Vacuum Evaporation
Introduction

• The objective is to controllably transfer atoms from a heated source (which can be a liquid or a solid) to a substrate located a distance away to grow a film.
• The source is heated directly or indirectly until the point is reached where it efficiently sublimes or evaporates.
• When analyzing this method, we need to start from evaporation rates and vapor pressure.
• Evaporation is normally done in the ballistic regime ($Kn > 1$).
• Other than pressure and temperature, the placement of the heater, source and substrate are important factors.
Process Summary

- Place a suitable material (the source) inside the vacuum chamber with a heater.
- Seal and evacuate the chamber.
- Heat the source. When the temperature reaches the evaporation temperature, atoms or molecules start to leave the surface of the source and travel in a more or less straight path until they reach another surface (substrate, chamber wall, instrumentation).
- Since these surfaces are at much lower temperatures, the molecules will transfer their energy to the substrate, lower their temperature and condense.
- Since the vapor pressure at the new temperature is much higher, they will not re-evaporate and adhere to the substrate.
- The deposition thickness is a function of the evaporation rate, the geometry of the source and the substrate and the time of evaporation.
Vapor Pressure

- Vapor pressure is the pressure at which the vapor phase is in equilibrium with the solid or the liquid phase at a given temperature.
- Below this pressure, surface evaporation is faster than condensation, above it it is slower.
- Theoretically, the vapor pressure can be found by the Clausius-Clapyeron equation.

\[
\frac{dP}{dT} = \frac{\Delta H(T)}{T\Delta V}
\]

where \( \Delta H \) is the change in enthalpy, and \( \Delta V \) is the change in volume between the solid (or liquid) and vapor phases.

- Over a small temperature range, the equation can be simplified as:

\[
P = P_0 \exp\left(-\frac{\Delta H_e}{RT}\right)
\]

where \( \Delta H_e \) is the molar heat of evaporation.
Vapor Pressure of Elements

• In reality, empirical formulas and experimental data are more useful to find the vapor pressure of an element.

• For example, the vapor pressure of liquid Al is given by:

\[
\log P(\text{torr}) = -\frac{15993}{T} + 12.409 - 0.999 \log T - 3.52 \times 10^{-6} T
\]

Main Terms

Smaller Terms
Evaporation Rate

• The basic equation for evaporation flux is given by:

\[ \Phi_e = \frac{\alpha_e N_A (P_v - P_h)}{\sqrt{2\pi MRT}} \]

where \( \Phi_e \) is the evaporation flux, \( \alpha_e \) is the coefficient of evaporation (0 < \( \alpha_e \) < 1), \( P_v \) is the vapor pressure and \( P_h \) is the ambient pressure.

• Maximum flux is obtained when \( \alpha_e = 1 \) and \( P_h = 0 \)

\[ \Phi_e = 3.513 \times 10^{22} \frac{P_v}{\sqrt{MT}} \text{ molecules cm}^{-2} \text{s}^{-1} \]

• This can also be put in mass units by multiplying flux with the atomic mass:

\[ \Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{M}{T}} P_v \text{ gr cm}^{-2} \text{s}^{-1} \]
Aluminum Example

- For Al, \( M = 27 \) gr
- From the vapor pressure diagram, to get \( P_v = 10^{-4} \) Torr, we need to heat Al to 980 °C.
- At this temperature, the mass evaporation rate is:

\[
\Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{27}{980}} 10^{-4} \frac{\text{gr}}{\text{cm}^2\text{s}} = 9.694 \times 10^{-7} \frac{\text{gr}}{\text{cm}^2\text{s}}
\]

- If the vapor pressure is chosen to be \( 10^{-2} \) Torr, then the temperature has to be increased to 1220 °C and the evaporation rate becomes:

\[
\Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{27}{1220}} 10^{-2} \frac{\text{gr}}{\text{cm}^2\text{s}} = 8.688 \times 10^{-5} \frac{\text{gr}}{\text{cm}^2\text{s}}
\]
Deposition Rate

