

Midterm 1 Review

Solid State Physics

- Solid matter forms can form in random (amorphous) or orderly (crystalline) fashion.
- Crystalline matter can be classified by the types of bonds they form.
 - Metallic, ionic, covalent, atomic, molecular.
- The bonds determine the electronic energy structure of the crystal.

Band Structure

- As individual atoms or molecules form bonds and larger crystals, their discrete energy levels split finer and finer until they form virtual continuums (energy bands) separated by prohibited levels (energy gaps).
- The available electrons of the atom fill these bands with the ones tightest bound to the nucleus having the lowest energy.
- The electrical and optical properties of the material is determined by the higher energy electrons and whether they fill the highest occupied band (valence band) completely or partially.

Semiconductors

- If the valence band is only partially filled we have a conductor.
- If it is completely filled we have an insulator or a semiconductor.
- Semiconductors are insulators with smaller band gaps and can be controllably doped with an acceptor (p-type) or donor (n-type) to change their conduction and the type of carriers.
- p- and n-type semiconductors can be put together to form diodes, LEDs, transistors or solar cells.

Defects

- Many electrical, optical, mechanical and thermal properties of materials are determined by the defects they have.
 - Vacancies (point defects) are thermal in nature.
 - Edge dislocations (line defects) arise from film growth problems.
 - Grain boundaries (surface defects) are seen in polycrystalline films.

Thermodynamics

- The possibility of a chemical reaction is determined by thermodynamics.

$$\Delta G = \Delta H - T\Delta S$$

where ΔG is the change in the Gibbs Free Energy, ΔH is the change in the enthalpy, ΔS is the change in entropy

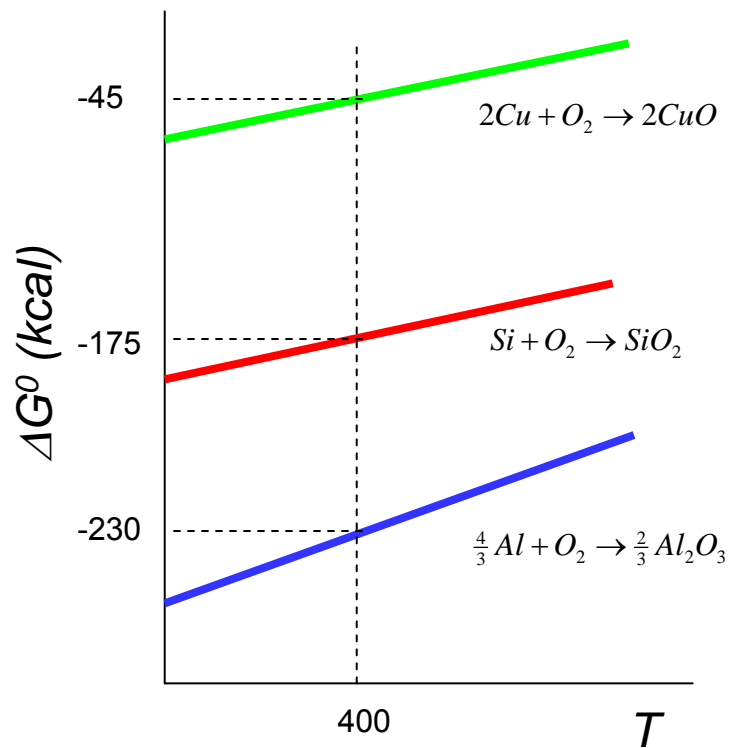
- If $\Delta G > 0$, the process is forbidden.
 - If $\Delta G < 0$, it is allowed.
 - If $\Delta G = 0$, there is equilibrium.
- In a chemical reaction involving three substances, in most cases, the Gibbs Free Energy can be taken as,

$$\Delta G = \Delta G^0 = RT \ln \left\{ \frac{a_{C,eq}^c}{a_{A,eq}^a a_{B,eq}^b} \right\}$$

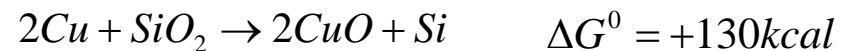
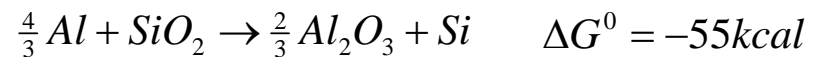
where where the a_i 's are the activities (kind of a thermodynamic concentration) and ΔG^0 is the standard state value of ΔG .

