Atomic Layer Deposition (ALD) - An Enabling Technology for NASA Space Systems

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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

Bare Substrate

Step 1

Step 2

Step 3

Step 4

Step 5

Step 6

Step 7

Step 8

Vent

Sputtering Gas

Thin Film

Substrate

Wafers

Vacuum Chamber

Heated Material

Rough Pump

Cryo or Turbo Pump

Air Inlet
Thin-Film Engineering

Vapor-phase deposition of inorganic materials

Microelectronics

Solar energy

Solid-state lighting

James River Semiconductor

First Solar

The New Ecologist
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.
Atomic Layer Deposition

A thin film “nanomanufacturing” tool that allows for the conformal coating of 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 Analogy (Checkers)

- Introduction of Precursor
- 1 Pair Stacked Chips
- Purge Excess & Reacted Species
- Random Precursor Surface Rxn
- Surface Limited State
- Cycle
- Surface Limited State
- Random Precursor Surface Rxn
- Purge Excess & Reacted Species
ALD Analogy Chemistry

1.1 Å / Cycle

\[ \text{OH} + \text{Al(CH₃)₃} \rightarrow 0\text{-Al(CH₃)₂} + \text{CH₄} \]

\[ 0\text{-Al(CH₃)₂} + 2\text{H₂O} \rightarrow 0\text{-Al(OH)₂} + 2\text{CH₄} \]
Precursor A + Precursor B → Solid film + Gas by-products
Cyclic operation: A → purge → B → purge → A → purge → ...

Atomic-level thickness control ...

... equivalent to a 60 μm layer over a city-sized wafer
ALD Advantageous Property

Epitaxial Growth

Batch Process

Substrate Independence

Multilayer consisting of:
- Al₂O₃ - 25 nm
- TIN - 20 nm
- Al₂O₃ - 25 nm

In the battery stack, as well as the candidate materials, always Al₂O₃/Al₂O₃/Al₂O₃ from 20 to 200 nm. See for more details.

Schematic of a 3D battery integrated in a Si-substrate.
• Elam, Jeffrey (2007). ALD Thin Film Materials. Argonne National Laboratory
An image labeled NASA Impacts shows a section with the following details:

**ISS Orbit 400 km**

Atomic O Density = $1 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$

$v = 7.2 \times 10^5 \text{ cm s}^{-1}$

$\rightarrow 1 \text{ O impact nm}^{-2} \text{ s}^{-1}$

KE = 4.2 eV

**Alumina ALD on Kapton substrate**

$$\text{Al}_2(\text{CH}_3)_6 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4$$

- Conformal, flexible, $O(100 \text{ nm})$, **nonvolatile oxide** coating
- Low temperature (100 °C) deposition process
**Ni ALD**

\[
\text{Ni(acac)}_2(g) + \text{MeOH}(g) \rightarrow \text{Ni}(s) + 2\text{Hacac}(g) + \text{CH}_2\text{O}(g)
\]
ZnO

UV Absorption

The graph shows the UV absorption of ZnO treated with different cycles. The x-axis represents the wavelength in nm, and the y-axis represents the absorption in a percentage scale. The treatments include Bare Quartz, 100 Cycles, 250 Cycles, and 500 Cycles.
ALD For Radiators - Pigments

Diagram showing a system with a Pressure Transducer, Precursor Injection, Pigments, Motor, Isolation Valve, and Vacuum connections.

Images of equipment related to the described ALD for radiators and pigments.
Spacecraft charging is the condition that occurs when a spacecraft accumulates excess electrons or ions. For a conducting spacecraft, the excess charges are on the surface. The term spacecraft surface charging (absolute charging) is used to clearly denote charging on the spacecraft surface as opposed to other charge distributions such as the voltage differences between electrically isolated parts of the spacecraft (differential charging).

HAZARD

If a charge builds up that is too big for the spacecraft’s material to hold, discharge arcs, which are essentially strong electrical currents, will occur.

And depending on where those arcs go, they can damage electronic components, destroy sensors, or damage important materials such as thermal control coatings.
Problem

ESA EURECA satellite solar array sustained arc damage. Credits: ESA

Arc damage in laboratory tests of the chromic acid anodized thermal control coating covering ISS orbital debris shields. Credits: NASA/T. Schneider
The space station’s radiator system, which is a critical component of the active system, consists of seven panels (each about 6 by 12 feet)

Wide Field Planetary Camera 2 (WFPC2) that was installed on the Hubble Space Telescope in December 1993, and removed during the last servicing mission in 2009

Origami Inspired
Motivation

• Most white pigments do not dissipate electrical charge without a dopant or additive
• Two most commonly used dissipative thermal coatings (Z93C55 and AZ2000) rely on indium hydroxide or tin oxide as charge dissipative additives utilizing sol gel wet chemistry
• ITO formed locally on a macroscopic scale due to seeding and ITO crystal formation on the boundaries of the pigment grains. Thickness and dispersion throughout the coating are difficult to control.

