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

CVD Process

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

Diagram of CVD Process:
- Step 1: Bare Substrate
- Step 2: Sputtering Gas
- Step 3: Thin Film
- Step 4: Sputtering Target
- Step 5: Sputtered Target Atom
- Step 6: Vent
- Step 7: Substrate

Diagram of Vacuum Chamber:
- Wafers
- Heated Material
- Vacuum Chamber
- Rough Pump
- Cryo or Turbo Pump

Diagram of Sputtering Process:
- Sputtering Gas
- Sputtering Target
- Sputtered Target Atom
- Thin Film
- Substrate
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 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

1.1 Å / Cycle

OH + Al(CH₃)₃ → O-Al(CH₃)₂ + CH₄

O-Al(CH₃)₂ + 2H₂O → O-Al-(OH)₂ + 2CH₄
Periodic Table of ALD Films

Acknowledgements

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

Precise Thickness Control

Thickness = \( F \) (# monolayers)

Example:

If 1 monolayer = 1 Å

# monolayers = 7

Thickness = 7 Å

Reproducibility
Advantageous Property

Substrate Independence
Advantageous Property

Epitaxial Growth

Batch Process

Artificial trench filled with an ALD nanolaminate.

Schematic of a 3D battery integrated in a Si substrate. The cross-section shows the various functional layers in the battery stack as well as the candidate materials. Kim, J.C., et al., ECS Trans., 33 (2013), pp. 333-344.

Multilayer consisting of:
- N2O2 - 25 nm
- TIN - 10 nm
- Al2O3 - 25 nm

Coating Silver with Aluminum Oxide: http://www.glasswebsites.com/
Building off a Commercial Reactor

Commercial Options
In-House Experimental ALD System
Open Source Solutions

Init Software Object

Define Scan Rate
Ar On/Off
DAQ On/Off

Define Arrays:
Precursors
Pulse Time
Wait Time
Cycles

Generate Valve State Map for One Cycle

Calculate Buffer Allocation

End

Calculate Buffer Size

Step Through the Valve States

Buffer > 1/2

Yes

Iterator = Cycles

No

Yes

No: Iterator += 1

Load The State Map into Labjack

No

Yes
Applications and Results

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

Effective area comparison

Gold+Al$_2$O$_3$ mirror
Gold mirror

Calorimeter system effective area

energy [keV]

effective area [cm$^2$]

0 100 200 300 400
0 2 4 6 8 10
\[ E = \frac{hc}{\lambda} \]

where:
- \( f \) = frequency in Hertz (Hz = \( 1/\text{sec} \))
- \( \lambda \) = 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 Elsm, Snurr, co-workers

AAO

AAO Pore 40 nm
Shrink Pore
Deposition of Catalytic Support
Deposition of Catalyst
NCM

20 - 400 nm
0.5 - 250 μm

reactant

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 °C
$\text{Al}_2\text{O}_3$

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

99% mass retention after a simulated 5 year flux
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Any Questions?