Example – Ellingham Diagrams

- Plots of ΔG^0 vs. T can be used to determine a preferred reaction.
- Consider the choice of depositing either Al or Cu on SiO_2 at 400 K.



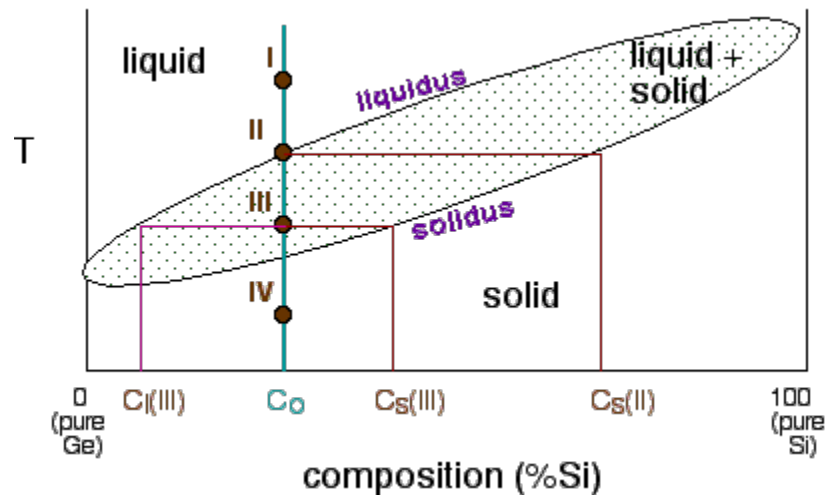
To get the relevant reduction equations for Si, add either the Al or Cu equation to the Si equation and algebraically eliminate O_2 . Apply the same factor to the free energy. Then you'll get:



Since the Al reaction has a lower free energy and will reduce SiO_2 , Cu would be the better choice for metallization.

Phase Diagrams

- Phase diagrams represent the equilibrium conditions for inorganic systems as a function of pressure, temperature and composition.



Kinetics - Diffusion

- Fick's first law governs one dimensional diffusion:

$$J = -D \frac{dC}{dx}$$

where J is the mass flux, D is the diffusion constant and C is the concentration

- The diffusion constant is temperature dependent.

$$D = D_0 \exp(-E_D/k_B T)$$

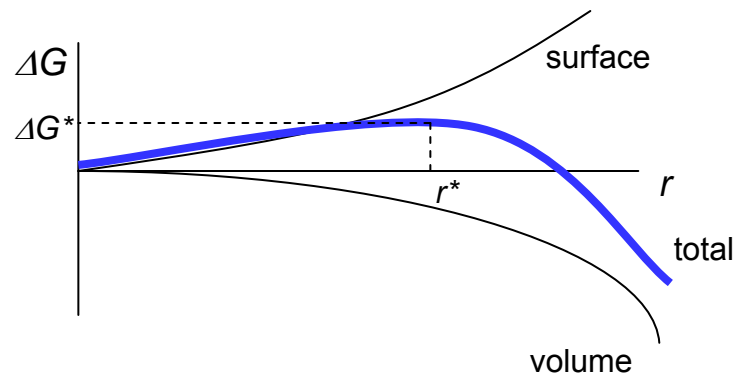
- Point defects promote diffusion as neighboring site vacancies increase atomic movement.

Nucleation

- If the formed nuclei are larger than a critical radius, then nucleation is possible.
- The volume transition free energy has to be negative and overcome the surface transition free energy.

$$\Delta G_v = \frac{k_B T}{\Omega} \ln \frac{P_S}{P_V}$$

$$\Delta G_{total} = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma$$



- The kinetics of nucleation depend on the following:

$$\dot{N} = N^* A^* \omega$$

where N^* is the equilibrium concentration of the stable nuclei, ω is the rate at which atoms impinge on to the nuclei of critical area A^* .

