520/530/580.495

Film Deposition

Lecture notes from

Physical Vapor Deposition by R. Darling

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

OUTLINE

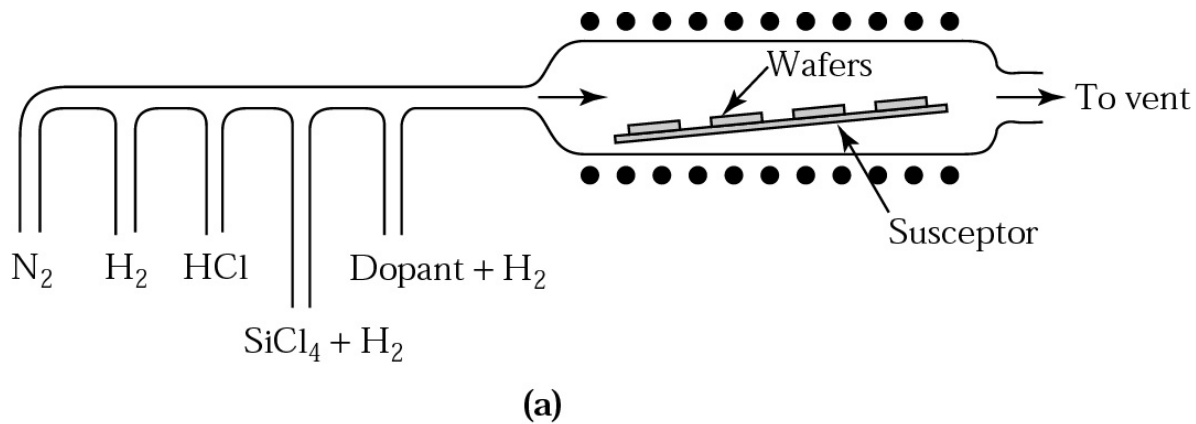
- Thin film deposition methods
- Evaporation
  - Physics and simple model
- Electrochemical deposition

METHODS

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

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

Chemical Vapor Deposition (CVD)



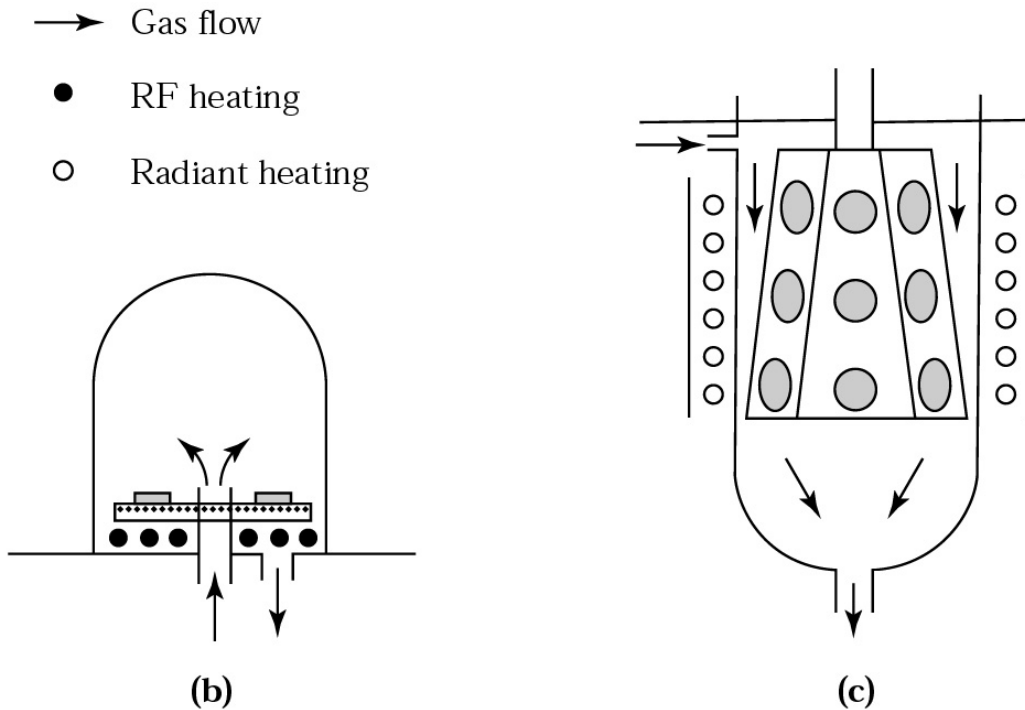


Figure 8.1 (p. 145 May and Sze)
Three common susceptors for chemical vapor deposition: (*a*) horizontal, (*b*) pancake, and (*c*) barrel susceptors.

