Thin film deposition techniques

Kristin Bergum, 07.05.2019, University of Oslo
### Thin film deposition techniques

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<th>Evaporative deposition</th>
<th>Sputter deposition</th>
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<td>Chemical vapour deposition</td>
<td>Atomic layer deposition</td>
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- How
- Properties of deposition processes
- Advantages
- Disadvantages
- Comparisons
Evaporative deposition: How

• Heat what you want to deposit until it has a high vapour pressure in vacuum

• Put substrate in «vapour cloud»
Thermal evaporation: How

• Heat target material (charge) with resistive heating
Thermal evaporation: How
E-beam evaporation:

• Use electron beam instead of current
E-beam evaporation: How
Thermal or e-beam?

- Reaction with crucible/boat/wire
  - Can become brittle and break

- Melting temperature of target material
  - 1600 °C
Figure 6.1: Equilibrium Vapor Pressures of Selected Materials. The Slashes Indicate the Melting Points (MPs)
Selective deposition of alloys

![Graph showing the equilibrium vapor pressures of lithium (Li) and silver (Ag) as a function of temperature. The graph displays two curves, one for Li and one for Ag, indicating the vapor pressure at different temperatures.](image)

*Figure 6.2: Equilibrium Vapor Pressures of Lithium (Li) and Silver (Ag)*
Properties of evaporative deposition

• Difficult to deposit alloys/mixtures
  • Selective deposition

• Radiative heating
  • Temperature sensitive samples
  • Increase distance

• Energy of atom corresponding to temperature, ~0.2 eV
  • Films often not completely dense
  • Tensile stress

• Line of sight deposition
  • Allow shadow-masks with no backside deposition
  • Easy to use shields to protect equipment
  • Little impurities from walls
  • Non-conformal on uneven substrates
Properties of evaporative deposition

- Low vacuum ($<10^{-5}$ Torr)
- Can allow high deposition rates
- Oxidation of target
- Large spread in thickness with angle
  - Design of chamber
- Easy to measure thickness in-situ
  - Quartz Crystal Microbalance
Sputter deposition
Sputter deposition
Sputter deposition: Higher energy and reactivity

• Why does it matter?

• With higher energies, the effective temperature of the film increases
  • Increase mobility of adatoms on the surface
  • Increase density
  • Can tune stress compressive/tensile
  • Influence reaction rates and pathways
  • Influence grain growth
E = 3/2 kT
k = 1.4 \times 10^{-16} \text{ ergs/}^{\circ}\text{K}

300^{\circ}\text{K} = 0.04 \text{ eV}
1500^{\circ}\text{K} = 0.2 \text{ eV}
E = 1/2 mv^2

Cu Sputtered by 600 eV Hg + ions

T (4eV) \approx 30,000^{\circ}\text{K}

Cu Evaporated AT 1500^{\circ}\text{C}
Compound deposition

• The target is sputtered layer by layer

• The composition of the sputtered material always the same as the bulk target

• Lighter atoms (oxygen, nitrogen, carbon) often lost in transport
  • Add gases to deposition chamber
Oxides, nitrides and carbides: Reactive deposition

• Oxides, nitrides and carbides can be deposited *reactively*
  - Oxygen, nitrogen or methane/acetylene introduced with argon

• Can shift the composition with changing amounts of reactive gas
  - No O$_2$: Cu
  - Cu + Cu$_2$O
  - Cu$_2$O
  - Cu$_2$O + CuO
  - CuO

• Can control the stoichiometry using optical emission spectrometry

• Poisoning of target
Reproducibility

• Many parameters in sputter deposition affect the film
  • Deposition pressure
  • Power of sputtering ions
  • Partial pressure of reactive gas
  • Density of plasma
  • «Racetrack» formation
  • Prefential sputtering of crystallographic...
Some comparisons: sputter and evaporative deposition

• More deposition parameters are available for sputtering
  • Allow non-equilibrium deposition
  • More complicated parameter-space
  • Denser films

• Sputtered films can have a higher energy impinging on the substrate
  • Energy can depend on voltage applied and pressure
  • Can change density and character of films by improving adatom mobility

• Sputtered atoms contain more reactive species
  • Radicals, ions

• Sputtering more complicated and expensive
Comparison: Sputter and evaporative deposition

• Evaporative deposition easier and more reproducible

• Sputter deposition not only line – of – sight.
  • Deposits on all surfaces in chamber
  • More difficult to keep clean
  • Can have impurities from chamber walls

• Sputter deposition better for temperature sensitive materials
Chemical vapour deposition (CVD)

- Relies on chemical bonding/chemical reactions rather than bombardment of atoms
- Less damage at interfaces