Example – SiO₂

- During SiO₂ formation, soot particles 250 Å in radius nucleate homogeneously in the vapor phase at 1200 °C. If the surface free energy of SiO₂ is 1 J/m², estimate the supersaturation (P_V/P_S). The density of SiO₂ is 2.63 g/cm³.

From the estimation of molecular size, Si has 28 nucleons and O has 16.

$$m_{SiO_2} = 60m_N = 9.96 \times 10^{-23} \text{ g} \quad \Omega_{SiO_2} = \frac{m_{SiO_2}}{\rho_{SiO_2}} = \frac{9.96 \times 10^{-24} \text{ g}}{2.63 \text{ g/cm}^3} = 3.79 \times 10^{-23} \text{ cm}^3 / \text{molecule}$$

Nucleation will start at the equilibrium radius (r^*)

$$r^* = -\frac{2\gamma}{\Delta G_v} \quad \text{then} \quad \Delta G_v = -\frac{2\gamma}{r^*} = \frac{k_B T}{\Omega} \ln \frac{P_S}{P_V} \quad \text{then} \quad \frac{P_V}{P_S} = \exp\left(\frac{2\gamma\Omega}{k_B T r^*}\right)$$

$$\frac{P_V}{P_S} = \exp\left(\frac{2(1 \text{ J/m}^2)(3.79 \times 10^{-29} \text{ m}^3)}{(1.38 \times 10^{-23} \text{ J/K})(1473 \text{ K})(250 \times 10^{-10} \text{ m})}\right) = 1.161$$

Pressure

- Pressure arises from the momentum transfer from the gas molecules to the walls of the container.
- For an ideal gas,

$$PV = N_m RT \quad \text{or} \quad PV = Nk_B T$$

where N_m is the total number of moles of the gas and N is the number of molecules

- 1 bar = 750 Torr = 10^5 Pa = 0.987 atm
- 1 atm = 760 Torr = 10100 Pa

Mean Free Path

- The average distance a molecule can move between collisions is called the mean free path.

$$MFP = \frac{\sqrt{2}k_B T}{2\pi d^2 P}$$

where T is in °C, P is in Torrs and d is the molecule diameter

- The flow of gas is characterized by the **Knudsen number (Kn)**.

$$Kn = \frac{MFP}{L}$$

If $Kn < 0.01$, the flow is viscous (like a fluid).
If $Kn > 1$, the flow is molecular and ballistic.

Example

- What is the mean free path of Argon ($d_{Ar} = 3.76 \text{ \AA}$) at 100°K and 10^{-2} Torr if at room temperature (298°K) and pressure (760 Torr) it is 650 nm?

$$MFP = \frac{\sqrt{2}k_B T}{2\pi d^2 P} \quad \text{then} \quad MFP|_{100K, 0.01Torr} = \frac{(100)(760)}{(298)(0.01)} MFP|_{RTP} = (2.55 \times 10^4) (650 \times 10^{-7} \text{ cm}) = 1.66 \text{ cm}$$

- What pressure should a 30 cm diameter chamber be pumped down at room temperature to in order to be safely in the ballistic regime?

$$Kn = \frac{MFP}{d} > 1 \quad \text{then} \quad MFP > d = 30 \text{ cm} \quad \text{and} \quad \frac{P_{chamber}}{P_{room}} < \frac{650 \text{ nm}}{30 \text{ cm}} = 2.17 \times 10^{-6}$$

$$P_{chamber} < 2.17 \times 10^{-6} (760) = 1.65 \times 10^{-3} \text{ Torr}$$

Gas Flow and Pumping

- Gas will flow when there is a pressure difference between different sections of a chamber.

$$Q = C(P_1 - P_2)$$

Conductance (Lt/s) is shape dependent

Throughput

- In a system with multiple components, the overall conductance is determined by how the components are hooked up.