Molecular Beam Epitaxy

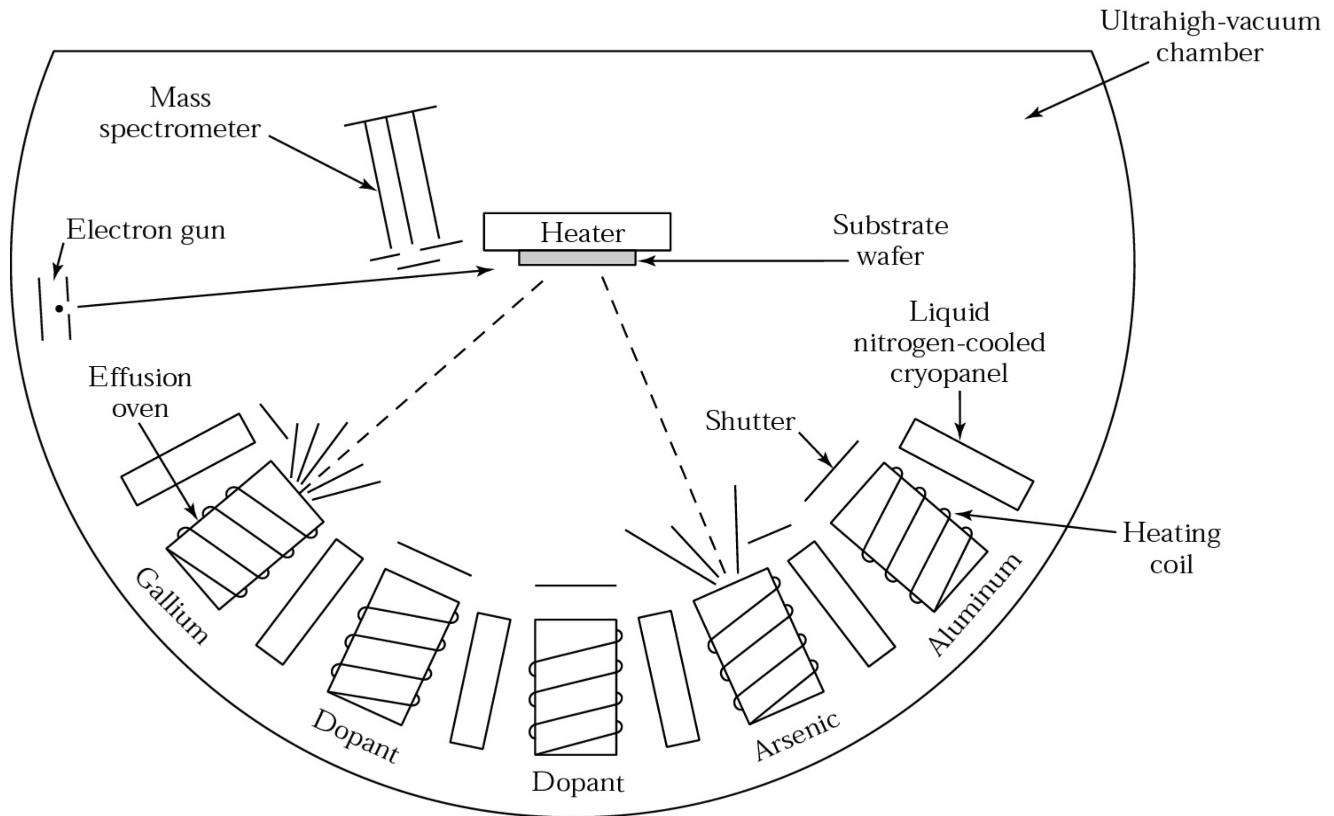
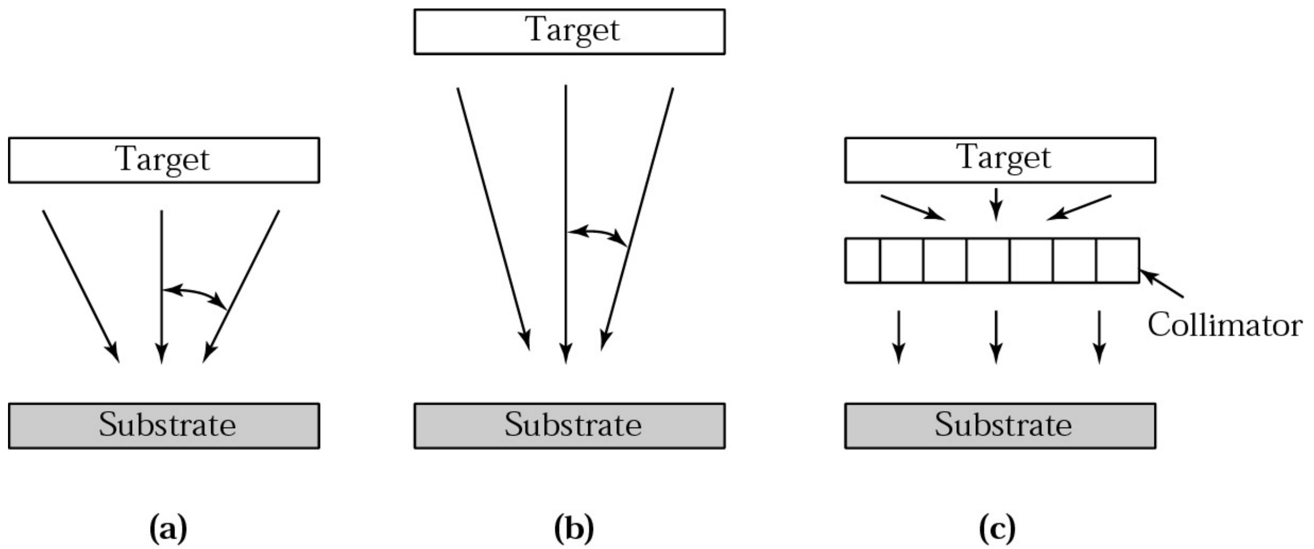


