An Introduction to Atomic Layer Deposition

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What is a Thin Film?

Thin film: thickness typically <1000nm.

Special properties of thin films: different from bulk materials, it may be –

• Not fully dense
• Under stress
• Different defect structures from bulk
• Quasi - two dimensional (very thin films)
• Strongly influenced by surface and interface effects
Other Deposition Techniques

1. Precursor gas phase reaction
2. Diffusion
3. Adsorption
4. Surface Process
5. Desorption
6. Diffusion
7. Purge

CVD Process

- Bare Substrate
- Step 1
- Step 2
- Step 3
- Step 4
- Step 5
- Step 6
- Step 7
- Sputtering Gas
- Thin Film
- Substrate

- Sputtering Target
- Sputtered Target Atom
- Ar^+
- U^+

Heated Material

Vacuum Chamber

- Wafers
- Rough Pump
- Cryo or Turbo Pump

Air Inlet

Valve

Valve
Common Denominator

- Deposition only occurs on substrates that “see” the target.
- Plasma process can damage the substrate
- Poor thickness control
- Poor Step Control
- High Pressure High Temperature Environment

**Step Coverage Example**

![Step Coverage Diagram](image)

Step coverage of metal over non-planar topography.

(a) Conformal step coverage, with constant thickness on horizontal and vertical surfaces.
(b) Poor step coverage, here thinner for vertical surfaces.
Introduction

Atomic Layer Deposition

A thin film “nanomanufacturing” tool that allows for the conformal coating materials on a myriad of surfaces with precise atomic thickness control.

Based on:

- Paired gas surface reaction chemistries
- Benign non-destructive temperature and pressure environment
  - Room temperature -> 250 °C (even lower around 45 °C)
  - Vacuum
ALD Procedure

Introduction of Precursor

Random Precursor Surface Rxn

Surface Limited State

Purge Excess & Reacted Species

Cycle

Introduction of Precursor

Surface Limited State

Random Precursor Surface Rxn

Purge Excess & Reacted Species

1-Cycle

1Pair Stacked Chips
ALD Procedure

1.1 Å / Cycle

OH + Al(CH₃)₃ -> O-Al(CH₃)₂ + CH₄

O-Al(CH₃)₂ + 2H₂O -> O-Al-(OH)₂ + 2CH₄

Al₂O₃
Periodic Table of ALD Films

Acknowledgements
• Elam, Jeffrey (2007). ALD Thin Film Materials. Argonne National Laboratory
Advantageous Property

Precise Thickness Control

Thickness = \( F (\# \text{ monolayers}) \)

Example:

If 1 monolayer = 1 Å

\# monolayers = 7

 Thickness = 7 Å

Reproducibility
Advantageous Property

Substrate Independence
Advantageous Property

**Epitaxial Growth**

Artificial trench filled with an ALD nanolaminate. Image courtesy of NASA Ames Research Center.

![Schematic of a 3D battery integrated in a Si substrate.](image1)

The cross-section shows the various functional layers in the battery stack as well as the candidate materials: AlOx, TiOx, etc. [Kuo, N.C. et al., ECS Trans., 33 (2009), pp. 333-344]

**Batch Process**

Multilayer consisting of:
- AlOx - 25 nm
- TiN - 10 nm
- Al2O3 - 25 nm

![Multilayer structure](image2)


Casting Silver with Aluminum Oxide: [http://www.glassome.com](http://www.glassome.com)
Building off a Commercial Reactor

Commercial Options
In-House Experimental ALD System
Applications and Results

~1600 Au Coated Mirrors
4x10” curved
50 cm/20”diameter cartridge

Effective area comparison

Gold+Al₂O₃ mirror
Gold mirror
Calorimeter system effective area
ZnO

\[ E = \frac{hc}{\lambda} \text{ where:} \]

- \( f \) = frequency in Hertz (Hz = \( \frac{1}{\text{sec}} \))
- \( \lambda \) = wavelength in meters (m)
- \( c \) = the speed of light (299792458 m/s)
- \( E \) = energy in electron Volts (eV)
- \( h \) = Plank’s constant (6.626068 \( \times 10^{-34} \) m\(^2\)kg/s)

\[ E_{\text{ZnO}} = 3.3 \text{ eV} \]
\[ \lambda_{\text{ZnO}} \approx 375 \text{ nm} \]
Blacker Than Black Carbon Nanotubes

Substrate + Catalyst + Gas = CNNT
Si,Ti, flat, 3d + Iron + Ethylene

Blacker than NASA Z306 Paint 10X Darker
“Build” Nanotubes

Formation of nanostructured catalytic membrane from AAO Els, Snurr, co-workers

AAO

AO Pore 40 nm

Shrink Pore

Deposition of Catalytic Support

Deposition of Catalyst

NCM

20-400 nm

0.5 - 250 μm

Reactant

Product

Oxidative Dehydrogenation (Alkane to Alkene)

Formation of nanotubes: Rubloff Group

Nano capacitor elements by Lee, Rubloff, coworkers. Nature 2008-09
Atomic Oxygen Protection

100 nm on Kapton
1000 Cycles
155 ºC
Al₂O₃

GPM Funded an experiment at Glenn to determine AO effects on materials.

99% mass retention after a simulated 5 year flux
Strategic Partnerships

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Questions?