Atomic Layer Deposition (ALD) overview

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Outline

• What is ALD?
• Processes
• System Features
• Application examples
• In situ diagnostics
• Control of ion energy
What is Atomic Layer Deposition (ALD)?

ALD is a sequential, self limiting surface reaction, based on two or more reactants

- Precise thickness control
- Growth rate is independent of precursor flux once surfaces are saturated
  - Conformal coating even in high aspect ratio structures
- Low pin hole levels
  - No gas phase reactions generating particles
- Very thin and dense films
  - Low deposition rates, typically 1Å/cycle
- Wide variety of materials possible
  - Limited by precursors
ALD cycle of Al$_2$O$_3$ thermal
ALD cycle of Al$_2$O$_3$ plasma enhanced
How to identify true ALD growth

- A plateau in GPC as dose times increase indicates self-limited, ALD. The metal precursor and plasma dose times should follow this trend.

- A linear trend indicates layer-by-layer deposition. Exponential trend indicates under-saturation or CVD.

- Low GPC at low T indicates slow deposition kinetics, i.e. under-saturation, poor nucleation. High GPC at high T indicates precursor decomposition.
• Differing possibilities depending on reaction mechanism
• ALD temperature window not always flat, since equilibrium density of reactive surface sites (e.g., OH), depends on temperature.
Strong points of ALD:

- **Growth control** at the subnanometer level
- **Uniformity** of the films on large substrates
- **Conformality** for complex surface features
- Choice of deposition temperature down to **low substrate temperatures** (using plasma)

Thermal and Plasma

**ALD benefits from Plasma**

- Improved material properties
  - Film density and composition can be influenced
  - Lower impurities
- Increased choice of precursors and materials
  - Nitrides
  - Metals
- Reduced substrate temperatures
- Surface pre-treatment
  - Surface activation and surface cleaning
- Increased growth rate
- Shorter nucleation periods

**Plasma not recommended for**

- Aspect ratios above 50:1
- Substrates reactive with plasma

Plasma essential for lower oxygen content and lower resistivities.

Plasma allows growth often at 100 °C or lower temperatures.

Often soft plasma conditions can be used to minimize damage.
Plasma ALD – reactor types

**Direct plasma:**
Substrate part of plasma creation zone
*Strong ion bombardment*
Plasma damage to sensitive devices

**Remote plasma:**
Substrate “downstream” of plasma creation zone
Mild ion bombardment at low pressure,
virtually no ion energy at high pressure
Excellent compromise between direct plasma ALD and radical enhanced

**Radical Enhanced:**
No plasma above substrate. Often bought in source.
No ions, low radical flux
Poor film quality and uniformity
FlexAL ALD system

• Cutting edge plasma ALD systems with thermal ALD as standard
• Mixed mode operation within a single recipe
  • No hardware changes required to switch mode between plasma and thermal ALD
    • start with thermal Al₂O₃ on sensitive interface but continue with plasma ALD for best material properties
    • for platinum start with plasma to minimise nucleation delay and continue with thermal
Outline

- What is ALD?
- **Processes**
- System Features
- Application examples
- In situ diagnostics
- Control of ion energy
Plasma ALD processing advantages

- Reduced substrate temperatures
  - Advantageous for temperature sensitive substrates such as LiNbO₃, LiTaO₃, polymers, plastics, etc.

- Improved material properties
  - Film density and composition can be influenced
  - Lower impurity levels

- Increased choice of precursors and materials
  - Nitrides including AlN, Si₃N₄, TiN
  - Metals

- Surface pre-treatment
  - Surface activation and surface cleansing, e.g. GaN

- Shorter nucleation periods, e.g. plasma ALD of metals

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Nitrides</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>AlN</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>GaN</td>
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<tr>
<td>Ga₂O₃</td>
<td>HfN</td>
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<tr>
<td>HfO₂</td>
<td>In₂O₃</td>
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<tr>
<td>In₂O₃</td>
<td>Li₂CO₃</td>
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<td>Li₂CO₃</td>
<td>MoO₃</td>
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<td>MoO₃</td>
<td>Nb₂O₅</td>
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<tr>
<td>Nb₂O₅</td>
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<tr>
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<tr>
<td>SiO₂</td>
<td>Si₃N₄</td>
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<tr>
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<td>ZnO</td>
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<tr>
<td>ZnO</td>
<td>ZrO₂</td>
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<tr>
<th>Metals</th>
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<tbody>
<tr>
<td>Pt</td>
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<td>Ru</td>
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<td>NiO</td>
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<tbody>
<tr>
<td>AlF₃</td>
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<th>Sulphides</th>
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<td>MoS₂</td>
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<tr>
<td>WS₂</td>
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<tr>
<td>TiS₂/TiS₃</td>
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</tbody>
</table>
Plasma surface pre-treatments