Figure 8.5 (p. 149) May and Sze

Arrangement of the sources and substrate in a conventional molecular beam epitaxy (MBE) system. (Courtesy of M. B. Panish, Bell Laboratories, Lucent Technologies).

Spattering



May and Sze Figure 8.18 (p. 168)

(*a*) Standard sputtering. (*b*) Long-throw sputtering. (*c*) Sputtering with a collimator.

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.

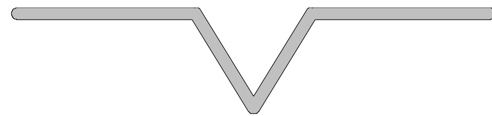
Evaporation Support Materials

- 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

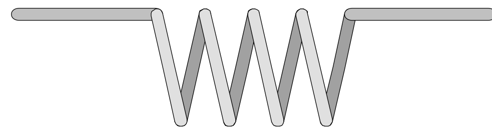
- Simple, robust, and in widespread use.
- Can only achieve temperatures of about 1800°C.
- Use W, Ta, or Mo filaments to heat evaporation source.
- Typical filament currents are 200-300 Amperes.
- Exposes substrates to visible and IR radiation.
- Typical deposition rates are 1-20 Angstroms/second.
- 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

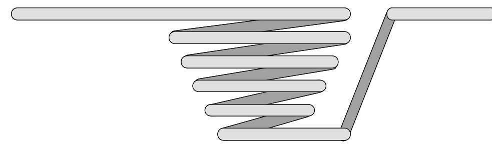

wire hairpin

foil dimple boat

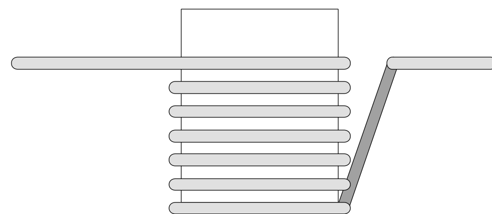
alumina coated foil dimple boat

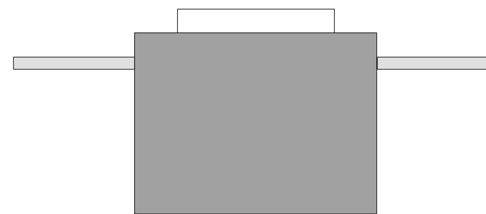

wire helix

foil trough


wire basket

chromium coated tungsten rod

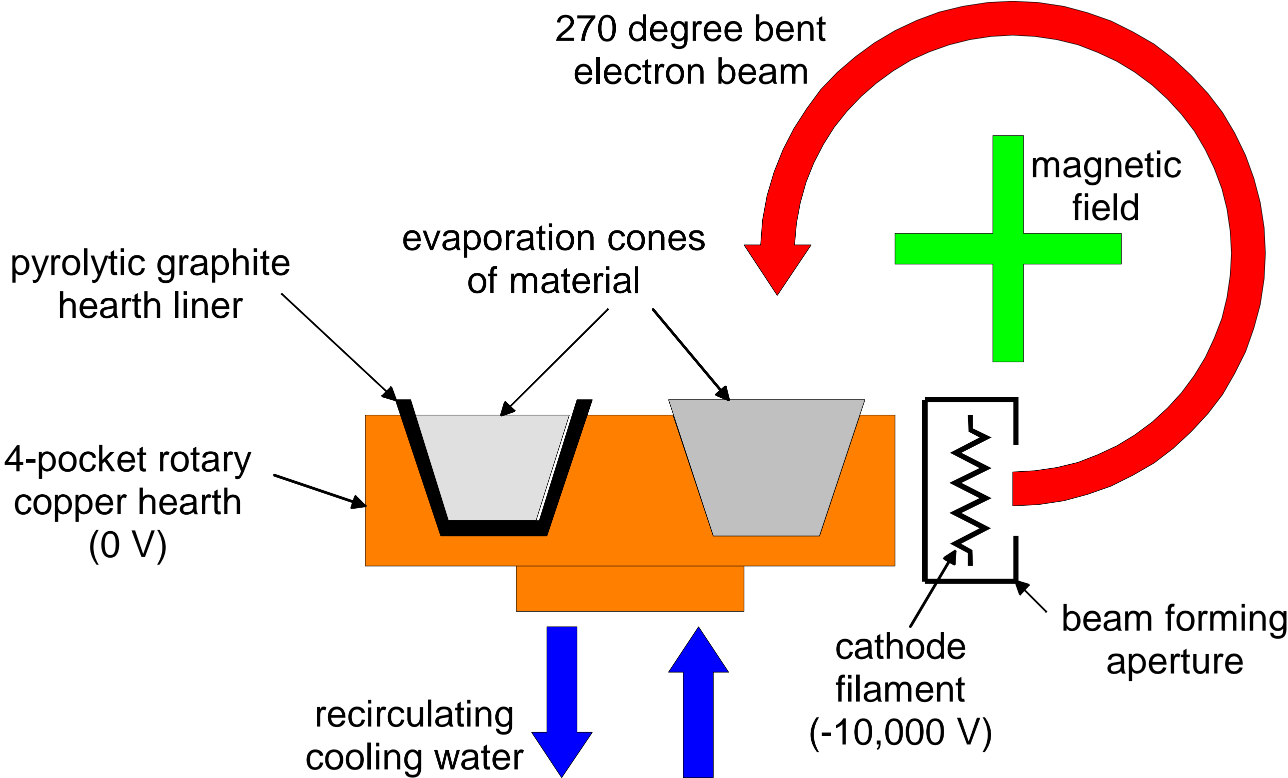

alumina crucible with wire basket