- Series connections:

$$C_{sys} = \left(\frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \dots \right)^{-1}$$

- Parallel connections:

$$C_{sys} = C_1 + C_2 + C_3 + \dots$$

- The pumping speed S_p , is defined as the volume of gas passing the plane of the inlet port per unit time when the pressure at the pump inlet is P_p .

$$S_{eff} = \frac{Q}{P} = \frac{S_p}{1 + S_p/C}$$

Flux and Deposition Rate

- The flux is the number of molecules that strike an element of a surface perpendicular to a coordinate direction, per unit time and area.
- The flux of molecules on the surface leads to deposition where the rate of film growth depends on the flux.

$$\Phi = 3.513 \times 10^{22} \frac{P}{\sqrt{MT}}$$

with P expressed in Torrs

$$\frac{dh_{film}}{dt} = \Phi \left(\frac{M_{film}}{\rho_{film} N_A} \right)$$

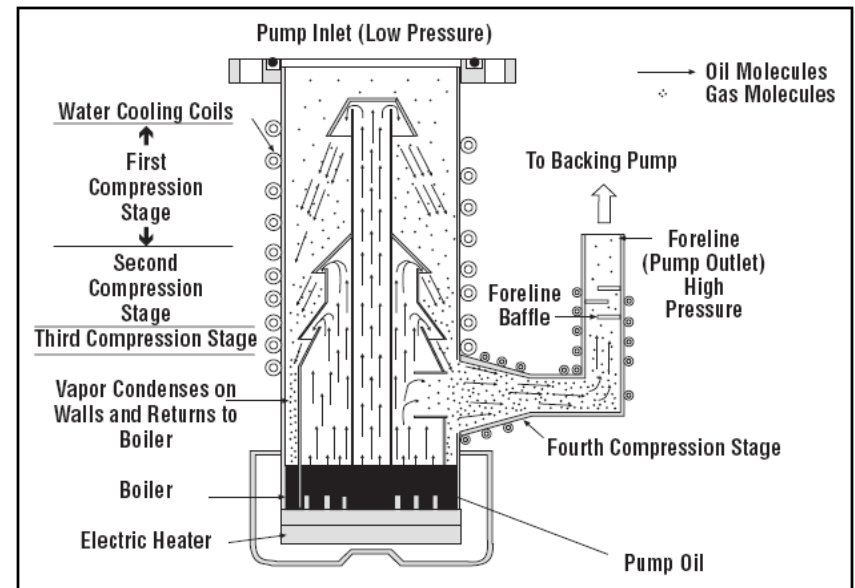
where M_{film} is the molar molecular mass (g/mol) and ρ_{film} is the film density (g/m³)

Vacuum Pumps

- Two general classes exist:
- Gas transfer – physical removal of matter
 - Mechanical, diffusion, turbomolecular
- Adsorption – entrapment of matter
 - Cryo, sublimation, ion

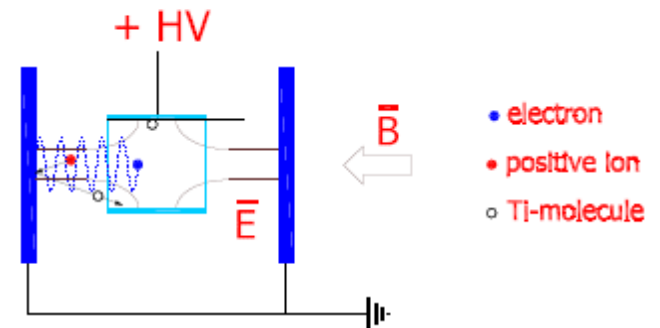
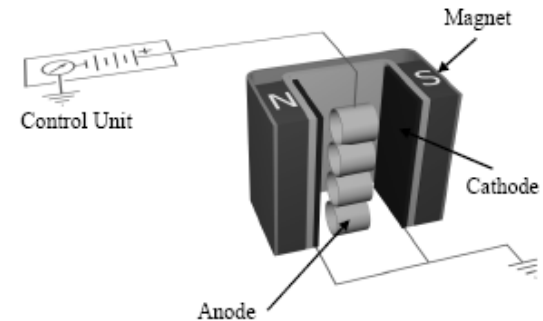
Diffusion Pumps

