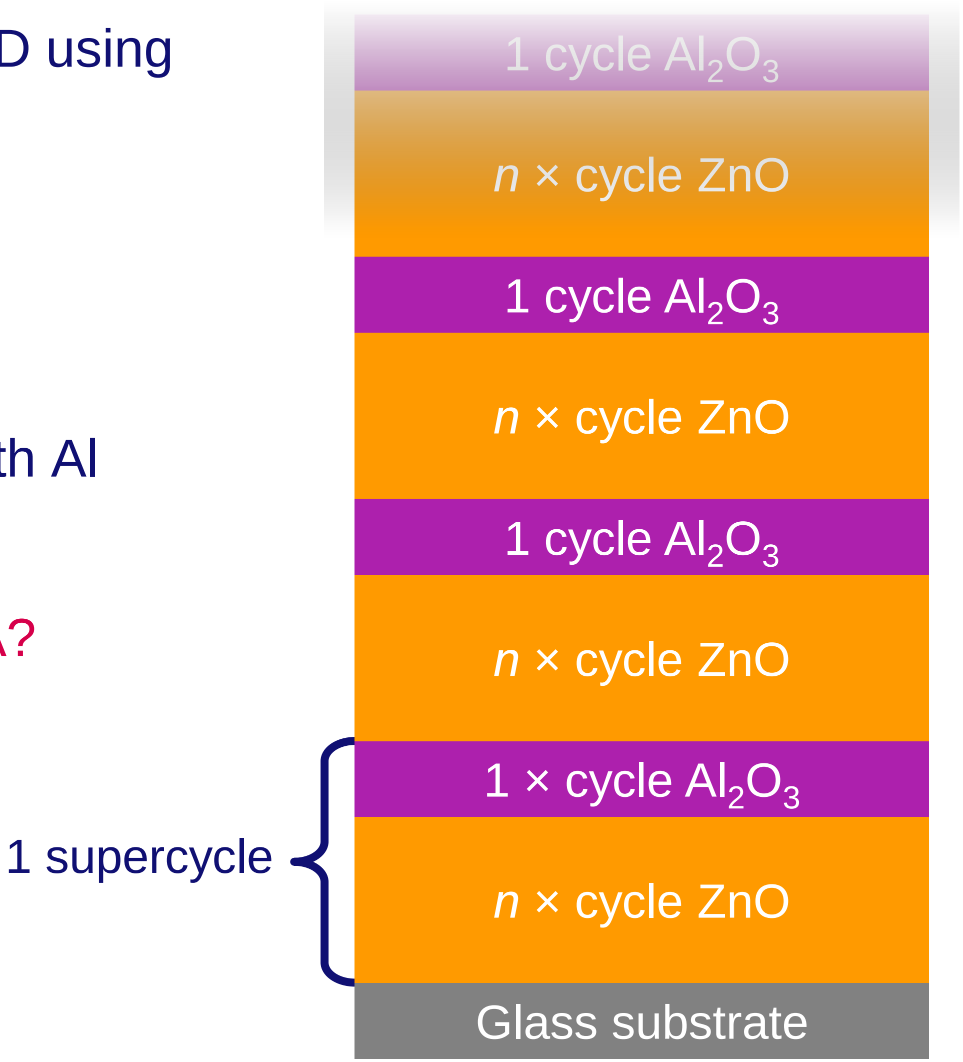


Injection (light) level = 5 × 10^{14} cm^{-3}

DMAI and TMA equivalent for plasma ALD

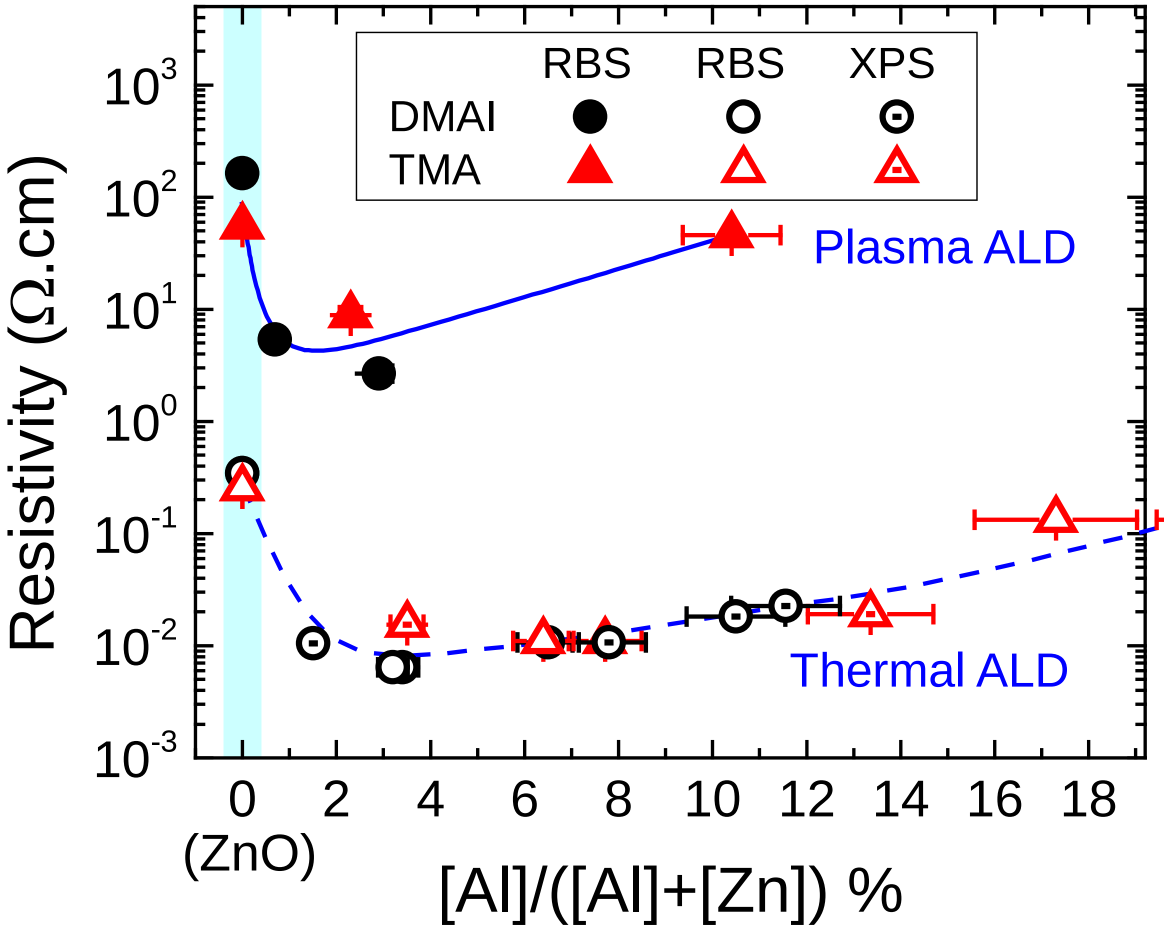
Experimental: Doping of ZnO

- Plasma-enhanced and thermal ALD using $ZnEt_2$ (DEZ) at 150 °C
- 40 nm thick films on glass
- Resistivity by four-point probe
- Aimed to replace 1-6% Zn sites with Al (RBS/XPS)
- Can DMAl perform as well as TMA?



Doping with TMA:
J. W. Elam and S. M. George., *Chem. Mater.*, **15**, 1020 (2003).
J. W. Elam *et al.*, *J. Electrochem. Soc.*, **150**, G339 (2003).
P. Banerjee *et al.*, *J. Appl. Phys.*, **108**, 043504 (2010).