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

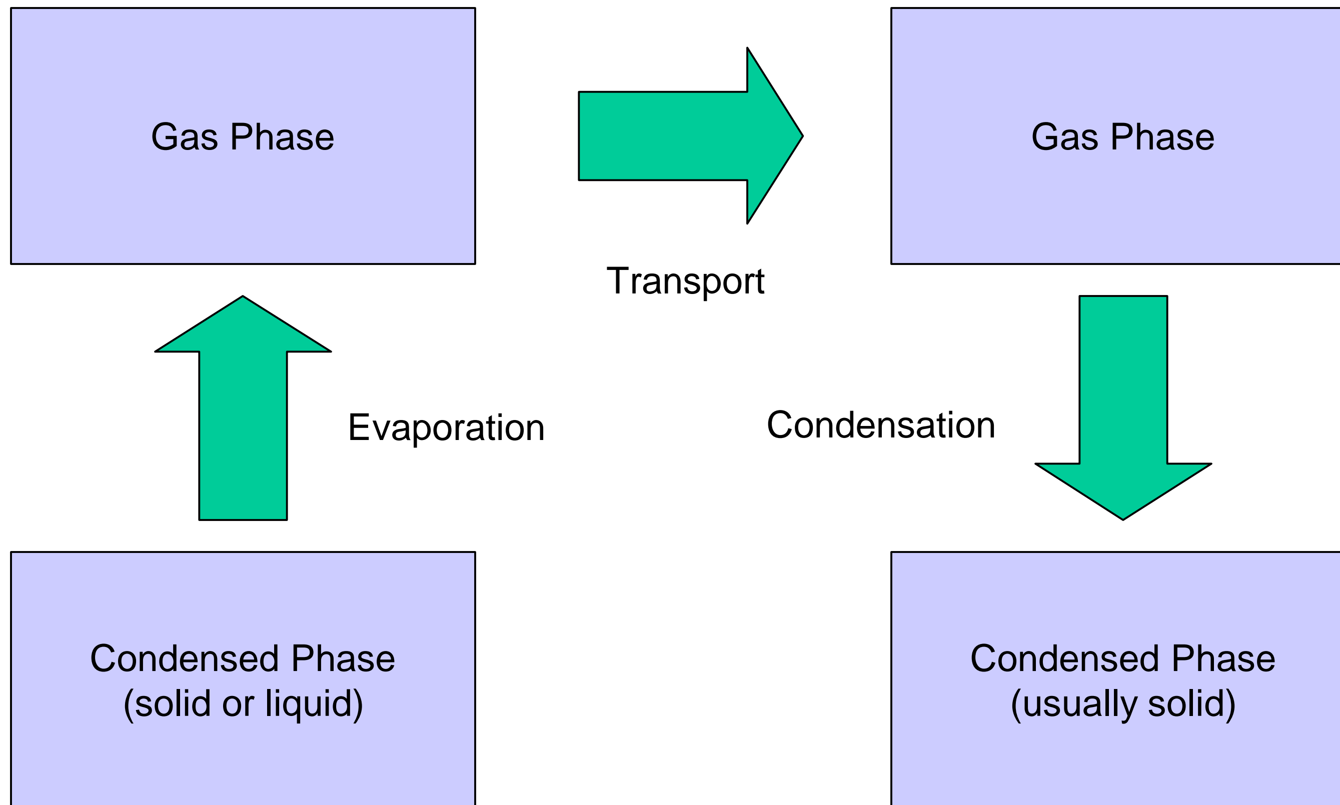
Electron Beam Heated Evaporation Source



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.

Physical Vapor Deposition



Equilibrium Vapor Pressure

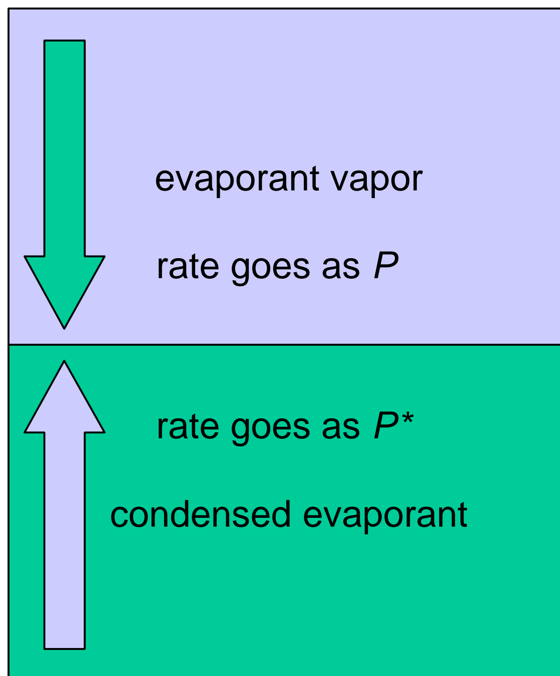
- $P*$ is the partial pressure of a gas in equilibrium with its condensed phase at a given temperature T.
  - No net transfer of material from one state to the other.
- For a given material, $P*$ is only a function of T.
  - But the dependence of $P*$ on T is rather complicated.

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.

