Atomic Layer Deposition: Pioneering Research with Atomic-Scale Precision

October 29th 2019

Presentation Given By: Dr. Andrew Lushington
Outline

- Introduction to Atomic Layer Deposition
- ALD - Energy Storage
- ALD - Catalyst Research
- Summary

*All information being presented may be found within the Public Domain*
Introduction to Atomic Layer Deposition
Introduction to ALD – Thin Film Deposition Techniques

- **ALD** is a thin film deposition technique that is a subset of **Chemical Vapor Deposition**

- In **CVD**, two precursors are introduced simultaneously to react in gas phase and/or on the surface to produce a film.

- In **ALD**, the reaction is split into two half reactions.

- Precursor gasses are temporally separated to maximize reaction with the surface – **Surface mediated technique**.
Introduction to ALD – Chemical Reactions

Simple ALD Design

Surface Mediated Technique – Surface functionality plays an important role

Examples of ALD: Growth of Aluminum Oxide (Al₂O₃) using Trimethylaluminum and Water

1 Complete ALD Cycle

Trimethylaluminum (TMA)

Water (H₂O)
Introduction to ALD – Parameters that Influence ALD

- Surface saturating dose of precursor is required

- Reaction temperature to facilitate ALD growth
Quartz has a very well defined piezoelectric response. This can be used to measure mass changes during film growth.

\[
\Delta f = -\frac{2f_0^2 \Delta m}{A \sqrt{\mu \rho}} = -C \Delta m
\]

- \( \Delta f \) = Change in resonant frequency
- \( f_0 \) = fundamental resonant frequency of the crystal
- \( \Delta m \) = Change in mass
- \( A \) = Surface area of exposed crystal
- \( \mu \) = Shear modul of crystal
- \( \rho \) = density of Quartz
- \( C \) = Crystal dependent constant
ALD vs Other Gas Phase Deposition Techniques

- ALD is a reaction-controlled deposition technique rather than a diffusion controlled deposition process.

- ALD is also a non-line-of-sight process. Allows for conformal pin-hole deposition around geometrically constrained complex objects.
Precursor Chemistry for ALD

1. Volatile: Coordinatively saturated, low molecular weight

2. Low Melting Point: Branching

3. Thermally Stable: Strong bonds to metal center

4. Chemically Reactive: bond formed during deposition are stronger than those broken

5. Self-limiting Monolayer: steric protection of the central atom keeping it from interacting with other precursor molecules
Thermal vs Plasma ALD

1st half-cycle

Starting surface → Precursor adsorption → After purge step

2nd half-cycle

Starting surface → Plasma exposure → Reactant exposure → After purge step

Thermal ALD

PEALD

- "Directionality"
- "Recombination Process"
- "Redeposition" etc.

Top surface

Sidewall

Good conformality

Plasma

Poor conformality

Trench bottom

Growth per cycle (Å)

Deposition temperature (°C)

Improper at-%

Si:O ratio

Refractive index

350°C Thermal

300°C Thermal

90°C PEALD

50°C PEALD

© 2004-2019 Arradiance® LLC. All rights reserved.
Materials Deposited by ALD

https://www.atomiclimits.com/
**Disadvantages of ALD**

- Deposition rate for ALD is much slower than other gas phase deposition technologies.

- Surface functionality plays a critical role in film growth. ALD will grow around initial surface functionality – typical of metals.

- High material waste, excess material gets pumped out.
Application of ALD - Microelectronics

Shrinking transistor size brought gate oxide size down to 1.2nm SiO2. Unfortunately, changes would tunnel through gate and cause leaking.

Moving to high k HfO2 gate using ALD ensures uniform gate thickness. Since field effect is increased, gate oxide can be made thicker. 100x reduction in gate dielectric leakage = lower power.