C. H. Ahn *et al.*, *Thin Solid Films*, **519**, 747 (2010).
D.-J. Lee, *Adv. Funct. Mater.*, **21**, 448 (2011).

DMAl as a Dopant Source for ZnO:Al



Lines are a guide to the eye.

- **Minima at 2% Al for 40 nm thick films**
- **Plasma ALD**
  - Higher resistivities
  - More O, less H than thermal
- **Thermal ALD**
  - DMAl and TMA overlap
- **DMAl and TMA give equivalent resistivities**

Conclusions

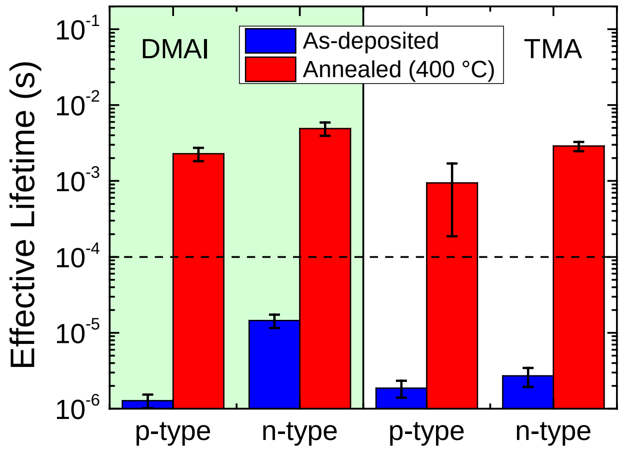
- **Al_2O_3 from ALD using DMAI**
  - Al–O^{i}Pr requires more thermal energy for reaction
  - ≥150 °C – equivalent to those from TMA