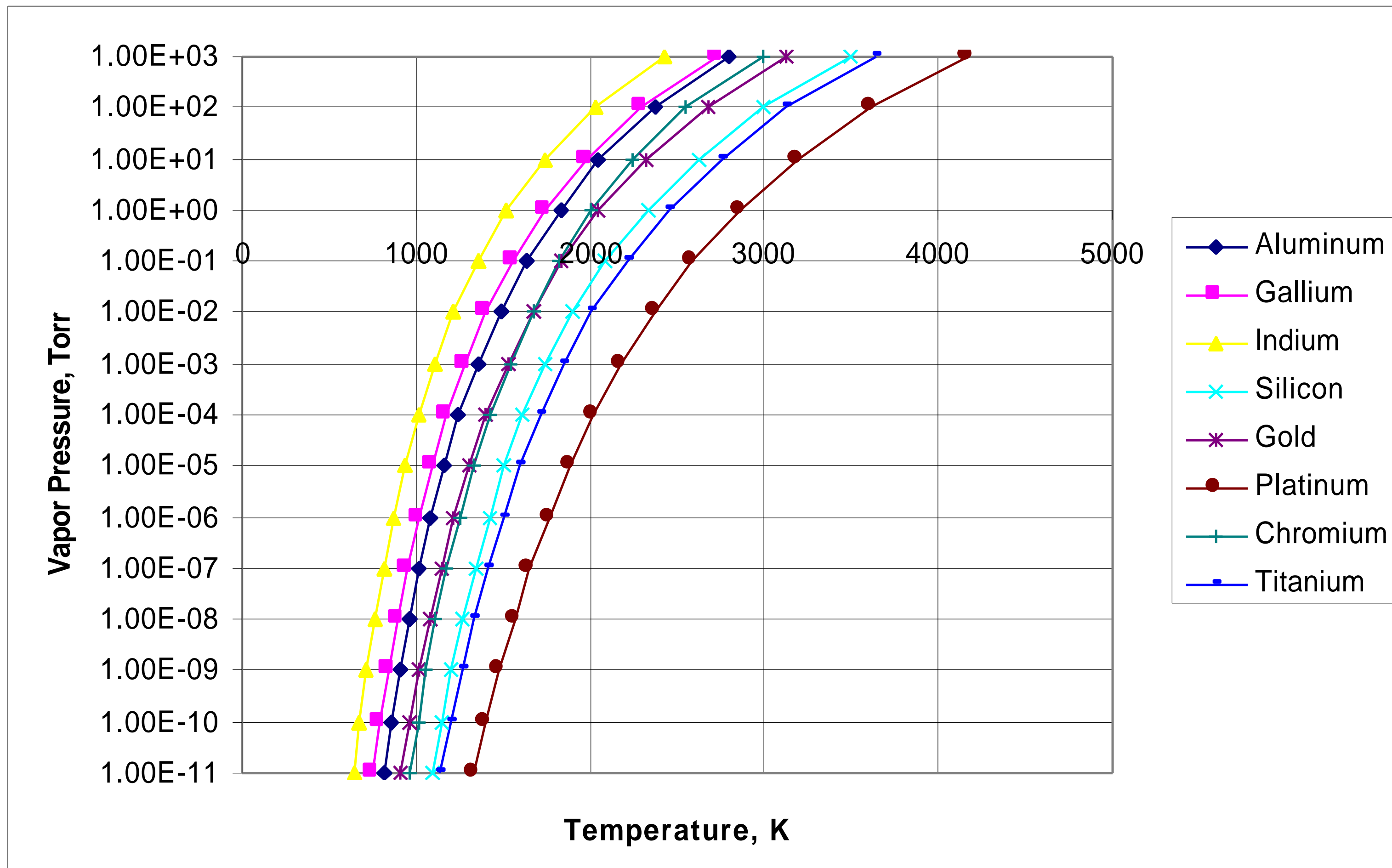
Equilibrium Vapor Pressure

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

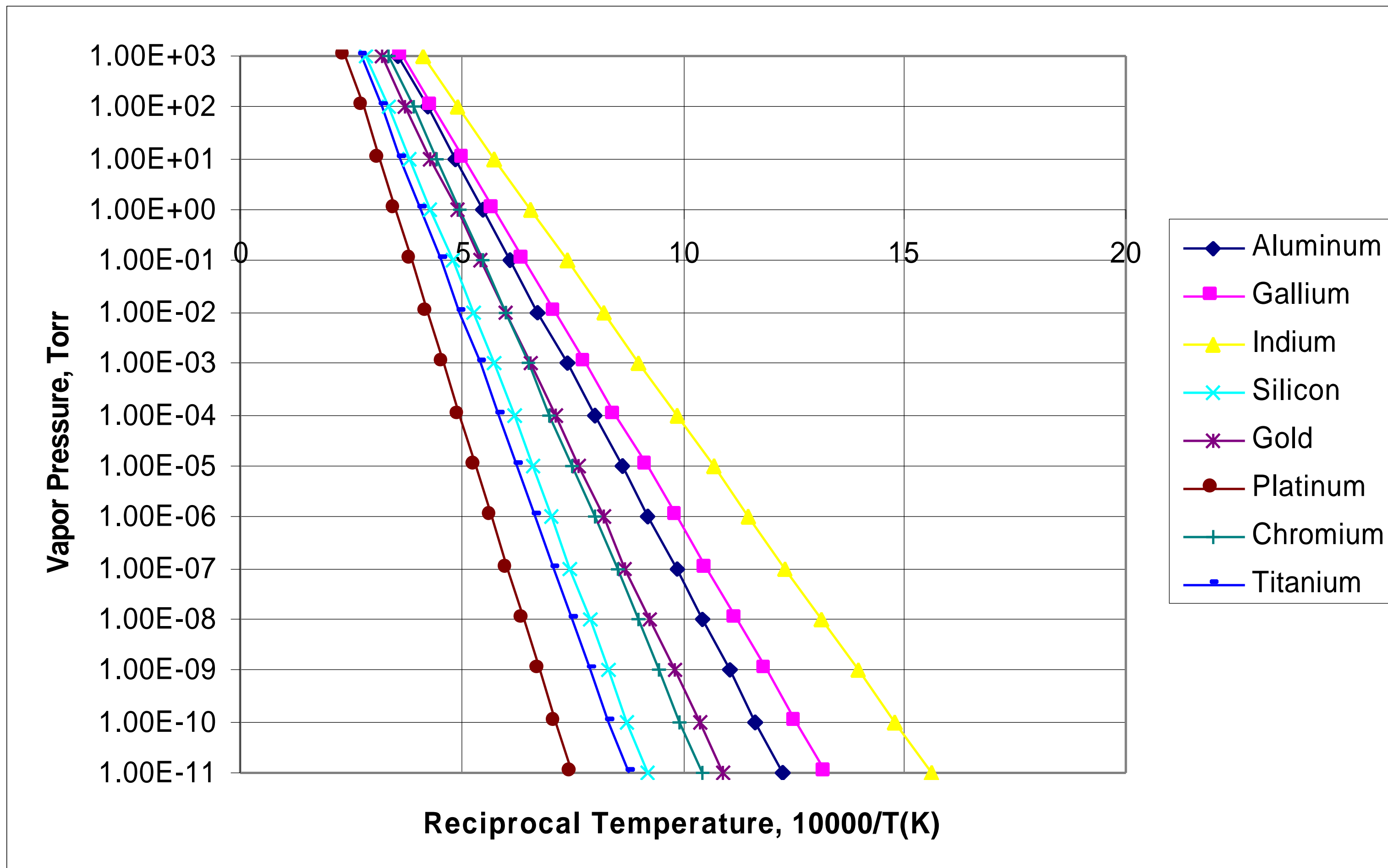
$$\ln P^* = -\frac{\Delta H_{eo}(298K)}{RT} + \frac{\Delta S_{eo}(298K)}{R} + \frac{1}{RT}\int_{298K}^{T}\int_{298K}^{T}\frac{\Delta c_p}{T}\,dT\,dT$$

  - 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



Electrochemical Deposition

- Introduction
- Electro-plating
- Immersion plating (electroless plating)