- Si oil is boiled and vaporized in a multistage jet assembly.
- Oil vapors emerging from the nozzles impart momentum on the residual gas molecules and drive them towards the bottom of the pump.
- The molecules are compressed and exhausted.
- No vibrations.
- From 1 mT to 10^{-10} T with LN cooling (works in the molecular flow regime).
- Wide range of flow rates.
- Requires mechanical pump.
- Backstreaming of the vapors are a problem and can be minimized with cooling coils are used to condense the oil before it enters the vacuum chamber.



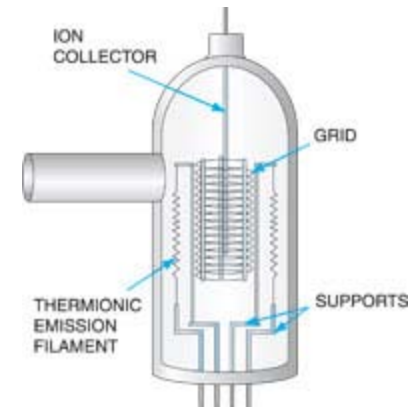
Ion Pumps

- A cold cathode electrical discharge creates an electron gas which is trapped by a small magnetic field.
- The electron gas ionizes residual gas particles in the chamber which are attracted to the cathode made of titanium.
- The incident ions sputter off titanium which forms a thin film on neighboring surfaces and form stable compounds with the residual gases in the chamber.
- Wide range of flow rate and pressure (still need mechanical pump)
- No moving parts or oil
- Need high voltage and magnetic fields.



Ion Gauge

- A filament is used to emit electrons which are attracted to a positively charged grid.
- Inside the grid is a negatively charged collector.
- The electrons collide with gas molecules around the grid and ionize them.
- The positively charged ions are attracted to the collector and create an ionic current.
- Works between $10^{-3} - 10^{-10}$ Torr





Crystal Monitor

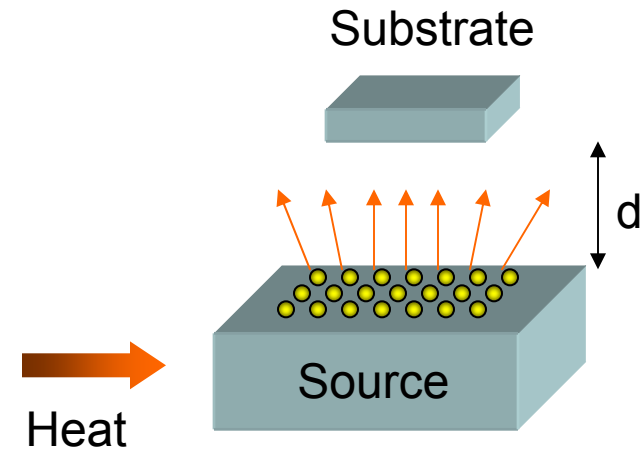


- Monitors thin film deposition rate and calculates thickness
- Quartz crystal has an oscillating electrical current, oscillates at a fixed frequency
- Oscillation frequency changes with changing mass
- Must input material density for each material
- Quartz crystal must be changed frequently
- Position needs to be calibrated



