520/580.495

Film Deposition

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Lecture notes from

Physical Vapor Deposition by R. Darling

http://www.engr.washington.edu/~cam/PROCESSES/physicalvapdeppdf.html

OUTLINE

- Thin film deposition methods
- Evaporation
- Physics and simple model

METHODS

- Conductors - metal films, polysilicon
- Insulators – dielectrics $Si0_2$
- Semiconductors – GaAs …

- Evaporation
  - Thermal (Filament)
  - Electron-beam
  - Flash
- Sputtering
- Chemical Vapor Deposition (CVD)
  - Low Pressure (LPCVD)
  - Plasma Enhanced (PECVD)
- Epitaxy
  - Vapor Phase (VPE)
  - Liquid Phase (LPE)
  - Molecular Beam (MBE)

EVAPORATION

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.

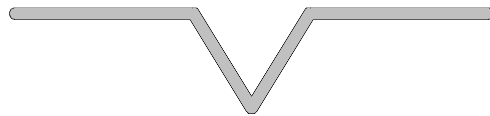
Evaporation Support Materials

- Refractory metals:
  - Tungsten (W); MP = 3380°C, P* = 10^{-2} torr at 3230°C
  - Tantalum (Ta); MP = 3000°C, P* = 10^{-2} torr at 3060°C
  - Molybdenum (Mo); MP = 2620°C, P* = 10^{-2} torr at 2530°C
- Refractory ceramics:
  - Graphitic Carbon (C); MP = 3700°C, P* = 10^{-2} torr at 2600°C
  - Alumina (Al_2O_3); MP = 2030°C, P* = 10^{-2} torr at 1900°C
  - Boron nitride (BN); MP = 2500°C, P* = 10^{-2} torr at 1600°C
- Engineering considerations:
  - Thermal conductivity
  - Thermal expansion
  - Electrical conductivity
  - Wettability and reactivity