- References

Introduction

- Plating is basically an application of REDOX chemistry
  - Electro-plating
  - Electroless plating
- Large industry for finishing parts
- Use in microelectronics for bonding posts and recently for copper interconnects
- Heavily regulated by EPA (not a basement or garage operation)

REDOX: Reduction / Oxidation Reactions

- **Electron transfer reactions**

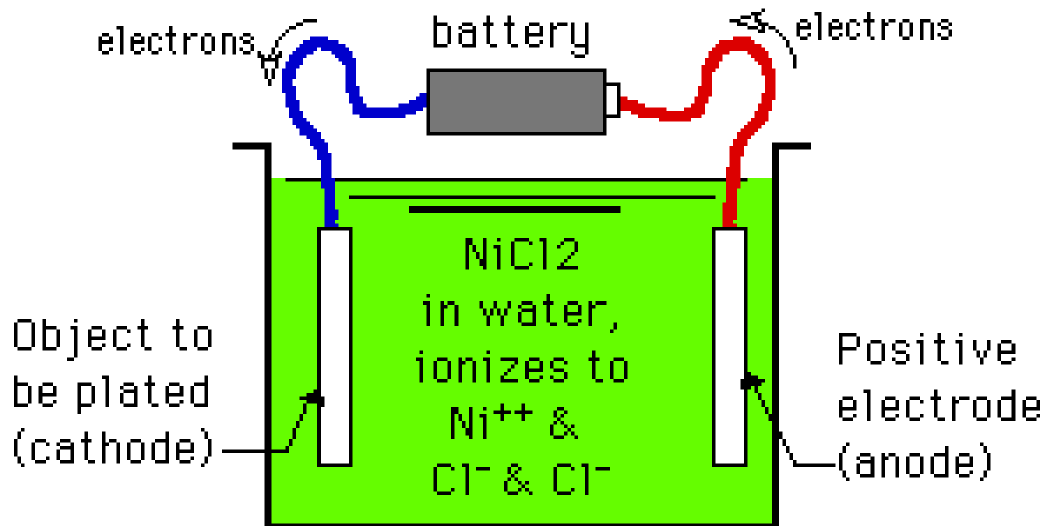
Oxidizing agent + n e^- = Reducing agent