• Optimal pre-treatment for surface can be integrated in recipe (plasma pressure, power, gas flow).
  • Improved nucleation for certain surfaces (short O\textsubscript{2} plasma on a-Si)
  • Functionalizing graphene, CNTs (O\textsubscript{2} or H\textsubscript{2} plasma)
  • Improving adhesion (H\textsubscript{2} plasma for Pt on TiO\textsubscript{2})
  • In-situ cleaning (TMA pulses to remove oxide, O\textsubscript{2} plasma for carbon)

With biasing chemical sputter clean of surfaces (e.g. Ar/H\textsubscript{2} to remove native oxide and carbon)
• Before deposition of dielectrics or metal contact
• Adhesion improvement
Ar sputter etch rates of $\text{Al}_2\text{O}_3$, $\text{HfO}_2$, $\text{SiO}_2$ and $\text{Si}_3\text{N}_4$

Etch rates (Å/min) under Ar plasma exposure were determined using the difference in film thickness, before and after etch as measured by ellipsometry.
Plasma cleaning by SF$_6$ for TiN

- Plasma cleaning using SF$_6$ plasma without bias

- Data available for TiN deposition (should also work for Si, W, Mo, and Ta compounds)

- Expected frequency of cleaning and downtime
  - Clean every >450 nm
  - <10 min plasma clean for TiN

Etch rates of TiN coated on Si test pieces placed at various locations in the system. Effective cleaning for surfaces >100 °C (temperature at which TiF$_x$ becomes volatile).
Low damage for depositing on polymers

- To limit etching of a polymer plasma conditions can be set to reduce etching.
- High pressure plasma allows growth on polymers without etching them.
- ALD deposit will also function as protective layer, so generally etching is minimal.

Rate of the resist removal during 50 plasma exposures of 5s each
We enable material property control by substrate biasing

A wide range of properties can be tuned by substrate biasing in ALD

- First to introduce substrate biasing in ALD
- >10 years of plasma ALD experience

Deposition of Nb₂O₅

- Plasma and thermal ALD using TBTDEN and O₂ plasma or H₂O.

Wide temperature range for plasma and thermal ALD with higher GPC for plasma process

<table>
<thead>
<tr>
<th>Material</th>
<th>Nb₂O₅</th>
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<tbody>
<tr>
<td>Precursor</td>
<td>TBTDEN</td>
</tr>
<tr>
<td>Co-reactant</td>
<td>O₂ plasma, H₂O thermal</td>
</tr>
<tr>
<td>Temperature range</td>
<td>150°C – 350 °C</td>
</tr>
<tr>
<td>Growth per cycle</td>
<td>0.56 Å/cycle (plasma) 0.38 Å/cycle (thermal) @ 200°C</td>
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<tr>
<td>Refractive Index</td>
<td>2.35 – 2.46</td>
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<tr>
<td>Uniformity</td>
<td>± 3-4% over 200mm</td>
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Nb₂O₅ on c-Si giving high surface passivation after anneal
Besides the regular AB process scheme, there are also ABC multistep and ABAB supercycle schemes, which are easily implemented in recipe based software.

ALD process schemes: multi-component materials

- **Regular** (AB)_m
  - e.g. Al₂O₃, TiO₂, Pt

- **Multistep** (ABC)_m
  - e.g. Pt at low temperature

- **Supercycle** ((A1B1)ₘ(A2B2)ₙ)ₓ
  - e.g. ZnO:Al, HfSiOₓ, SrTiO₃

Conclusions

• Extremely flexible thermal and plasma ALD system
• Wide range of precursors and films
• Low temperature capability for temperature sensitive deposition
• Pretreatments prior to deposition to improve interface and nucleation
• Turbopumping for superior nitride films
• Substrate bias capability for film densification and stress control
• Clusterable with other modules for transfer without vacuum break