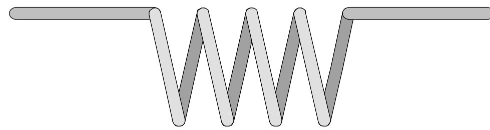
Resistance Heated Evaporation

- 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, $PbCl_2$

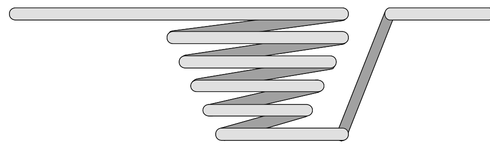
Resistance Heated Evaporation Sources



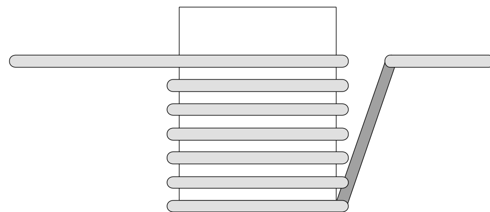
wire hairpin



wire helix



wire basket



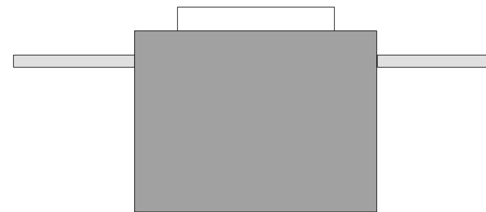
alumina crucible with wire basket

foil dimple boat

alumina coated foil dimple boat

foil trough

chromium coated tungsten rod

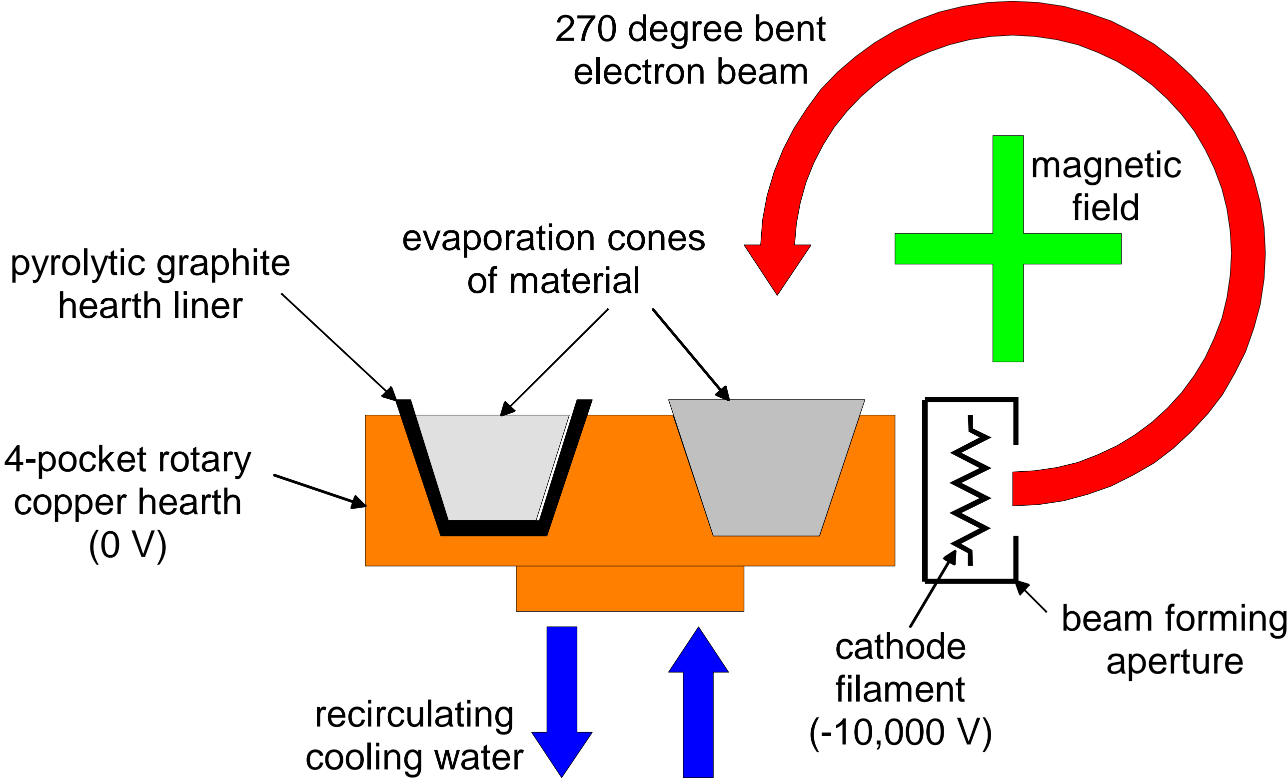


alumina crucible in tantalum box

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

Electron Beam Heated Evaporation Source



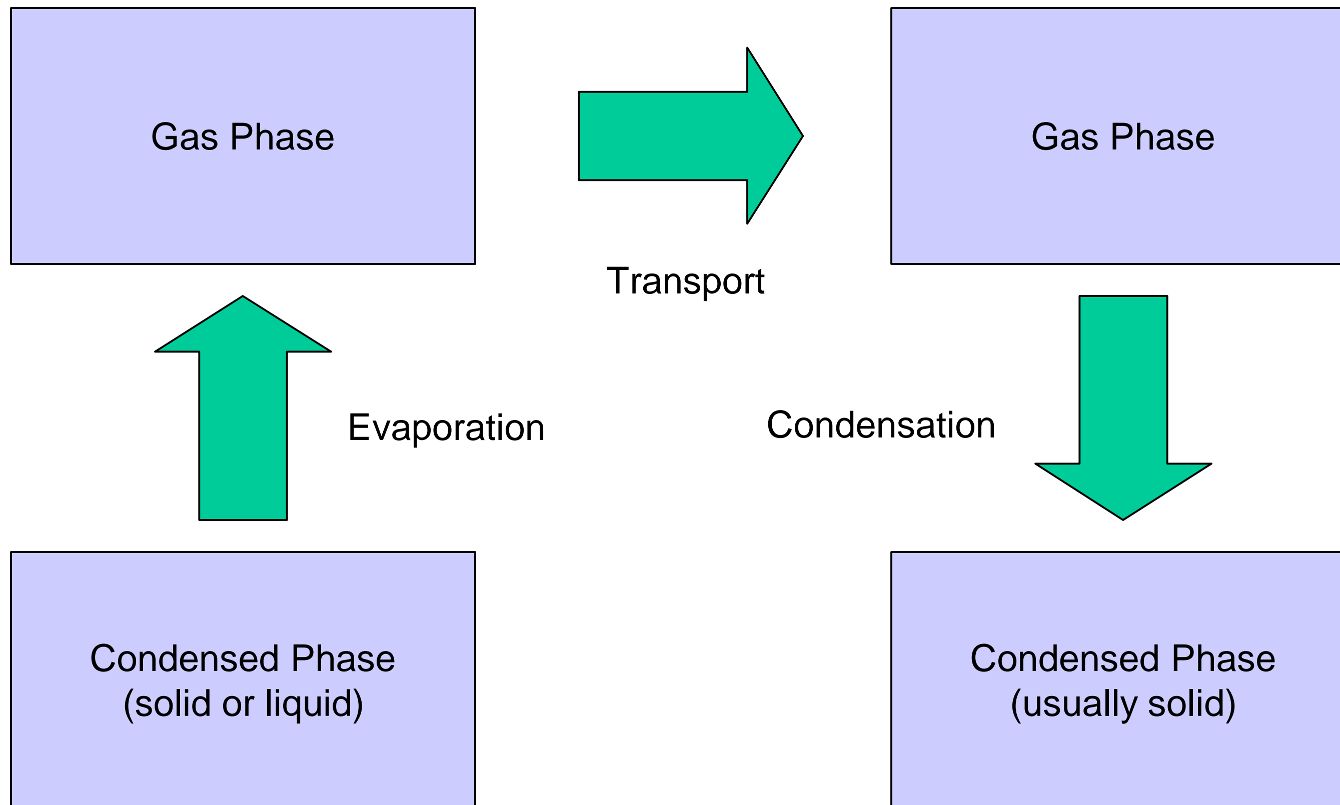
Electron Beam Heated Evaporation - 2

- 270° bent beam electron gun is most preferred:
  - Filament is out of direct exposure from evaporant flux.
  - Magnetic field can be used for beam focusing.
  - Magnetic field can be used for beam positioning.