CVD
- Plasma or thermally assisted

Atomic Layer Deposition (ALD)
- Plasma or thermally assisted
- ALD is a subset of CVD

- Impurities depend on the chemical reaction completeness
Chemical vapour deposition (CVD)

Reactants and carrier gas in →

\[ \text{CH}_3\text{SiCl}_3 \quad \text{H}_2 \quad \text{CH}_3\text{SiCl}_3 \quad \text{H}_2 \quad \text{CH}_3\text{SiCl}_3 \quad \text{H}_2 \quad \text{CH}_3\text{SiCl}_3 \quad \text{H}_2 \quad \text{CH}_3\text{SiCl}_3 \]

Unused reactants, bi-products and carrier gas out →

\[ \text{H}_2 \quad \text{CH}_3\text{SiCl}_3 \quad \text{H}_2 \quad \text{CH}_3\text{SiCl}_3 \quad \text{H}_2 \quad \text{CH}_3\text{SiCl}_3 \]

Substrate
Chemical vapour deposition (CVD)

Reactants and carrier gas in → Unused reactants, bi-products and carrier gas out →

SiC

Substrate
Chemical vapour deposition (CVD)

• Non-line of sight process
  • Conformality also on uneven substrates
  • Up to ~1:50 ratio
  • Can coat trenches

• Great flexibility in films deposited
  • Carbides, nitrides, polymers

• Deposition temperature can be reduced using plasma

• From ultra-high vacuum to atmospheric pressure

• Can tune deposition rate, microstructure, stoichiometry, morphology, orientation
Atomic layer deposition (ALD)

- The chemical reaction divided into two «half-reactions»
- Reactants separated in time
- Surface saturation
Atomic layer deposition (ALD)

V. Miikkulainen et al., «Crystallinity of inorganic films grown by atomic layer deposition: overview and general trends»
Atomic layer deposition (ALD)

- Can deposit on very high aspect-ratio substrates
  - Conformal and dense films

- Deposition temperature can be reduced using plasma
  - Some chemistries require plasma to occur
  - Can reduce conformality

- No pinholes

- Excellent thickness control (nm control)

- Often expensive and time-consuming
  - Batch process (not spatial ALD)
  - Precursors can be expensive
  - Low deposition rates
## Systems in our labs

<table>
<thead>
<tr>
<th></th>
<th>Evaporative deposition</th>
<th>Sputter deposition</th>
<th>Atomic layer deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lund</td>
<td></td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Chalmers</td>
<td>9</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>Uppsala</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>DTU</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>UiO</td>
<td>3</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>USN</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>KTH</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Aalto</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Properties</td>
<td>ALD</td>
<td>PEALD</td>
<td>CVD</td>
</tr>
<tr>
<td>-----------------</td>
<td>----------------------------------------</td>
<td>---------------------------------------</td>
<td>-----------------------------------------</td>
</tr>
<tr>
<td>Temperature</td>
<td>Lower &lt; 400 °C common</td>
<td>Lower than similar ALD processes</td>
<td>Higher &gt; 1000 °C possible</td>
</tr>
<tr>
<td>Pressure</td>
<td>mbar range common, can go to AP</td>
<td>mbar range common</td>
<td>mbar range for LPCVD and higher for APCVD</td>
</tr>
<tr>
<td>Growth rate</td>
<td>Very low 1 Å/s is a fast process, sALD can go higher</td>
<td>Higher than comparable thermal ALD processes</td>
<td>Moderate to high µm/min range possible</td>
</tr>
<tr>
<td>Uniformity</td>
<td>Excellent</td>
<td>Very good</td>
<td>Good, but can be worse on larger surfaces</td>
</tr>
<tr>
<td>Step coverage</td>
<td>Excellent</td>
<td>Worse than ALD due to reactive plasma species</td>
<td>Good for a surface controlled process</td>
</tr>
<tr>
<td>Impurity levels</td>
<td>Moderate Precursor contamination due to low temperature</td>
<td>Higher or lower than ALD due to plasma effects and temp.</td>
<td>Moderate Low cont. can be obtained at high temp.</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Very good</td>
<td>Very good</td>
<td>Very good</td>
</tr>
<tr>
<td>Film density</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
Figure 6.10: Geometrical Shadowing of the Deposition Flux by a Particle on the Surface and by Surface Features
Evaporative deposition

Easy

Little energy during film formation (temperature and condensation)

Films tensile stress and less dense

Sputter deposition

Complex

More energy deposited during film formation (higher speed, plasma presence)

Can deposit wide range of properties in films

Thank you!
• There is a threshold energy below which nothing will sputter (25 eV)
  • No sputtering by electrons

• Sputtering yields decrease at high energies due to energy lost far beneath surface