Oxidation is a loss of electrons
Reduction is a gain of electrons

Oxidizing agents get reduced

Reducing agents get oxidized

Electroplating



- Copper object (cathode)
- Salt (nickel chloride) –molten or in water-
- Source of metal used for plating (anode)
- Nickel (ionic) gets REDUCED and gets deposited at the cathode
- Nickel (metal) gets OXIDIZED at the anode and gets into the solution

Electroplating @Home

- Cathode: is clean shiny US penny
- Anode: is sand down modern US penny (to expose zinc core)
- Solution: water based zinc salt
  - Vinegar
  - Add 100g/l Epsom salts
  - Add 120g/l table sugar
  - Mix in a pyrex container

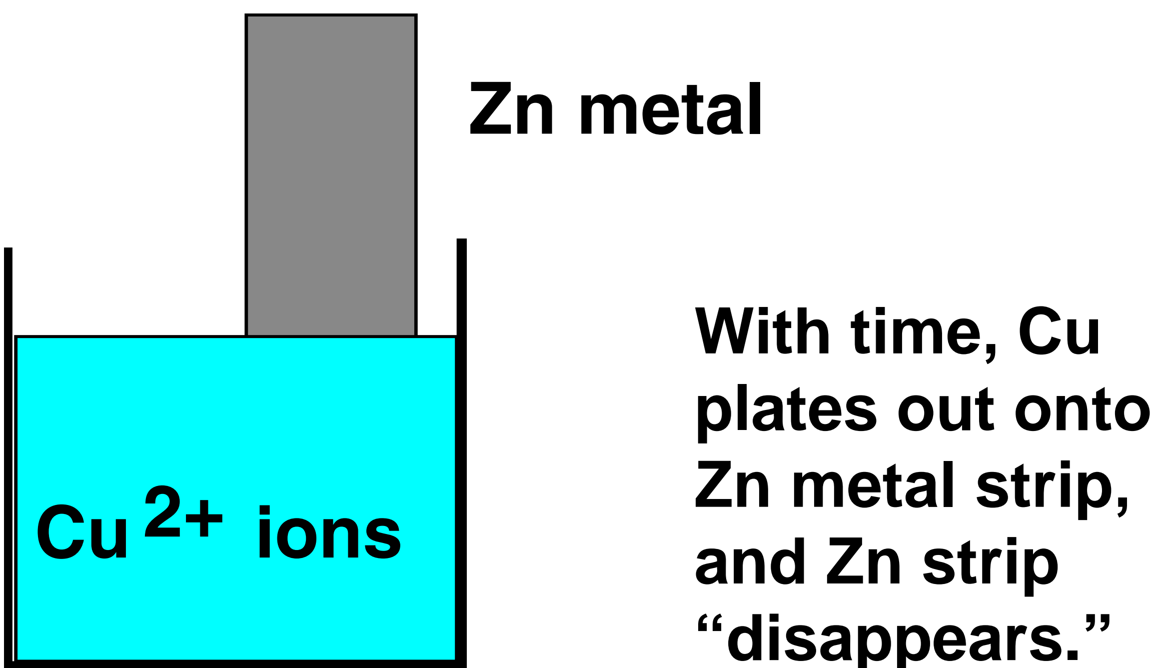
Put zinc penny in the vinegar and let sit for a few hours (dissolve zinc).

Add epsom salts and table sugar.

Use a 1.5 Volt flashlight battery to supply the current.

Sit and watch your copper penny zinc plated (silvery coating).

Immersion plating (electrroless plating)



- Zn is oxidized and is the reducing agent

  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

- Cu^{2+} is reduced and is the oxidizing agent

  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

CHEMICAL CHANGE → ELECTRIC CURRENT

Green processes

- No cyanides
- No phosphates
- No caustic amines
- Commercial products employ proprietry chemistry that companies do not make public (such as our Technics plating solutions)

References

- http://www.finishing.com

(general information)

- http://www.finishing.com/Library

(library)