  - Additional lateral magnetic field can be used produce X-Y sweep.
- Sweeping or rastering of the evaporant source is useful for:
  - Allows a larger evaporant surface area for higher deposition rates.
  - Allows initial charge to be “soaked” or preheated.
  - Allows evaporant source to be more fully utilized.
- Multiple pocket rotary hearth is also preferred:
  - Allows sequential deposition of layers with a single pump-down.
  - Allows larger evaporation sources to be used.

PHYSICS AND MODELS

(First order effects)

Physical Vapor Deposition



Equilibrium Vapor Pressure

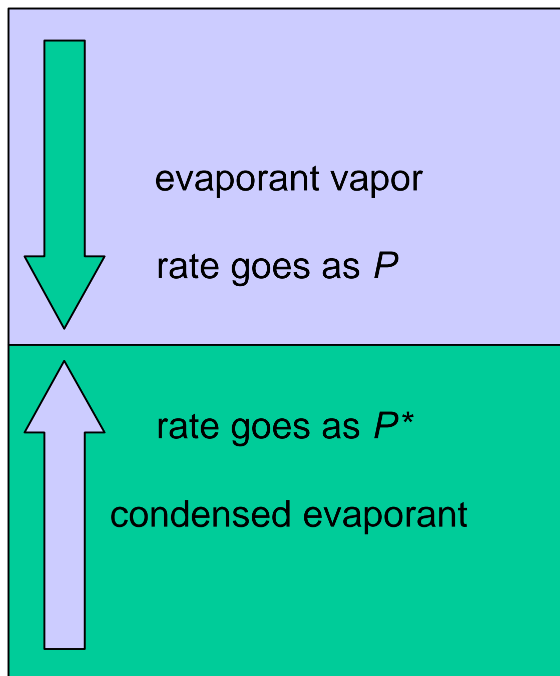
- P^* is the partial pressure of a gas in equilibrium with its condensed phase at a given temperature T.
  - No net transfer of material from one state to the other.
- For a given material, P^* is only a function of T.
  - But the dependence of P^* on T is rather complicated.

