Introduction to ALD

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Outline

1. The need for atomic layer deposition (ALD)

2. What is ALD? - ALD of Al$_2$O$_3$ illustrated

3. Materials that can be deposited by ALD

4. A few words on ALD equipment
Very demanding applications

Nanoelectronics

Flexible electronics

Protective thin films

Photovoltaics
Vapor phase deposition technologies

Physical Vapor Deposition (PVD) – sputtering –

Chemical Vapor Deposition (CVD)

Energetic ions! Heat!
Increased growth control required

Atomic layer deposition (ALD)

Vapor-phase deposition technique of metal oxides, sulfides, nitrides & metals:
1. Cycle wise, atomic layer-by-layer growth (typically 0.5-1 Å per cycle)
2. Self-limiting (saturating) surface reactions ruled by surface chemistry
3. ALD yields precise growth control, excellent conformality and uniformity
4. Substrate temperature typically 150-400 °C
Atomic layer deposition (ALD) of Al₂O₃ - movie
Thickness versus ALD cycles (Al$_2$O$_3$)

Slope:
Growth-per-cycle (GPC) = ~1 Å/cycle
ALD saturation curves (Al₂O₃)

1. Precursor
2. Purge
3. Reactant
4. Purge

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ALD surface chemistry ($\text{Al}_2\text{O}_3$)

1. Precursor
2. Purge
3. Reactant
4. Purge

- Mass spectrometry signal (A)
- Time (s)
- Infrared absorbance
- Wavenumber (cm$^{-1}$)
- OH stretching
- CH$_x$ stretching
- CH$_x$ deformation
- H$_2$O dosing

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**ALD surface chemistry (Al$_2$O$_3$)**

A: $\text{AlOH}^* + \text{Al}(\text{CH}_3)_3 \rightarrow \text{AlOAl}(\text{CH}_3)_2^* + \text{CH}_4$

B: $\text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{AlOH}^* + \text{CH}_4$

* are surface species
ALD process: substrate temperature (ideal case)

A. Condensation
B. Insufficient thermal energy
C. CVD
D. Evaporation

Substrate/film surface
ALD temperature window ($\text{Al}_2\text{O}_3$)

(a) Growth rate (nm/cycle)

(b) # Al atoms per cycle ($10^{15} \text{ cm}^{-2}$)

Energy-enhanced ALD (O₂ plasma or O₃)

More Precursor Freedom

Energy-Enhanced
Atomic Layer Deposition

Plasma

Low-Temperature ALD Enabled

Ozone

Room-Temperature ALD

25°C

CVD

>= 200°C

<= 150°C

<= 150°C ALD Enabled

25°C

H₃C

H₃C

H₃C

H₃C

H₃C

H₃C
ALD of metal oxides

1. Al(CH₃)₃
2. SiH₂{N(C₂H₅)}₂
3. Ta{N(CH₃)₂}₅
4. Zn(CH₂CH₃)₂
5. Ti(Cp*)(OCH₃)₃

Film thickness is ruled by the number of cycles chosen

H₂O, O₃ or O₂ plasma

H₂O, O₃ or O₂ plasma

ALD of metals and nitrides

Pt

(MeCp)PtMe₃ + O₂

Ru

CpRuEt(CO)₂ + O₂

Pd

Pd(hfac)₂ + H₂ plasma

TiN

TiCl₄ + H₂-N₂ plasma

TaN

Ta(NMe)₅ + H₂ plasma

SiNₓ

SiH₂(NHᵗBu) + N₂ plasma
Materials deposited by ALD

Periodic Table | ALD Films

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<th>Symbol</th>
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Recipe for this material is available from CNT staff or customer base.

Website: www.cambridgenanotechald.com

Surface controlled vs. flux controlled

(a) Surface controlled

(b) Flux controlled

uniformity

conformality

Nanolayers

Al₂O₃ film in vias

Double TiN/Al₂O₃ stack in trench

Al₂O₃ and ZnO on GaP nanowires

Planar Pt/SrTiO₃/Pt stack

Hoogeland et al., ECS Trans. 25(4), 389 (2009)
Nucleation delay for metals

Metals (on oxides) show typically a considerable long nucleation delay

\[(\text{CpCH}_3)\text{Pt(CH}_3)_3\]

\[+\]

\[\text{O}_2\]

(pressure varied)

Nucleation delay: from nanoparticles to film

ALD of Pt (300 °C) on Al₂O₃

- < 100 cycles: Island size and density increases.
- 100 - 150 cycles: Island coalescence
- > 200 cycles: Film closure

Nanoparticles

Pt nanoparticles on InP nanowires

Pd-Pt core-shell nanoparticles

Bimetallic Pt-Ru nanoparticles on multiwall carbon nanotubes

Weber et al., Chem. Mater. 24, 2973 (2012)
Johansson et al., J. Catalysis 311, 481 (2013)
(Plasma) ALD reactor

Oxford Instruments OpAL reactor
ALD reactors

Flow-type

Single wafer • Thermal • Temporal

Batch

Energy Enhanced

Spatial

Kessels et al., MRS Bulletin 36, 907 (2011)
Knoops et al., Handbook of Crystal Growth, 2nd edition (Oct. 2014)
ALD reactors

Flow-type

Showerhead

Temporal

Time $t$

Spatial

Position $x$

Kessels et al., MRS Bulletin 36, 907 (2011)
Knoops et al., Handbook of Crystal Growth, 2nd edition (Oct. 2014)
Regular and advanced ALD cycle configurations

(a) Regular

\((AB)_m\)

(b) Multistep

\((ABC)_m\)

(c) Supercycle

\(((A1B1)_m(A2B2)_n)_x\)

- Purge
- Time
- \(m\) cycles
- \(n\) cycles
- \(x\) supercycles