MSN 551
THIN FILM DEPOSITION

EVAPORATION

What is evaporation?

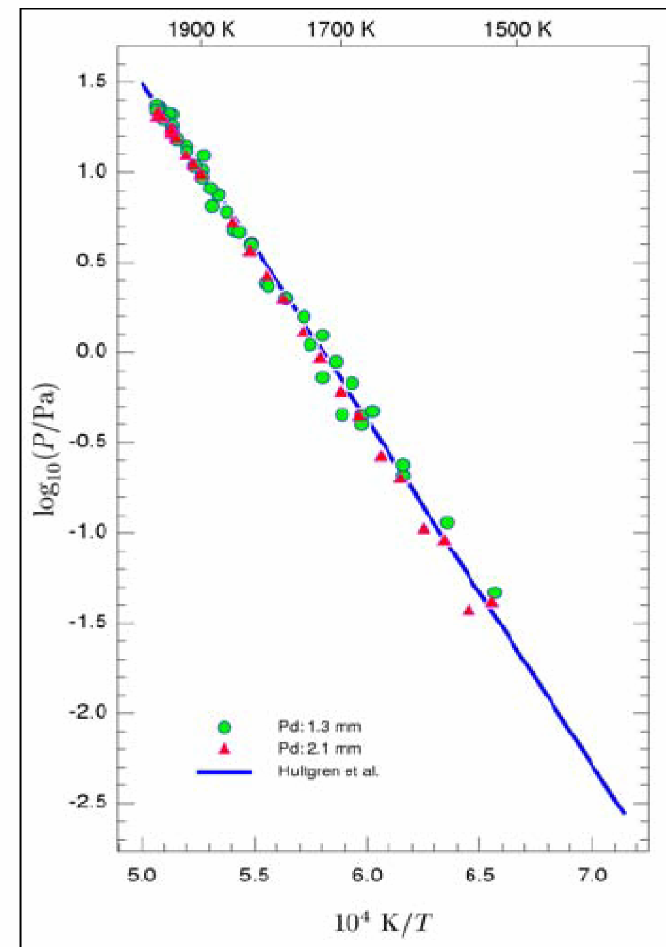
- Material to be evaporated is heated to increase vapor pressure
- In a reasonably high vacuum, material atoms fly to a target and stick onto the surface
- Source material is coated onto the target surface

Vapor pressures

at their melting points (approx., in torr):

Gallium (essentially zero; too low to measure)
Tin (less than 1e-11 torr)
Indium (less than 1e-11 torr)
Lithium 1e-10
Bismuth 2e-10
Lanthanum 3e-10
Aluminum 2e-9
Lead 3e-9
Uranium 1e-8
Sodium 1e-7
Mercury 2e-6

Chromium 5
Magnesium 2
Manganese 1
Zinc 1e-1
Iron 2e-2
Titanium 3e-3
Nickel 2e-3
Copper 3e-4



Evaporation

- Resistive evaporation
  - Uses resistive heating to evaporate a metallic filament
  - Drawbacks
    - Limited to low melting point metals
    - Small filament size limits deposit thickness
- Electron-beam evaporation
  - Uses a stream of high energy electrons (5-30 keV) to evaporate source material
  - Can evaporate any material
  - Electron-beam guns with power up to 1200 kw
  - Drawbacks
    - At >10 kv (emission voltage), incident electrons can produce x-rays
    - Re-deposition of metal droplets blown of source by vapor
- Ion beam evaporation
- Inductive heating evaporation

Molecular Transport

- We can calculate 2 important quantities:
  - ------Details omitted
- Mean free path (lambda)
  - How far does a molecule go before it strikes another?
- Impingement rate --- Surface Flux
  - How many molecules strike the surface in a given period of time?