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

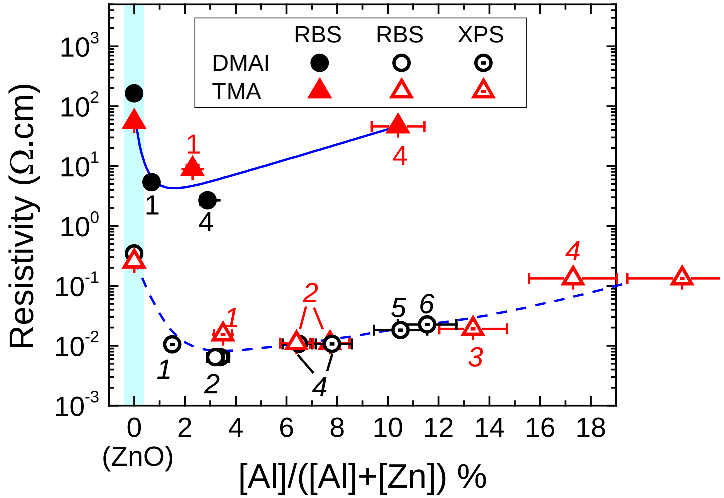
- **DMAI can be used to dope ZnO to achieve similar resistivities to those with TMA**

- **DMAI is a viable alternative to TMA