• Of course the ultimate quantity we are looking for is a deposition rate.
• This is not only related to the evaporation rate but also the angle and distance between the source and substrate.
• Our basic assumption remains that we are in the ballistic regime and the evaporated atoms travel in a straight line from the source to the substrate.
• We start by looking at the mass lost from the source.

\[ M_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt \]  

where \( A_e \) is the surface area of the source

• The expansion of that mass in the chamber depends on whether the source is a point or a surface source.
• A portion of that mass is incident on the target. The orientation of the target will determine the actual mass that is deposited.
Point and Surface Sources

\[ \frac{dM_s}{dA_s} = \frac{M_e \cos \theta}{4\pi r^2} \]

Point Source

Surface Source

\[ \frac{dM_s}{dA_s} = \frac{M_e (n+1) \cos^n \phi \cos \theta}{2\pi r^2} \]
Film Thickness Variation

Maximum film thickness occurs at $l = 0$. If we express the thickness relative to the maximum thickness:

\[
\frac{d}{d_0} = \frac{1}{\left(1 + \left(\frac{l}{h}\right)^2\right)^{3/2}}
\]

Point Source

\[
d = \frac{M_c h}{4\pi\left(h^2 + l^2\right)^{3/2} \rho_{\text{density}}}
\]

Surface Source

\[
d = \frac{M_c h^2}{\pi\left(h^2 + l^2\right)^2 \rho_{\text{density}}}
\]
An Arrangement for Uniform Films

- If both the source and the substrate are located on the surface of a sphere, the angular dependence on $\theta$ or $\phi$ is eliminated.

\[
\frac{dM_s}{dA_s} = \frac{M_e}{4\pi r_0^2}
\]
Film Purity

There are several sources of impurity:

• Contamination of source materials
  – Use high purity (99.99999%) materials
• Contamination from the heater
  – Use materials with low diffusion
• Residual gas in chamber
  – Better vacuum
  – Higher deposition rate
Compounds

- Evaporation of multi-element materials like compounds present some problems.
- Compounds can decompose or dissociate during evaporation.
- Different components of the material can have different vapor pressure/temperature requirements leading to different vapor concentrations and different stochiometry.

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Chemical Reaction</th>
<th>Examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No dissociation</td>
<td>MX(I or s)→MX(g)</td>
<td>SiO, CaF$_2$, MgF$_2$</td>
<td>Stoch. maintained</td>
</tr>
<tr>
<td>Decomposition</td>
<td>MX(s)→M(s or l)+½ X$_2$(g)</td>
<td>III-V semiconductors</td>
<td>Separate sources are required</td>
</tr>
<tr>
<td>Dissociation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chalcogenides</td>
<td>MX(s)→M(g)+½ X$_2$(g)</td>
<td>CdS, CdSe, CdTe</td>
<td>Separate sources are required</td>
</tr>
<tr>
<td>Oxides</td>
<td>MO$_2$(s)→MO(g)+½ O$_2$(g)</td>
<td>SiO$_2$, TiO$_2$</td>
<td>Deposit in O$_2$ partial pressure</td>
</tr>
</tbody>
</table>
Alloys

• An alloy is a multi-component system where the constitutive elements are completely miscible in each other and can have varying stochiometry.
• The problem arises due to the different vaporization rates of the components.
• Even if initial concentration ratios are adjusted to take this into account, as evaporation proceeds, the flux of each component will vary leading to a graded film composition along the film thickness.
Vacuum Evaporation Sources

• Physical evaporation
  – A “source” container is heated.
  – The material to be evaporated is placed in or near the source.
  – The radiative and conductive heating evaporates the source.