Instead of postprocessing the dissipative coating can we preprocess the dissipative coating before binding directly on the pigment itself?
Experimental Procedures

- The first set of experiments were conducted on flat substrates for the ALD of In$_2$O$_3$ and ITO, the films were deposited on a variety of substrates including n-type Si(100) wafers for thickness measurements and glass microscope slides for sheet resistivity determination.
- The In$_2$O$_3$ ALD on the particle substrates was applied to Z93P pigments provided by Alion Science and Technology; these particles had a mean size of 2 microns.
- Thickness and conformity of the ALD films on the Si wafers of In$_2$O$_3$ and ITO were measured using a J.A. Woollam M-2000D Spectroscopic Ellipsometer. The sheet resistivity of the ALD films on the microscope glass substrates was measured using a Lucas Signatone S-302 four-point probe.
- The bulk resistivity of the ALD deposited pigment system is measured in air after the formation of a pellet of 1 in. diameter and a thickness of approximately .5 in. The pigment is compressed lightly by hand and held in place by a 3D printed electrically insulating hollow nylon/Teflon annulus spacer held on an aluminum plate. Resistivity was measured in air and vacuum.
Results

Uncoated Pigment

Coated Pigment
Results
## Results

### XPS of Particle Composition

<table>
<thead>
<tr>
<th>Spectrum Label</th>
<th>Zinc Oxide Particles</th>
<th>Indium Oxide Coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>57.73</td>
<td>73.72</td>
</tr>
<tr>
<td>O</td>
<td>33.23</td>
<td>24.76</td>
</tr>
<tr>
<td>Zn</td>
<td>9.04</td>
<td>1.28</td>
</tr>
<tr>
<td>In</td>
<td>-</td>
<td>0.23</td>
</tr>
</tbody>
</table>

**Notes:**
- The table above shows the atomic percentage for each element in the spectrum.
- The XPS spectrum confirms the presence of zinc oxide particles and indium oxide coating.
- The survey plot displays the binding energy (eV) across different elements.
- The peaks at various binding energies correspond to the elements C, O, Zn, and In, indicating their presence in the sample.

**Image Description:**
- The image features a survey plot with peaks at binding energies corresponding to C, O, Zn, and In.
- The plot highlights the presence of zinc oxide particles and indium oxide coating.
- The atomic percentages are aligned with the theoretical composition, validating the analysis.
As vacuum is increased the resistivity of the Z93 pigment powders increases several orders of magnitude while the indium oxide treated Z93P pigment remains relatively stable. This increase in resistivity can be attributed to either the removal of moisture within the bulk powder or the compression of the powder filling the void space allowing for an increased number of conduction paths.
Results

Reflectance measurements were taken on lightly compressed pellets of the untreated and indium oxide treated Z93P pigment and show approximately one percent reflectance differences across the solar spectrum.
ISS Opportunity
The Materials ISS Experiment Flight Facility (MISSE-FF) with MISSE Sample Carriers (MSCs) in the fully open position exposing samples/experiments to the harsh environment of space in low-Earth Orbit (LEO). Image courtesy of Alpha Space.

An earlier MISSE mission
Catch the Nov. 15 Antares Launch from Wallops

Get up early Nov. 15 to view the Northrop Grumman’s Antares rocket launch from the Mid-Atlantic Regional Spaceport at NASA’s Wallops Flight Facility.

The NASA Wallops Flight Facility and Virginia’s Mid-Atlantic Regional Spaceport are set to support the launch of the Antares rocket, carrying the company’s Cygnus cargo spacecraft to the International Space Station at 4:49 a.m. EST, Nov. 15.

The launch may be visible, weather permitting, to residents throughout the East Coast of the United States.

The NASA Visitor Center at Wallops opens at 1 a.m. on launch day for public viewing. Additional locations for catching the launch are Robert Reed Park on Chincoteague Island or Beach Road spanning the area between Chincoteague and Assateague Islands. Assateague Island National Seashore/Chincoteague National Wildlife Refuge in Virginia will not be open for viewing the launch.

Credits: Northrop Grumman
The numerical values in each colored circle indicate the time (in seconds) after liftoff. This value can be used to determine when the rocket become visible within the associated colored region. Viewing availability is based on clear weather conditions.
Acknowledgments

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