for photovoltaic applications**

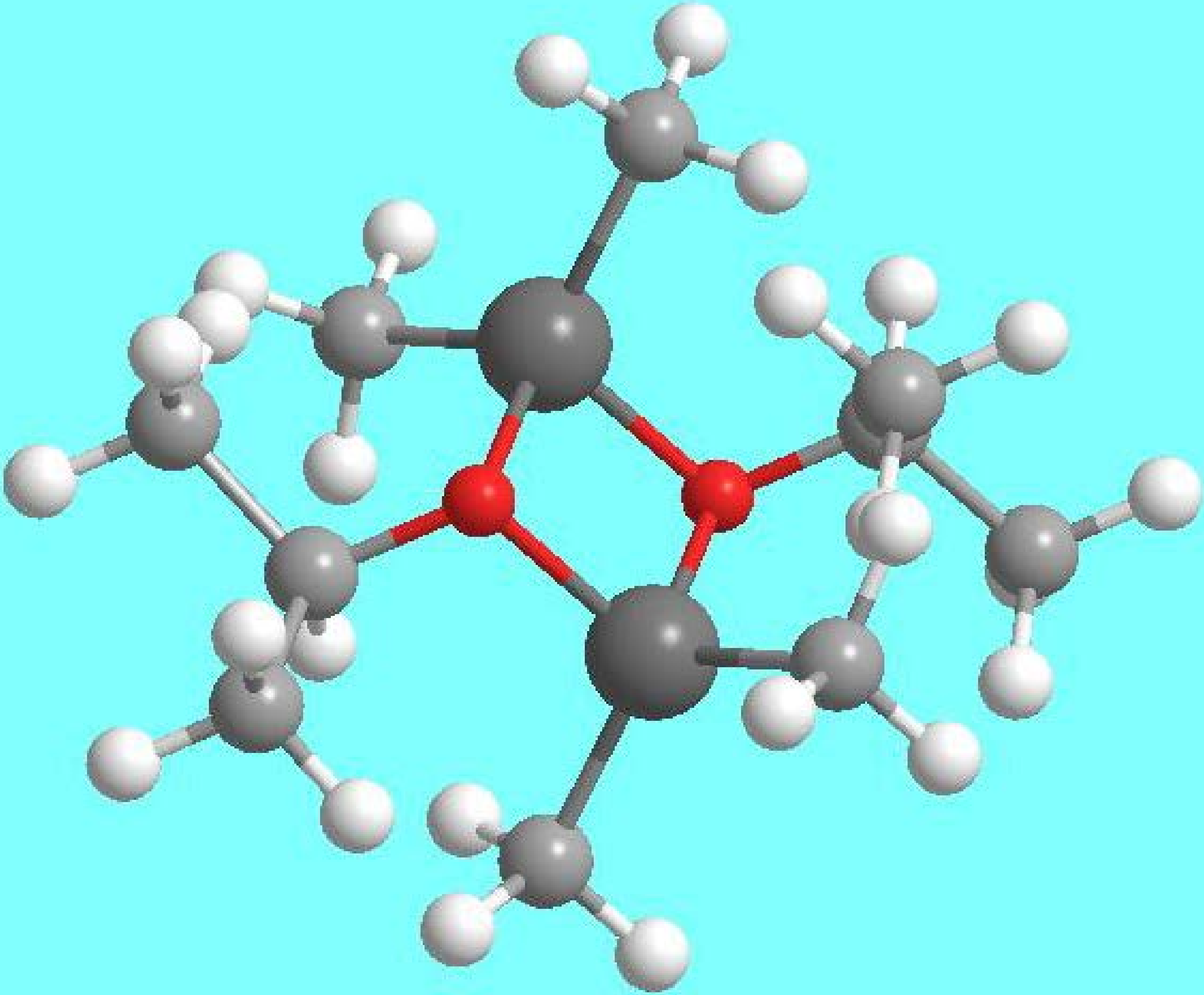
Effective Lifetimes



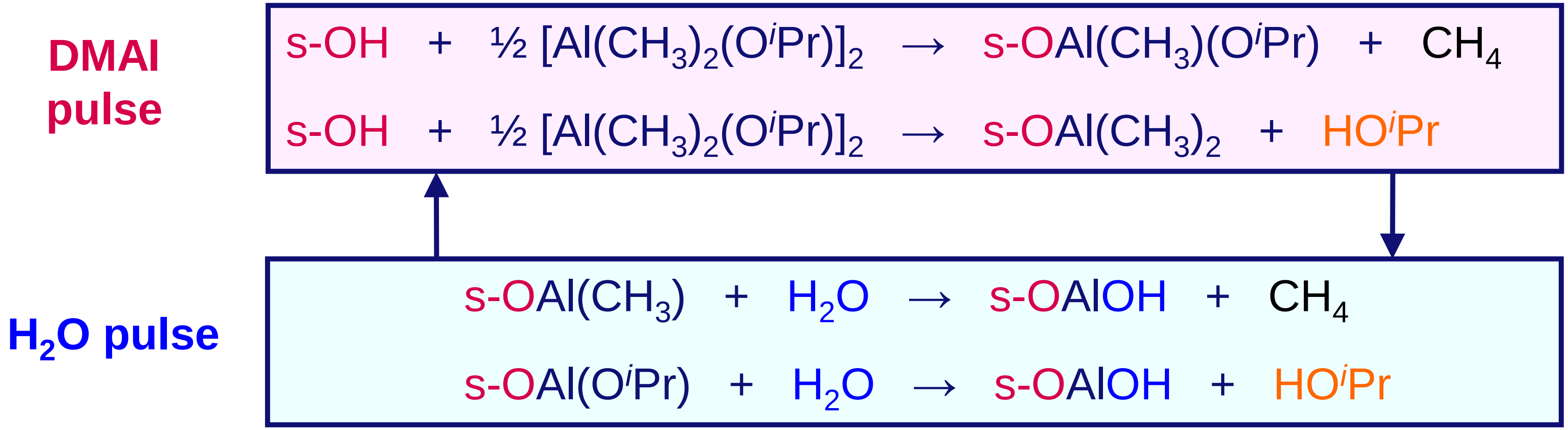
ZnO:Al Resistivities



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).