At atmosphere, MFP is very short and Surface Flux is very high

At high vacuum, MFP is very long and Surface Flux is very low

Mean Free Path

- **Mean free path:**
  - **d = molecular diameter**

$$\lambda = \frac{1}{\sqrt{2}\pi n d^2}$$

$$\lambda_{cm} = \frac{5*10^{-3}}{P_{torr}}$$

  - **For Air:**

$$\lambda_{cm} = \frac{5}{P_{millitorr}}$$

Flow Regimes

Fluid like

- MFP << "a"

  "crowded"

  - Molecules interact with each other more than walls
  - Act as a "fluid"
  - Flow
  - Diffusion
  - Viscosity
- Familiar region
- Molecules act on each other
- We can act on the gas " as a whole"
- Essentially most of "rough" vacuum range

Viscous Flow

Molecule like

- MFP >> "a"

  "sparse"/ "vacant"

  - A "sparse" gas on the scale of the tube dimension
  - Molecules interact only with the walls
  - Every molecule to itself
  - No intermolecular forces or energy transfer
- We can only act on ONE MOLECULE AT A TIME
- A VERY UNFAMILIAR REGIME.
- Most of mid, high and ultra high vacuum

Free Molecular Flow

Physical vapor deposition (PVD): thermal evaporation

$$N = N_o \exp\text{-}\left(\frac{\Phi_e}{kT}\right)$$

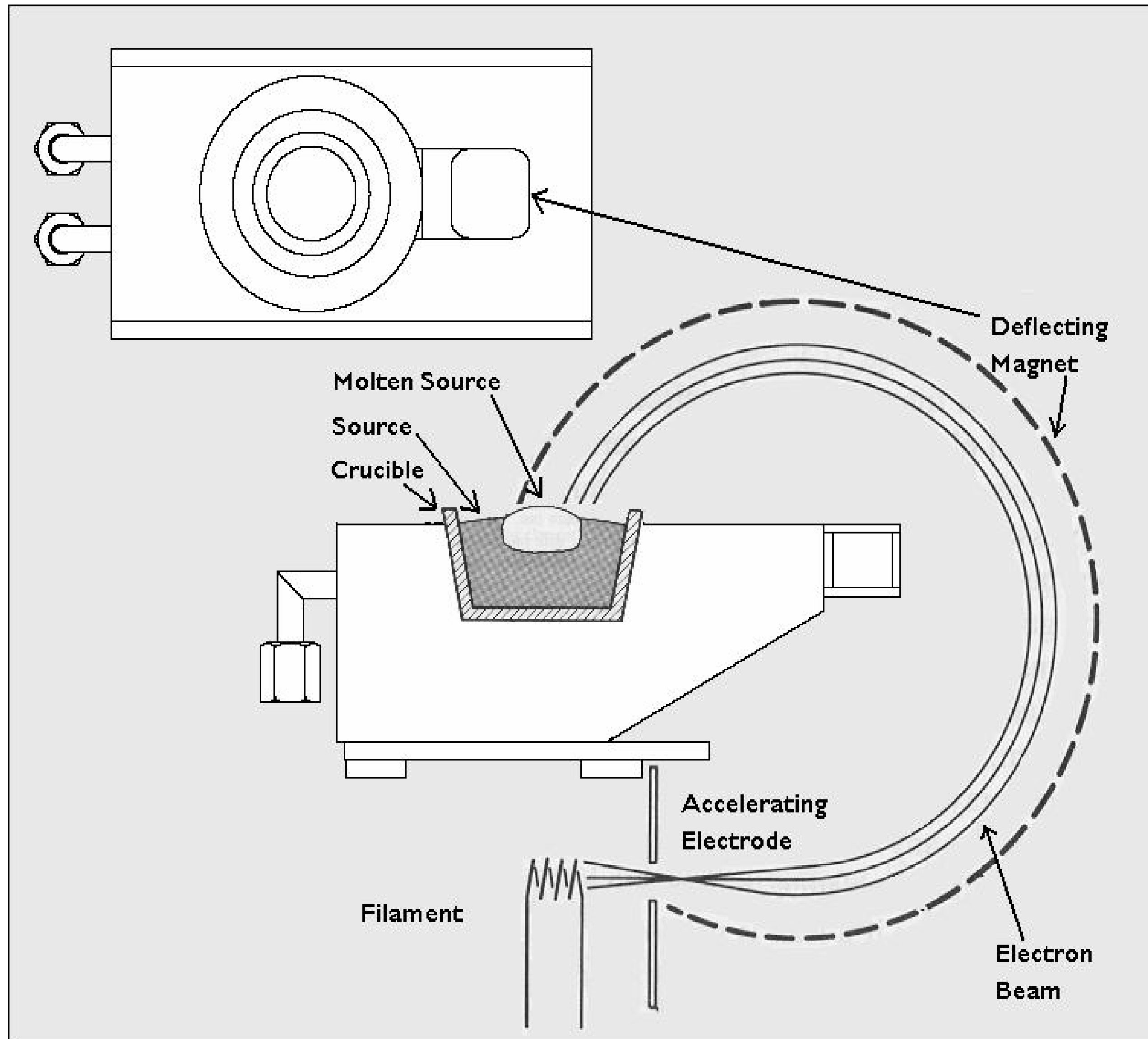
The number of molecules leaving a unit area of evaporant per second