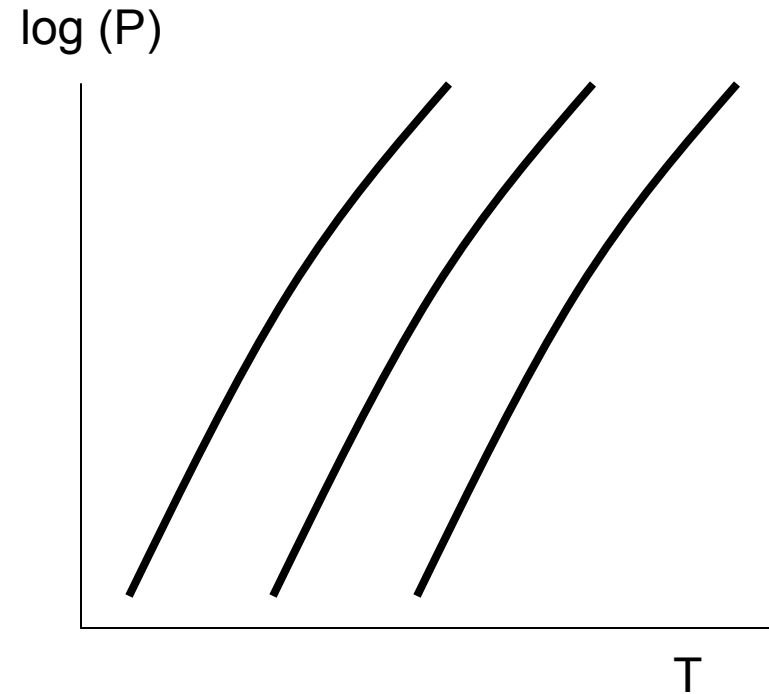
Vacuum Evaporation

- 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 sublimates 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.



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.
- It has an important role in determining the deposition rate for a given source temperature.
- In reality, empirical formulas and experimental data are used to find the vapor pressure of an element which mostly follows a $\log(P) \propto -1/T$ dependence.



Evaporation and Deposition Rates

- Evaporation flux from the source is given by:

$$\Phi_e = 3.513 \times 10^{22} \frac{P_v}{\sqrt{MT}} \frac{\text{molecules}}{\text{cm}^2\text{s}} \quad \text{or} \quad \Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{M}{T}} P_v \frac{\text{gr}}{\text{cm}^2\text{s}}$$

- The total mass evaporated from the source is:

$$M_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt \quad \text{where } A_e \text{ is the surface area of the source}$$

- The deposited mass per substrate area is:

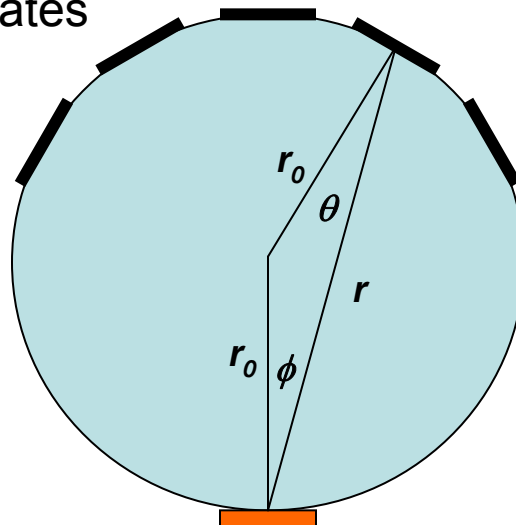
$$\frac{dM_s}{dA_s} = \frac{M_e \cos \theta}{4\pi r^2} \quad \text{or} \quad \frac{dM_s}{dA_s} = \frac{M_e (n+1) \cos^n \phi \cos \theta}{2\pi r^2}$$

point source surface source

Film Uniformity

- Film thickness varies over the length of the substrate due to varying distance from the source.
- A constellation arrangement of substrates arranged around a sphere as well as the source would eliminate this problem and result in uniform films.