In Situ QMS: Thermal ALD



DMAI pulse

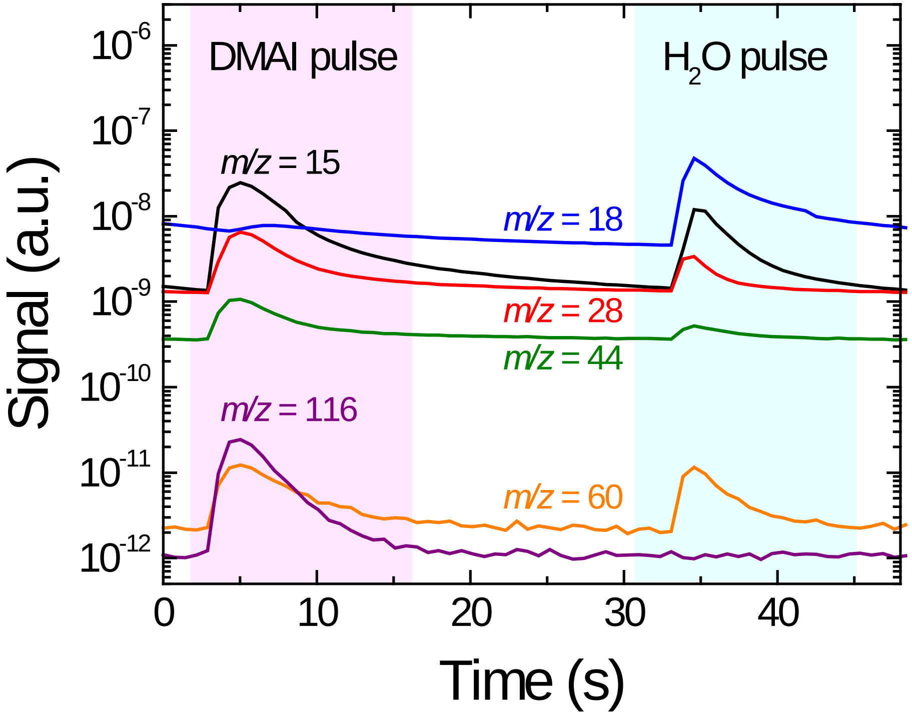
$s\text{-}OH + \frac{1}{2}\,[Al(CH_3)_2(O^iPr)]_2 \rightarrow s\text{-}OAl(CH_3)(O^iPr) + CH_4$

$s\text{-}OH + \frac{1}{2}\,[Al(CH_3)_2(O^iPr)]_2 \rightarrow s\text{-}OAl(CH_3)_2 + HO^iPr$

H_2O pulse

$s\text{-}OAl(CH_3) + H_2O \rightarrow s\text{-}OAlOH + CH_4$

$s\text{-}OAl(O^iPr) + H_2O \rightarrow s\text{-}OAlOH + HO^iPr$



- 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).

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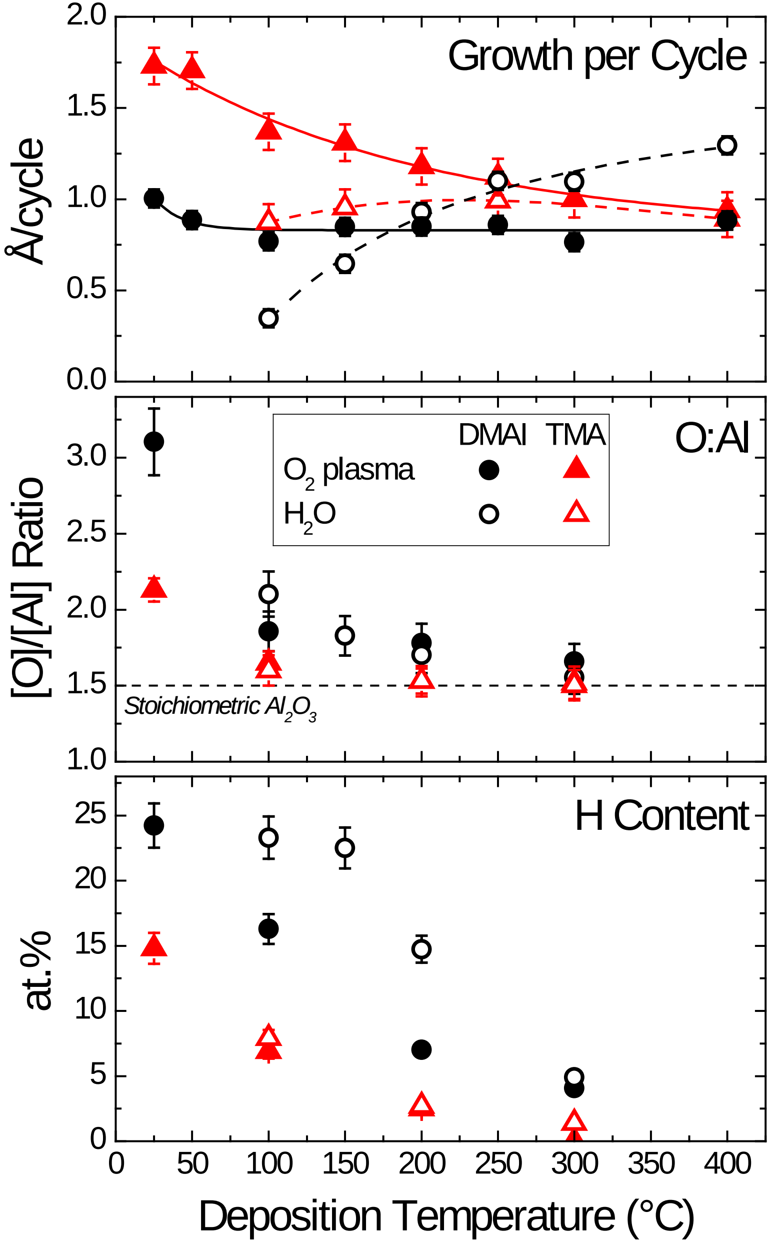
Film Composition