Evaporation Rates - 1

- P^* is the equilibrium vapor pressure of the evaporant at T.
- P is the ambient hydrostatic pressure acting upon the evaporant in the condensed phase.
- Heinrich Hertz found experimentally that the evaporation rate was proportional to (P^* - P).
  - This is consistent with kinetic theory in which the impingement rates are proportional to pressure.
  - Hertz also found that the evaporation rate could not be increased by supplying more heat unless the equilibrium vapor pressure was also increased by this action.
  - Thus, there is a maximum evaporation rate set by P^*, and this is only achieved in a vacuum, where $P = 0$.

Evaporation Rates - 2

- This can be viewed as two opposing fluxes:



The net evaporation flux is the difference between the impingement rates for the two fluxes:

$$\frac{dN_e}{A_e dt} = \left(2\pi m k_B T\right)^{-1/2}\left(P^* - P\right)$$

Evaporation Rates - 3

- Hertz only measured rates of about 1/10 of the above using Hg vapor.
- Knudsen postulated that the evaporant vapor molecules impinging upon the condensed phase surface may be reflected back.
  - α_v = sticking coefficient for vapor molecules onto the surface.
  - Then a (1 - α_v) fraction of the vapor molecules contribute to the evaporant pressure, but not to the evaporant flux.
  - Therefore, the vapor pressure must be higher by a factor of $1/\alpha_v$ to obtain the same evaporation rate.
- This gives the general Hertz-Knudsen equation:

$$\frac{dN_e}{A_e dt} = \alpha_v (2\pi m k_B T)^{-1/2} (P^* - P)$$

Mass Evaporation Rates

- Γ = mass evaporation rate in g/cm^2-sec:

$$\Gamma = m \frac{dN_e}{A_e dt} = \alpha_v \left(\frac{m}{2\pi k_B T} \right)^{1/2} \left(P^* - P \right)$$

- For most elements, $\Gamma \sim 10^{-4}$ g/cm^2-sec at $P^* = 10^{-2}$ torr.
- The mass of the evaporated material is

$$M_e = \int_0^t \int_0^{A_e} \Gamma \, dA_e \, dt$$

Free Evaporation Versus Effusion

- Evaporation from a free surface is termed Langmuir evaporation.
- Because α_v is often much less than unity, the general Hertz-Knudsen expression must be used.
- Effusion refers to evaporation through an orifice by which the area of the orifice appears as an evaporation source of the same area.
- Free evaporation is isotropic.
- Effusion is somewhat directional.
  - Ideally, it is a Lambertian angular distribution.