Heat Sources	Advantages	Disadvantages
Resistance	No radiation	Contamination
e-beam	Low contamination	Radiation
RF	No radiation	Contamination
Laser	No radiation, low contamination	Expensive

Kinetic Data for Air as a Function of Pressure

Pressure (Torr)	Mean Free Path (cm)	Number Impingement Rate ($s^{-1} \cdot cm^{-2}$)	Monolayer Impingement Rate (s^{-1})
10^{1}	0.5	3.8×10^{18}	4400
10^{-4}	51	3.8×10^{16}	44
10^{-5}	510	3.8×10^{15}	4.4
10^{-7}	5.1×10^{4}	3.8×10^{13}	4.4×10^{-2}
10^{-9}	5.1×10^{4} 6	3.8×10^{11}	4.4×10^{-4}

E-beam evaporation

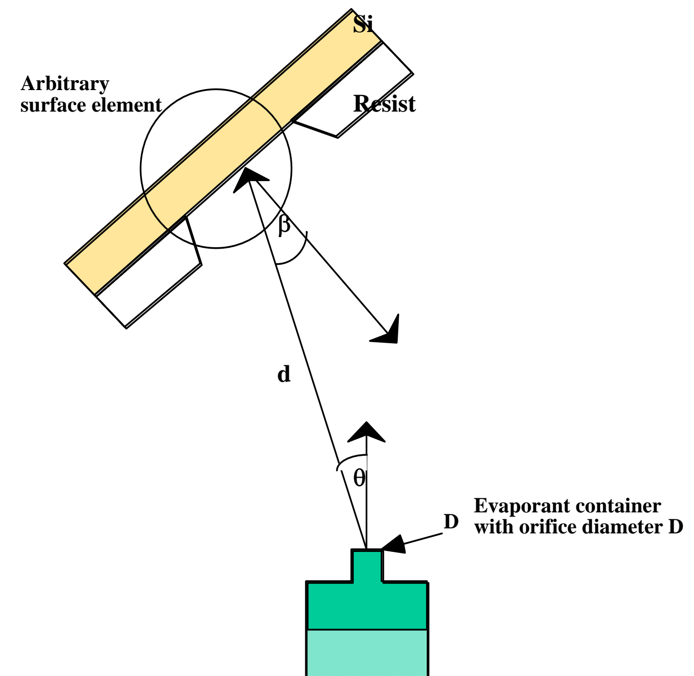


Physical vapor deposition (PVD): thermal evaporation

N (molecules/unit area/unit time) =
$3.513 \cdot 10^{22} P_v(T) / (MT)^{1/2}$

This is the relation between vapor pressure of the evaporant and the evaporation rate. If a high vacuum is established, most molecules/atoms will reach the substrate without intervening collisions. Atoms and molecules flow through the orifice in a single straight track,or we have free molecular flow :

$$K_n = \lambda/D > 1$$



The fraction of particles scattered by collisions with atoms of residual gas is proportional to:

$$1-\exp(+d/\lambda)$$

The source-to-wafer distance must be smaler than the mean free path (e.g, 25 to 70 cm)