- 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^iPr

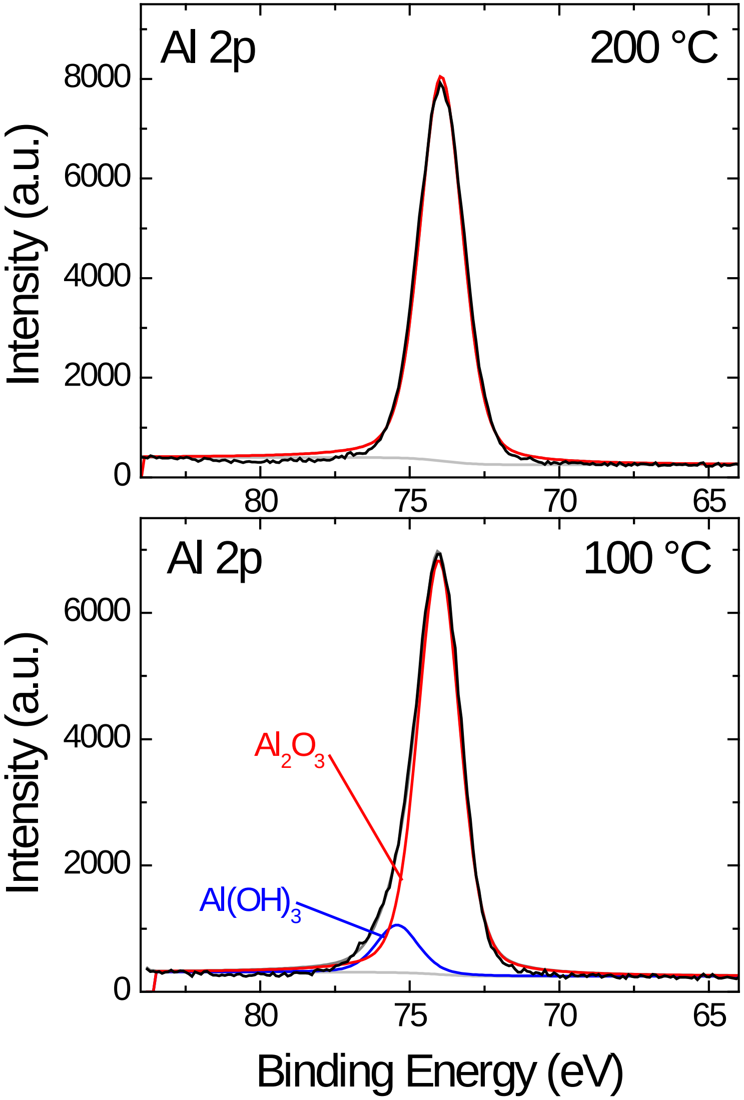
XPS: Thermal ALD

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

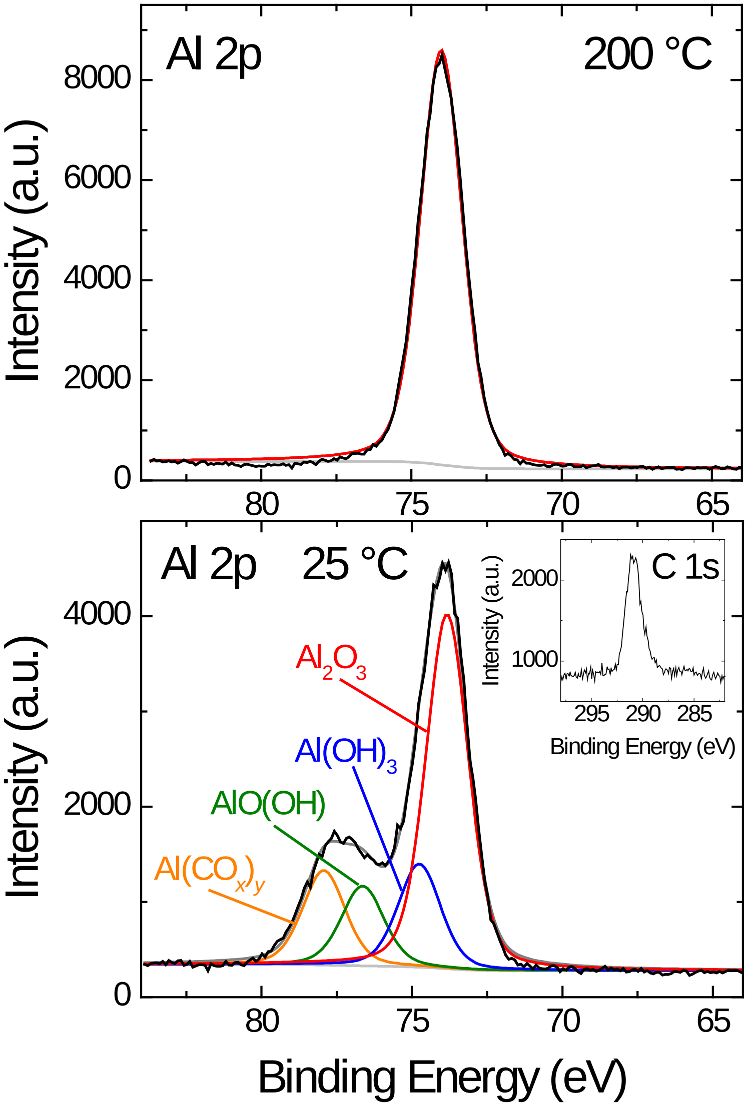
200 °C ‘standard temperature’