• Electron beam evaporation
  – A filament is heated and emits electrons.
  – The electrons heat the evaporant and vaporize it.
The Basic V-Groove Source

- Place the evaporant at the tip of the V.
- Uses radiative and conductive heating (through wetting) to evaporate material.
- Filament is good for one use.
- Not for depositing films thicker than 1500 Å.
- Point source (fairly even coating over a spherical surface)

Diagram:
- 3-strand Tungsten wire
- Low voltage feedthrough
- Step down transformer
- Variable transformer
- 110 VAC
Other Arrangements

- **Multiple Loop Source**
  - Better for heavier coatings
  - As many as 15 loops, wound helically
  - Need trial and error to find best position for even coating.

- **Wire basket source**
  - More flexible
  - Better able to handle evaporants that melt

- **Dimpled boat source**
  - Made of Mo, Ta, Tu
  - Can hold bigger charges
  - Can deposit thicker layers
  - Evaporation occurs only in the upward direction
  - Higher power requirements
Closed Sources

• Evaporant is placed in dimpled volumes inside the source.
• The source is sealed creating a simple furnace.
• As current is passed through the source, evaporant vapors are emitted through the holes in the source.
• Creates speck-free vapor.
Electron Beam Sources

- Resistive heating first heats a source and then uses radiant or convection heating to heat the evaporant. This can be inefficient.
- By applying a high voltage to a filament, we can create an electron beam.
- When the beam contacts the evaporant, it will heat it directly.
- Since the evaporant is water cooled, it will not wet the source and remains pure.
- Since there are no boats, wires, etc., higher temperatures can be reached.
- Electrical arcing and discharges may occur.
Thickness Measurements

• Gravimetric Method
  – Measure substrate weight before and after coating
  – Calculate thickness from known substrate dimensions
  – Not real-time but surprisingly accurate

• Stylus Method (Profilometer)
  – A stylus is drawn across a step in the film
  – Scratching can occur
  – Needs calibration
  – Can do repeated measurements
  – Not real-time
Process Control

• Resistance monitoring
  – For metallic (conductive) films
  – Resistance is the ratio of voltage to current.
  – It is a function of the dimensions of the film (thickness and length) as well as the material it is made of (resistivity).
  – Should be calibrated against the gravimetric method.
Quartz Crystal Monitors

- Install a quartz oscillator in the vacuum chamber.
- Quartz will have a specific oscillation frequency.
- Expose one side of the quartz wafer to the vapor.
- As the vapor coats the wafer, the oscillation frequency changes.
- Many assumptions are being made including proper calibration, quartz quality and proper usage.
- With a 6 MHz oscillator, it is possible to measure nanogram changes which in turn means about 0.1 A.
Substrate Cleaning

• A clean substrate is essential to achieve good film adhesion.
• The “Tape Test” is the qualitative measure for good adhesion.
• Sample cleaning for ITO:
  – 30 min ultrasonic bath in acetone
  – 30 min ultrasonic bath in methanol
  – 15 min ultrasonic bath in isopropanol
  – 90 min UV/Ozone cleaning
Vacuum Evaporator Diagrams

Complete vacuum evaporator
Operating situation 1: Making low vacuum in chamber

Roughing valve open: MP makes low vacuum in chamber
Operating situation 2: Standby situation

Backing valve open: MP removes air molecules from DP
Operating situation 3: Condition for evaporation

Backing valve and main valve both open: MP removes air molecules from DP while DP removes air from main chamber
Vacuum Chamber

- 304 stainless steel base plate ~1 in. thick
- Glass bell jar: usually Pyrex
- Viton rubber boot on bottom of bell jar (greased)

SAFETY:
1. Do not handle bell jar with gloves on
2. Line inside of bell jar with aluminum foil to keep surface clean/no abrasives
3. Never touch components of chamber or interior of bell jar with bare hands
Final Words

• Vacuum evaporation is most suitable for deposition of metallic thin films.
• Compounds and alloys don’t deposit well because they tend to dissociate at the temperatures required.
• While patterning using masks are routinely done, step coverage is not very good because the vapor flows ballistically (shadowing).