Surface Functionalization by Atomic Layer Deposition

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Atomic layer deposition (ALD)

- **Gas-phase** thin film deposition technique
- Cyclic process of **self-limiting surface reactions** → layer-by-layer growth

**Example:**
ALD growth of Al₂O₃ from trimethyl aluminum (TMA) and H₂O

- TMA pulse
- Self-saturated chemisorption
- One (sub)monolayer of Al₂O₃
- New OH groups at the surface
- Water pulse
Advantages of ALD

- Ultimate control of layer thickness
- Excellent conformality
- Excellent control of stoichiometry
- Highly uniform
- Easily upscalable

Limitations of ALD

- Slow – limited to nanocoatings and surface engineering
Materials that can be deposited by ALD

Advantages and limitations of ALD

Layer-by-layer deposition

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ALD is ideal tool for 3D surface engineering

- Controlling surface properties: adhesion, friction, hydrophobicity
- Surface functionalization: catalysis
- Surface passivation: diffusion barriers, encapsulation, anti-corrosion

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Applications of ALD

- Functional nanocoatings in micro-electronics
- Encapsulation
- Surface engineering – hydrophobic/hydrophilic
- Surface engineering – adhesion
- Coating nanoporous materials for catalysis
- Coating nano-objects
- Powder coating
Functional nanocoatings in micro-electronics
Applications of ALD

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ALD nanocoatings for encapsulation: Protecting silver objects from tarnishing

Problem: silver objects require cleaning after some time

ALD solution: 10nm Al$_2$O$_3$ “sapphire-like” coating

Accelerated tarnishing test:

uncoated

ALD coated
ALD can be scaled to large batches

**Batch size**

Crown Size Coins
120 x 17 = 2040 pcs/batch

Jewelry
2000 pcs/batch

Photo: courtesy of Kalevala Jewelry
ALD nanocoatings for encapsulation: Protecting CaS:Eu phosphor powders from moisture

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ALD for surface engineering:
Making a Kleenex tissue hydrophobic ...

“Original” tissue

ALD coated tissue (200 cycles Al₂O₃)

Thermal ALD, TMA + H₂O, 50°C
ALD for surface engineering: Making Teflon hydrophilic.

+ High thermal stability (melting at 320-327°C)
+ High chemical resistance
+ Low coefficient of friction
+ Low dielectric loss (RF applications)
- Poor adhesion, not glueable
- Lack of reactivity makes it challenging to functionalize the PTFE surface

Native Teflon - hydrophobic

ALD coated Teflon - hydrophilic

Patent application (WO 2014111492 A1)
ALD for surface engineering: Making Teflon gluable.

14-fold improvement of adhesion after PE-ALD

20mm wide strips
Peeling speed 5 mm/s
Peeling angle 180 °

Patent application (WO 2014111492 A1)
ALD for surface engineering: Making Teflon glueable.

Native Teflon Poor adhesion

PE-ALD coated Teflon glueable !!

Aluminum plate
superglue
PTFE sheet

Uncoated PTFE peels off

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ALD coating of nanoporous materials for catalysis

ALD coating throughout the interior surface of a nanoporous material
Photocatalysis

- ALD of amorphous TiO$_2$ inside mesoporous silica particles
- Calcination leads to uniformly distributed anatase TiO$_2$ nanoparticles

Photocatalysis

- Excellent dispersion of anatase particles in accessible mesopores
- Excellent photocatalytic activity
- Method can be extended to other metal oxides
- Potentially useful concept for lab-on-a-chip applications

Applications of ALD

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Multilayer ALD coating of a carbon nanotube

$\text{TiO}_2/\text{V}_2\text{O}_5/\text{TiO}_2$ multilayer coating of a carbon nanotube
Platinum ALD coating of carbon nanotubes

After calcination: Pt nanoparticles transformed into interconnected nanowires.
Applications of ALD

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ALD for coating powders

Particles are 3D objects – conformal coating by ALD

Easy concept: Put a cup of powder in a regular flow-type or pump-type ALD reactor.

Problem: Precursors and reactants cannot diffuse easily down to the particle bed!

Diffusion time of TMA at 10 mbar pressure in a cubically stacked bed of spherical particles with 100 nm diameter.

Rotary reactor for thermal and PE-ALD on powders

- Advantages of PE-ALD:
  - Lower processing temperatures
  - Higher quality coatings
  - Cheaper precursor chemistry available

- Demonstrated oxide/nitride coatings on oxide/metal particles.

ALD on powders

FUNC:
Tools for dry nanofunctionalization of particles and fibrous materials
Summary

• Atomic layer deposition offers
  • Ultimate thickness control
  • Ultimate conformality

• Wide range of applications
  • Nanocoatings for micro-electronics
  • Encapsulation
  • Surface engineering – hydrophobic/hydrophilic
  • Surface engineering – adhesion
  • Coating nanoporous materials for catalysis
  • Coating nano-objects

• ALD is being explored for powder coating within SIM-FUNC
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