- 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

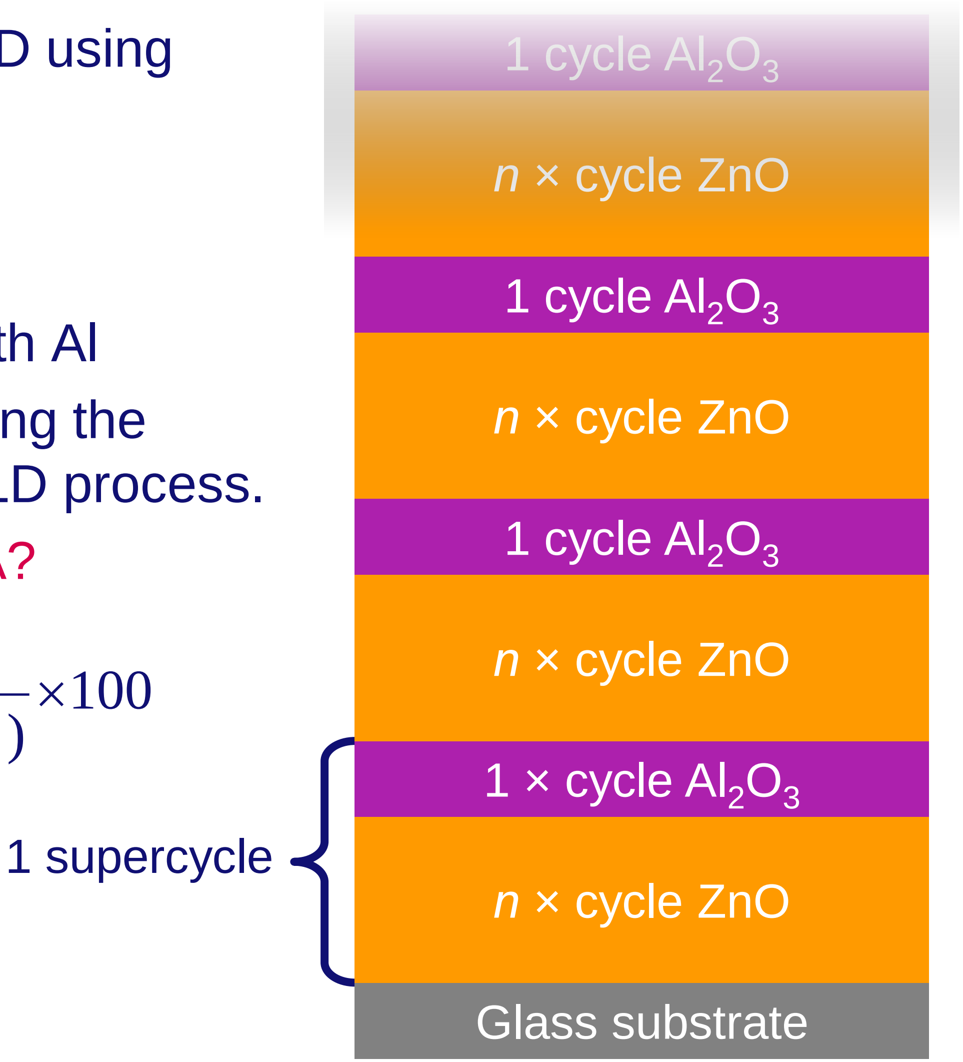


Al assignments: T. Gougousi *et al.*, *Chem. Mater.*, **17**, 5903 (2005).