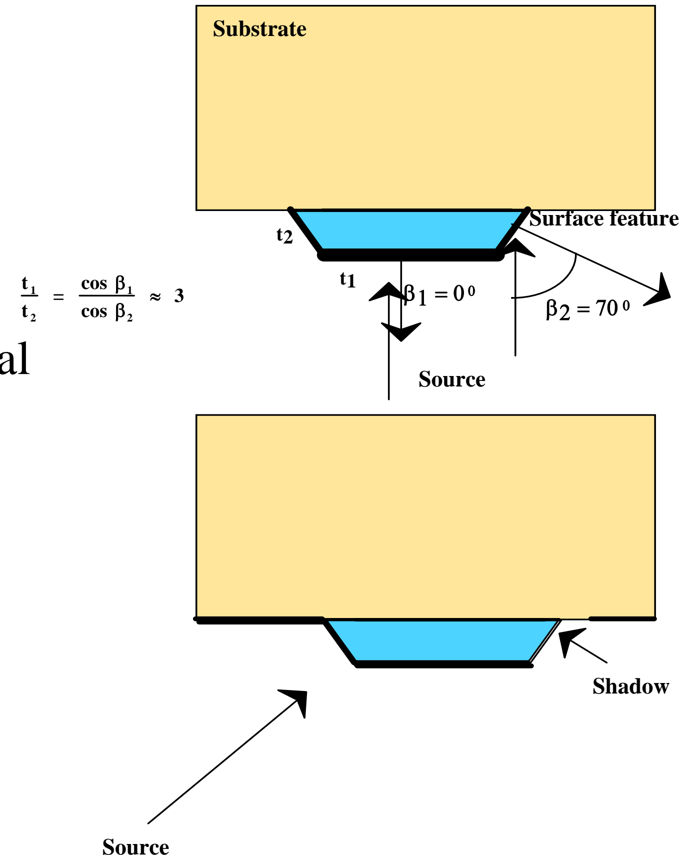
The cosine law

$$A \sim \cos\beta \cos\theta/d^2$$

Physical vapor deposition (PVD): thermal evaporation

From kinetic theory the mean free path relates to the total pressure as:

$$\lambda = (\pi RT/2M)^{1/2}\ \eta/P_T$$



Since the thickness of the deposited film, t, is proportional To the cos β, the ratio of the film thickness shown in the Figure on the right with θ = 0° is given as:

$$t_1/t_2 = \cos\beta_1/\cos\beta_2$$

Advantages

• High film deposition rates;
• Less substrate surface damage from impinging atoms as the film is being formed, unlike sputtering that induces more damage because it involves high-energy particles;
• Excellent purity of the film because of the high vacuum condition used by evaporation;
• Less tendency for unintentional substrate heating.

Disadvantages

1) more difficult control of film composition than sputtering;
2) absence of capability to do *in situ* cleaning of substrate surfaces, which is possible in sputter deposition systems;
3) step coverage is more difficult to improve by evaporation than by sputtering;
4) x-ray damage caused by electron beam evaporation can occur.

Evaporation System Requirements

- Vacuum:
  - Need 10^{-6} torr for medium quality films.
  - Can be accomplished in UHV down to 10^{-9} torr.
- Cooling water:
  - Hearth
  - Thickness monitor
  - Bell jar
- Mechanical shutter:
  - Evaporation rate is set by temperature of source, but this cannot be turned on and off rapidly. A mechanical shutter allows evaporant flux to be rapidly modulated.
- Electrical power:
  - Either high current or high voltage, typically 1-10 kW