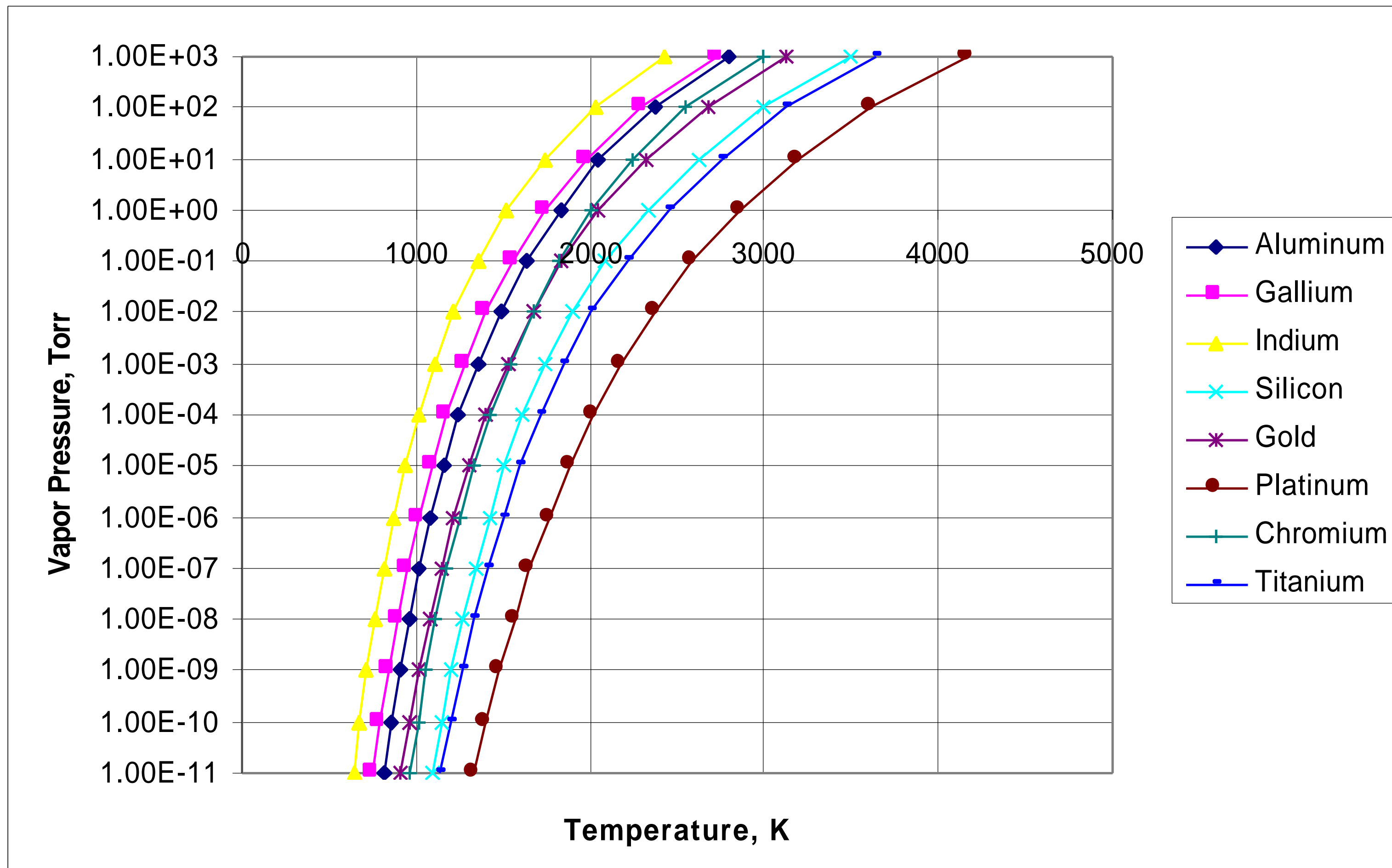
Equilibrium Vapor Pressure

- A working formulation of the equilibrium vapor pressure from standard thermochemical data is therefore:

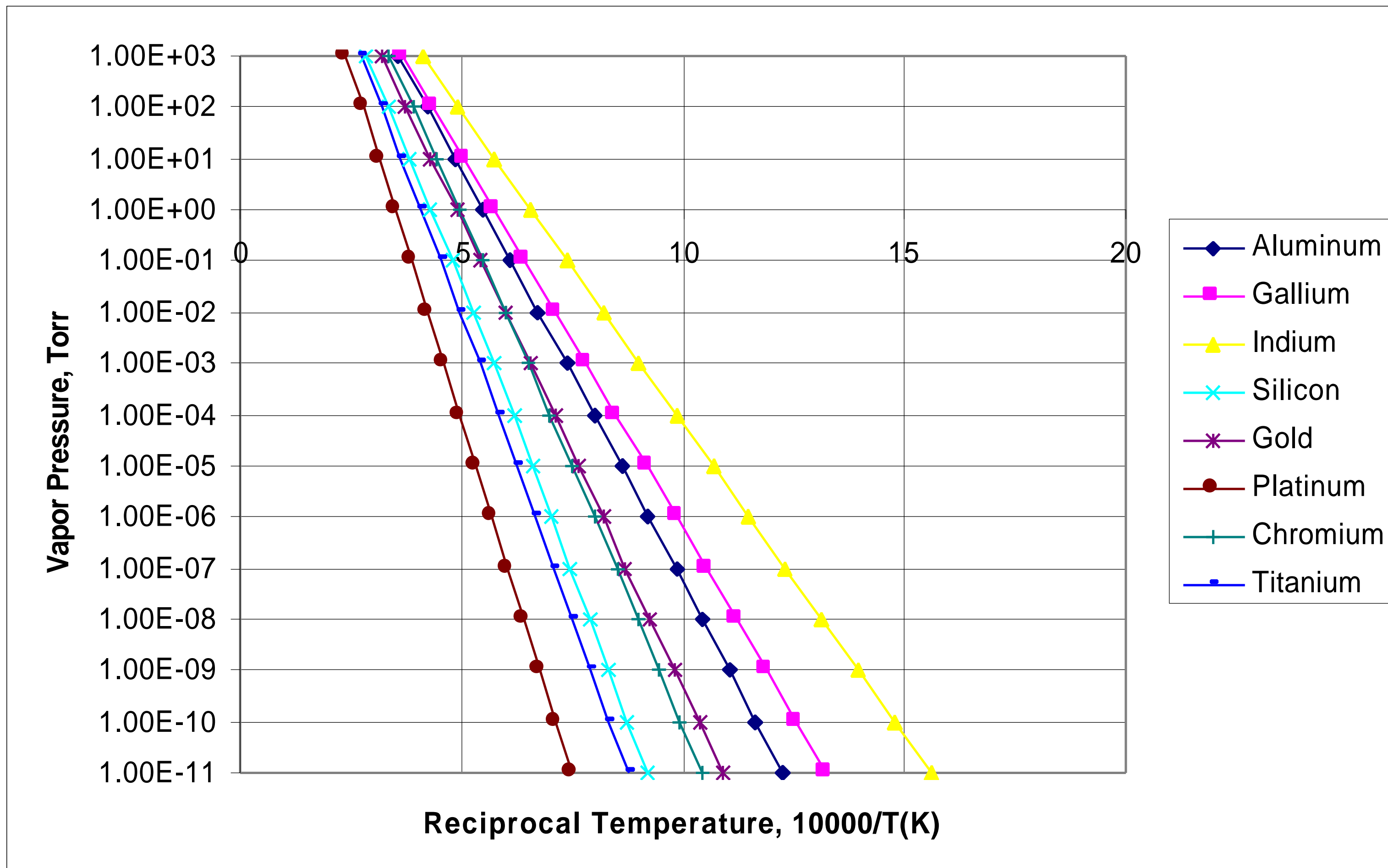
$$\ln P^* = -\frac{\Delta H_{eo}(298K)}{RT} + \frac{\Delta S_{eo}(298K)}{R} + \frac{1}{RT}\int_{298K}^{T}\int_{298K}^{T}\frac{\Delta c_p}{T}\,dT\,dT$$

  - P^* is in units of atmospheres.
  - ΔH_{eo}(298K), ΔS_{eo}(298K), and c_p(T) may be found in standard tables of thermochemical data.
  - Note: 1 kcal = 1 Cal = 1000 cal = 4186.8 J = 3.97 BTU
  - See Section D of the CRC Handbook of Chemistry and Physics.
  - Example: Aluminum:
    - ΔH_{eo}(298K) = 70 kcal/mole, ΔS_{eo}(298K) = 30 kcal/mole-K, at the boiling point of P = 1 atm and T = 2327°C = 2600 K.
    - ΔH_{mo}(298K) = 2.57 kcal/mole, at the melting point of P = 1 atm and T = 658.5°C = 931.7 K.

Equilibrium Vapor Pressure



Equilibrium Vapor Pressure



Adsorption

- Adsorption is the sticking of a particle to a surface.
- Physisorption:
  - The impinging molecule loses kinetic (thermal) energy within some residence time, and the lower energy of the molecule does not allow it to overcome the threshold that is needed to escape.
- Chemisorption:
  - The impinging molecule loses its kinetic energy to a chemical reaction which forms a chemical bond between it and other substrate atoms.