Experimental: Doping of ZnO

- Plasma-enhanced and thermal ALD using ZnEt$_2$ (DEZ) at 150 °C
- 40 nm thick films
- Resistivity by four-point probe
- Aimed to replace 1-6% Zn sites with Al
- Nominal Al content determined using the growth per cycle (GPC) of each ALD process.
- Can DMAI perform as well as TMA?

$$\text{Fraction Al}^{\%}_{\text{Nominal}} = \frac{GPC_{Al}}{GPC_{Al} + (n \times GPC_{Zn})} \times 100$$



1 cycle Al$_2$O$_3$

n × cycle ZnO

1 cycle Al$_2$O$_3$

n × cycle ZnO

1 cycle Al$_2$O$_3$

n × cycle ZnO

1 supercycle

1 × cycle Al$_2$O$_3$

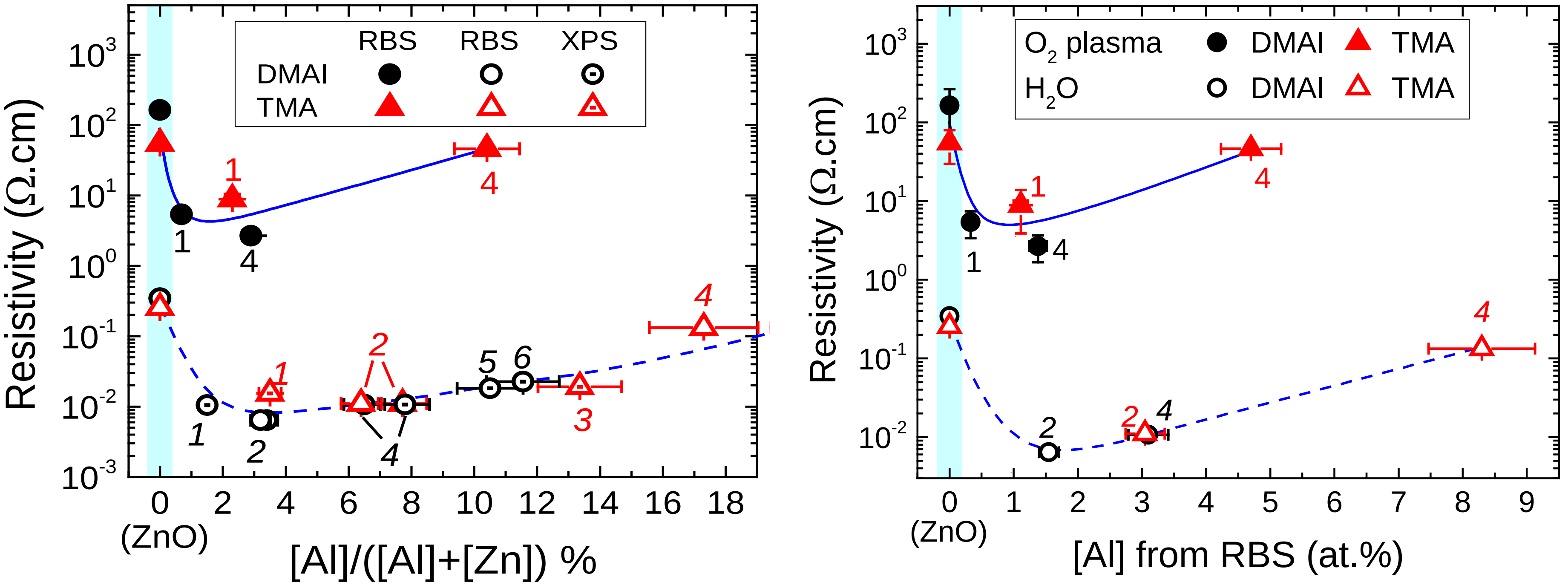
n × cycle ZnO

Glass substrate

Doping with TMA:

J. W. Elam and S. M. George., *Chem. Mater.*, **15**, 1020 (2003).
J. W. Elam *et al.*, *J. Electrochem. Soc.*, **150**, G339 (2003).
P. Banerjee *et al.*, *J. Appl. Phys.*, **108**, 043504 (2010).
C. H. Ahn *et al.*, *Thin Solid Films*, **519**, 747 (2010).
D.-J. Lee, *Adv. Funct. Mater.*, **21**, 448 (2011).

Resistivities as a Function of Atomic Percent



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