Resistance Heated Evaporation

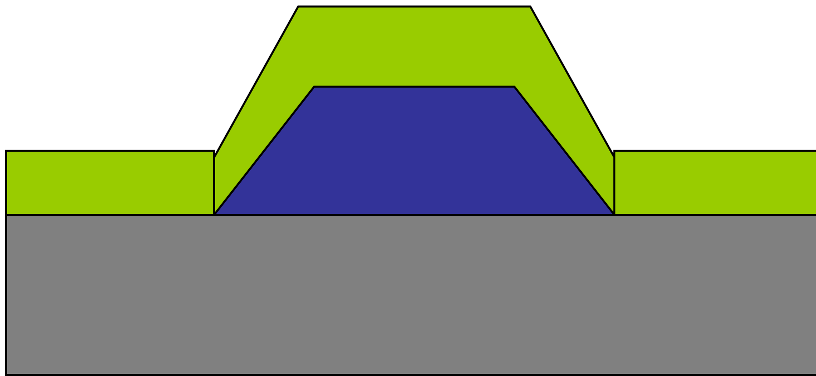
- Simple, robust, and in widespread use.
- Can only achieve temperatures of about 1800°C.
- Use W, Ta, or Mo filaments to heat evaporation source.
- Typical filament currents are 200-300 Amperes.
- Exposes substrates to visible and IR radiation.
- Typical deposition rates are 1-20 Angstroms/second.
- Common evaporant materials:
  - Au, Ag, Al, Sn, Cr, Sb, Ge, In, Mg, Ga
  - CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF_2, CaF_2, $PbCl_2$

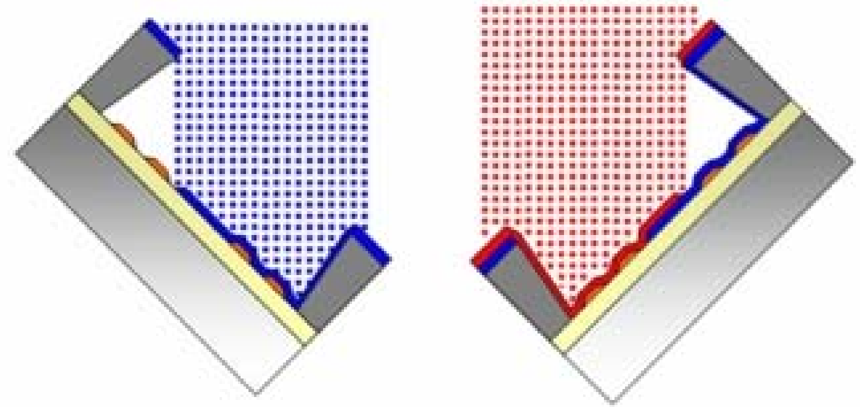
Electron Beam Heated Evaporation - 1

- More complex, but extremely versatile.
- Can achieve temperatures in excess of 3000°C.
- Use evaporation cones or crucibles in a copper hearth.
- Typical emission voltage is 8-10 kV.
- Exposes substrates to secondary electron radiation.
  - X-rays can also be generated by high voltage electron beam.
- Typical deposition rates are 10-100 Angstroms/second.
- Common evaporant materials:
  - Everything a resistance heated evaporator will accommodate, plus:
  - Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo
  - Al_2O_3, SiO, SiO_2, SnO_2, TiO_2, ZrO_2

Non-Conformal Coatings

- Due to line-of-sight evaporation, sidewalls will not be coated as thick as the surface faces.