With introduction of tri-gate transistor, ALD is a key process in coating high aspect ratio fins protruding from surface with a gate oxide that is pinhole free.
Extension of ALD: Molecular Layer Deposition

- In MLD molecular bifunctional monomer units are reacted together to form polymeric organic materials.
**ALD vs MLD**

- **ALD**: Alternating sequences of vapour precursors allow for layer by layer growth

![ALD Diagram](image)

- **ALD and MLD** can be mixed together to form new metalcone compounds

![MLD Diagram](image)
Merging ALD and MLD

**Organic (MLD)**
- Soft
- Flexible
- Low Modulus
- Low Refractive Index
- Low Density

**Inorganic (ALD)**
- Hard
- Brittle
- High Modulus
- High Refractive Index
- High Density

**Hybrid Organic-Inorganic Films with Composite Properties**
ALD and Energy Storage
Growing Electric Vehicle Market

Electric vehicle market has significantly grown in the past decade

An increasing number of manufactures are entering the electric vehicle market
Energy Storage Device of Choice

- Lithium is the lightest metal
- Lithium has a very high electrochemical potential
- Provides the largest energy density for weight out of any other battery system
New Materials Required for Future Energy Storage Devices

To meet future demand and extend EV range, adoption of new materials is required.
Lithium Ion Battery Operation and Challenges at the Interface

ALD is one coating strategy that can be used to address challenges at both the anode and cathode of lithium ion batteries.

Required Coating Properties

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform Coverage</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Lithium-ion Conductive</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Electronically Conductive</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Prevent Metal Dissolution</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Enhance Mechanical Stability</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
ALD Coating Enhancing Cathode Performance

- ALD provides unique surface coverage required to mitigate metal dissolution.
- ALD nanolaminates used to tune film properties, such as lithium ion diffusion.
ALD Enhancing Anode

1. High Reactivity of Lithium
2. Uncontrolled Formation of Solid Electrolyte Interface (SEI)
3. Infinite Volume Change
Use of ALD and MLD to Engineer Surface

- **TMA-H₂O**
  - $\text{CH}_3\text{AlCH}_3 + \text{H}_3\text{C} \rightarrow \text{HOAlOH}$
  - Previous research indicates positive results
  - Can be done at low temperatures (RT)

- **TMA-EG**
  - $\text{CH}_3\text{AlCH}_3 + \text{HOCH}_2\text{OH} \rightarrow \text{HOAlOH}$
  - Increase film flexibility by MLD linkage
  - Relatively low deposition temperature (90°C)
  - Does not include water
  - Increase chance of double side reactions
  - Long purge times

- **TMA-GLY**
  - $\text{CH}_3\text{AlCH}_3 + \text{HOCH}_2\text{OH} \rightarrow \text{HOAlOH}$
  - Highly Robust
  - Continued reaction (dbl side reactions do not limit surface sites)
  - Increased cross linking
  - Requires high deposition temperatures (150°C)
  - Long purge times

- Water can react with Li
- Dense film may not allow for good Li⁺ conduction

© 2004-2019 Arradiance® LLC. All rights reserved.
Coating Lithium with ALD/MLD

Current Density (mA cm$^{-2}$): How quickly Li is transferred from electrode $\rightarrow$ electrode

Capacity (mAh cm$^{-2}$): How much Li is transferred per charge/discharge cycle
Cell Testing

1 mA cm\(^{-2}\) 1 mAh cm\(^{-2}\)

A) Bare Li

B) TMA-H2O

C) TMA-EG

D) TMA-GLY

Soft short circuit
Cell Testing Continued

Current Density (mA cm\(^{-2}\)): How quickly Li is transferred from electrode \(\rightarrow\) electrode

Capacity (mAh cm\(^{-2}\)): How much Li is transferred per charge/discharge cycle