Condensation of Evaporant - 1

- Condensation of a vapor to a solid or liquid occurs when the partial pressure of the vapor exceeds the equilibrium vapor pressure of the condensed phase at this temperature.
- The vapor is "supersaturated" under these conditions.
- This is only true if condensation takes place onto material which is of the same composition as the vapor.
- When a material is first deposited onto a substrate of a different composition, a third adsorbed phase must be included to describe the process.

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 of Evaporant - 3

- Thermal accomodation coefficient:

$$\alpha_T = \frac{E_v - E_r}{E_v - E_s} = \frac{T_v - T_r}{T_v - T_s}$$

  - E_v, T_v = energy, temperature of impinging vapor molecules.
  - E_r, T_r = energy, temperature of resident vapor molecules;
    - (Those which have adsorbed, but have not permanently found a site.)
  - E_s, T_s = energy, temperature of substrate surface.
- If $\alpha_T < 1$, ($E_r > E_s$), then some fraction of the impinging molecules will desorb from the surface.

Condensation of Evaporant - 4

- Mean residence time for an adsorbed molecule:

$$\tau_a = \frac{1}{\upsilon_0} \exp\left(\frac{\Delta G_{\mathrm{des}}}{\mathrm{k_B} T} \right)$$

  - $\upsilon_0 = k_B T/h$ = vibrational frequency of adsorbed molecule ($\sim 10^{14}$ Hz)
    - This is the frequency at which the molecule "attempts" to desorb.
  - ΔG_{des} = free activation energy for desorption.
- Under a constant impinging vapor flux of R, the surface density of the deposit is then:

$$n_s = R\tau_a = \frac{R}{\upsilon_0} \exp\left(\frac{\Delta G_{\mathrm{des}}}{\mathrm{k_B} T} \right)$$

  - R = deposition rate in molecules/cm^2-sec.
  - n_s = surface density of deposited molecules in cm^{-2}.

Condensation of Evaporant - 5

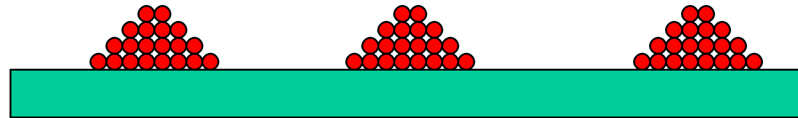
- If the impingement rate stops, then the adsorbed molecules will all eventually desorb.
- Condensation of a permanent deposit will not occur, even for low substrate temperatures, unless the molecules interact.
- Within the mean residence time, surface migration occurs and clusters form.
- Clusters have smaller surface-to-volume ratios, and therefore desorb at a reduced rate.
- Nucleation of a permanent deposit is therefore dependent upon clustering of the adsorbed molecules.

Stages of Thin Film Growth

- Island Stage
- Coalescence Stage
- Channel Stage
- Continuous Film Stage

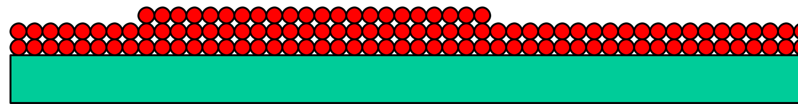
Modes of Thin Film Growth

(1) Volmer-Weber: (island growth):



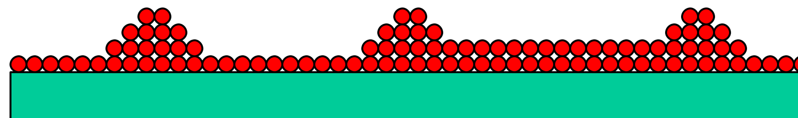
M. Volmer and A. Weber, *Z. Phys. Chem.* **119**, p. 277 (1926).

(2) Frank-Van der Merwe: (layer growth; ideal epitaxy):



F. C. Frank and J. H. Van der Merwe, *Proc. R. Soc. London*, Ser. A **198**, p. 205 (1949).

(3) Stranski-Krastanov: (layers + islands):



J. N. Stranski and L. Krastanov, *Ber. Akad. Wiss. Wien* **146**, p. 797 (1938).

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…)