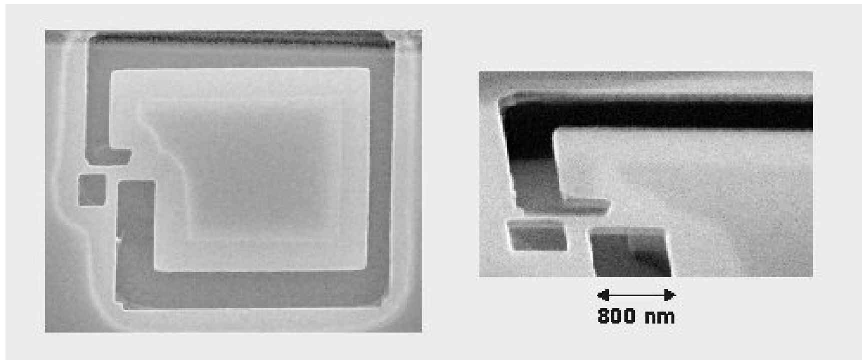




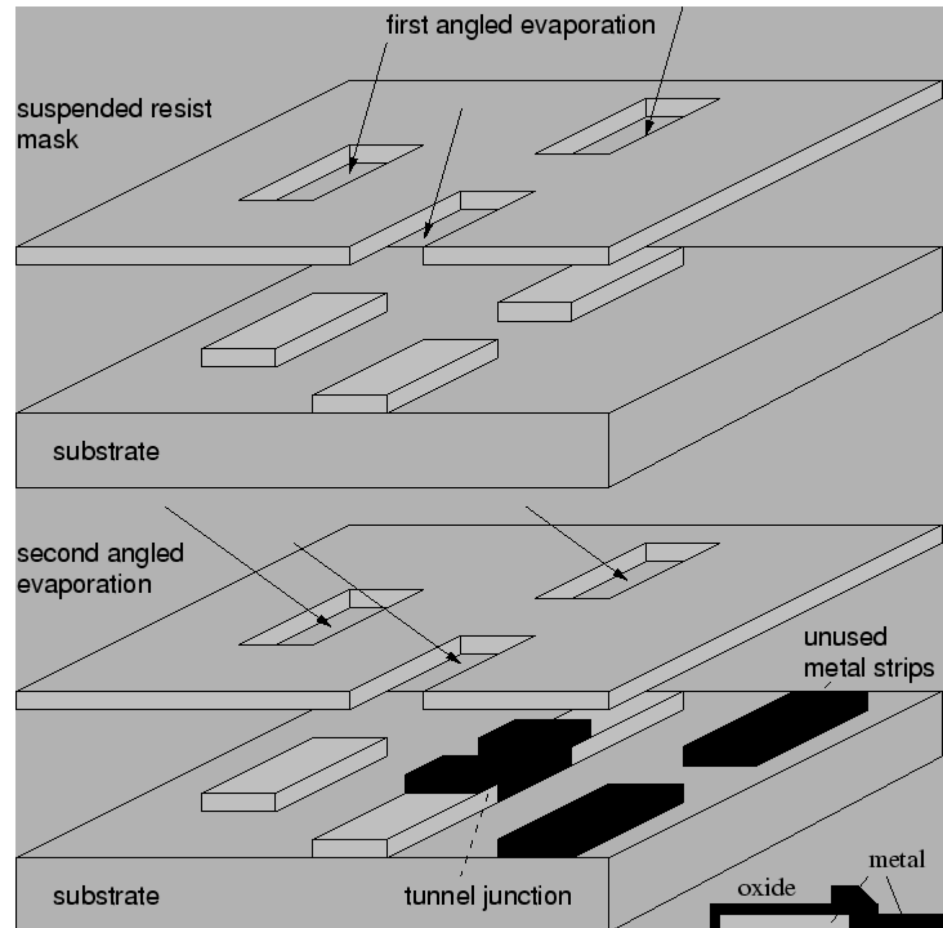
Intentional shadowing

Shadow evaporation

- Routinely used for nanoelectronics fabrication



The pictures show shadow-masks for niobium rings containing a Josephson-junction, prior to evaporation. The metals are evaporated under different angles without breaking the vacuum. The mask consists of Germanium while the sacrificial layer is made of high-temperatur capable plastic (polyether sulphone).



Condensation of Evaporant - 2

- Molecules impinging upon a surface may:
  - Adsorb and permanently stick where they land (rare!).
  - Adsorb and permanently stick after diffusing around on the surface to find an appropriate site.
    - This can lead to physisorption or chemisorption.
  - Adsorb and then desorb after some residence time τ_a.
  - Immediately reflect off of the surface.
- Incident vapor molecules normally have a kinetic energy much higher than $k_B T$ of the substrate surface.
- Whether an atom or molecule will stick depends upon how well it can equilibrate with the substrate surface, decreasing its energy to the point where it will not subsequently desorb.

Condensation Control

- Control of condensation of the evaporant is achieved through the control of substrate temperature T_s.
- Higher substrate temperatures:
  - Increase thermal energy of adsorbed molecules.
    - (Shortens the residence time.)
  - Increase surface diffusivity of adsorbed molecules.
  - Performs annealing of deposited film.
- Substrate heaters:
  - Quartz IR lamps from frontside
  - Ta, W, or Mo foil heaters from backside
  - Graphite impregnated cloth heaters from backside
- Too much heat will desorb the deposited film, evaporating it away! (But this can be used for cleaning…)