**1mA cm\(^{-2}\) 1mAh cm\(^{-2}\)**

- A) Bare Li
- B) TMA-H2O
- C) TMA-EG
- D) TMA-GLY

**5mA cm\(^{-2}\) 1mAh cm\(^{-2}\)**

- A) Bare Li
- B) TMA-H2O
- C) TMA-EG
- D) TMA-GLY

**3mA cm\(^{-2}\) 1mAh cm\(^{-2}\)**

- A) Bare Li
- B) TMA-H2O
- C) TMA-EG
- D) TMA-GLY

**3mA cm\(^{-2}\) 2mAh cm\(^{-2}\)**

- a) Bare Li
- b) TMA-H2O
- c) TMA-EG
- d) TMA-GLY
Full Cell Battery Data

- **LFP – Lithium Ion Battery**
  - Considered a more environmentally friendly material compared to LiCoO₂
  - Coin cells tested using loading of ~10mg
  - Carbonate based electrolyte (1M LiPF₆ in EC, DEC, EMC w FEC)
  - Constant current in a voltage range of 2.5-4.2V

- **Carbon/Sulfur – Lithium-Sulfur Battery**
  - Much higher energy density compared to Lithium ion
  - Coin cells tested using loading of ~1mg
  - Ether Based electrolyte (1M LiTFSI in DOL, DME w LiNO₃)
  - Constant current in a voltage range of 1.8-2.8V
There is a consumer demand for Energy Storage devices with increased Energy Density. However, this requires the adoption of new materials.

Many problems exist at the interface of electrode materials – ALD is one solution for addressing these problems.

For cathode materials, tuning and ALD material to be lithium ion conducting prevents metal dissolution and prolongs cycle life and capacity.

For anode materials, ALD stabilizes the interface between the electrolyte and electrode, allowing for prolonged cycling behavior.
ALD and Catalysis

Graphene

Controlled nucleation sites creation

Pt ALD 1st cycle

MeCpPtMe₃

Self-limiting

Pt ALD 2nd cycle

Pt single atoms

Pt dimers

O₂
Nobel Metals Empower Catalyst Reactions

Supported noble metal catalysts nanoparticles are among the most important catalyst that enable many critical technologies.
Reducing Size of Catalyst Particles

High price and low natural abundance of noble metals is an issue.

Important aspect that determines catalytic performance is nanocatalyst size

ALD has unique advantages for deposition of particles by allowing control over:

- **Increased surface area** also increases the rate of reaction by increasing the collision frequency

---

© 2004-2019 Arradiance® LLC. All rights reserved.
Depositing Single Atoms using ALD

Controlled nucleation sites creation

Graphene ➔ Pt ALD 1st cycle

MeCpPtMe₃ ➔ Pt ALD 2nd cycle

Pt single atoms

O₂

O₃

Pt dimers

Reaction Temperature = 150°C

Control temperature for selective deposition

H₃C-Pt-CH₃

H₃C-CH₃

Reaction Temperature = 250°C

© 2004-2019 Arradiance® LLC. All rights reserved.
TEM Images of ALD Deposited Platinum
Hydrogen Production

Tested Pt Dimer on graphene for hydrogen production via hydrolysis of ammonia borane

\[ \text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{BO}_2^- + 3\text{H}_2 (g) \]

17x increased hydrogen vs single atom Pt
45x vs Pt nanoparticles
ALD and Catalysis Summary

- Nobel Metals are important for a number of catalytic reactions

- Nobel metals are expensive and there is a commercial drive to reduce the utilization of these expensive materials. Furthermore, decreasing size can also increase catalytic activity

- ALD is one technique that can be used to deposit nanoparticles of noble particles down to the single atom range, providing excellent control over particle size and dimension
Conclusions and Final Remarks

- ALD is a technique that is capable of depositing angstrom level films over high aspect ratio nanostructures surfaces.

- There are number of parameters that can be tuned to optimize films properties. The process is not as simple as A-B deposition.

- ALD can be used to address changes in lithium ion battery devices at both the anode and cathode.

- Nanoparticles can be deposited by ALD, down to the single atom.