Substrates



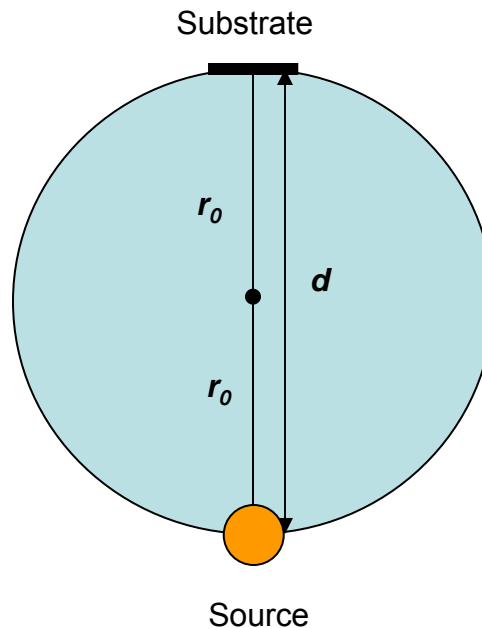
$$\frac{dM_s}{dA_s} = \frac{M_e}{4\pi r_0^2}$$

Source

Example

- If we want to deposit Al at a 50 \AA/s rate on a 1 cm^2 substrate 10 cm away from the source directly below it using a 3 mm radius ball of pure Al ($M_{\text{Al}}=27$, $\rho_{\text{Al}}=2.7\text{g/cm}^3$), what should be the substrate temperature? Assume uniform deposition and the following P_v vs. T relationship:

$$\log P(\text{torr}) = -15993/T + 12.409$$



Example (cont.)

$$\frac{dM_s}{dA_s} = \frac{M_e}{4\pi r_0^2} = \frac{\int_0^t \int_{A_e} \Gamma_e dA_e dt}{4\pi r_0^2} = \frac{t\Gamma_e A_e}{4\pi(d/2)^2}$$

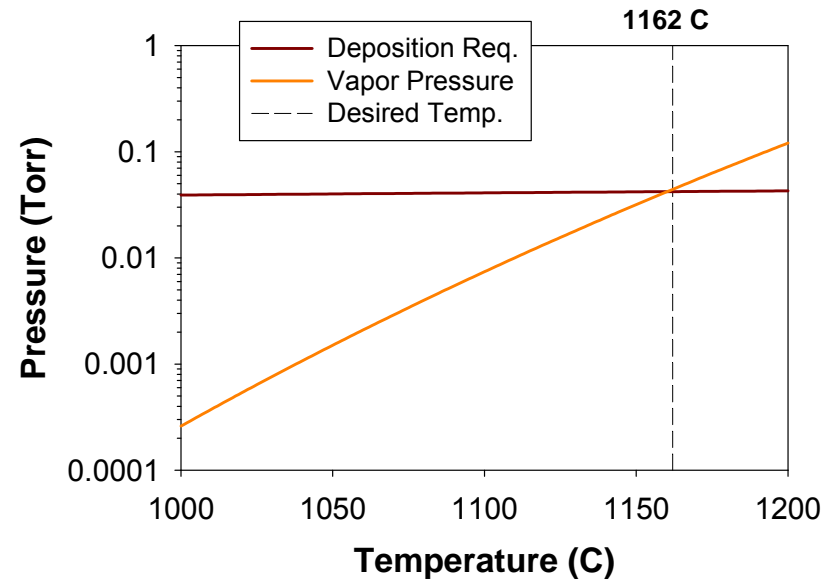
$$\frac{M_s}{A_s} = \frac{t\Gamma_e A_e}{4\pi(d/2)^2}$$

$$V_{dep} = A_s h_{dep} = \frac{M_s}{\rho_{Al}}$$

$$\frac{h_{dep}}{t} = \frac{M_s}{\rho_{Al} t A_s} = \frac{t\Gamma_e A_e}{t\rho_{Al} 4\pi(d/2)^2}$$

$$\Gamma_e = \frac{h_{dep}}{t} \frac{\rho_{Al} 4\pi(d/2)^2}{A_e} = 5.84 \times 10^{-2} \sqrt{\frac{M}{T}} P_v$$

$$P_v = \frac{h_{dep}}{t} \frac{\rho_{Al} 4\pi(d/2)^2}{A_e (5.84 \times 10^{-2})} \sqrt{\frac{T}{M}} = 1.236 \times 10^{-3} \sqrt{T}$$



Evaporating Multielement Materials

- Due to the varying vapor pressures, and possible dissociation/decomposition, maintaining stoichiometric ratios in compounds and alloys is difficult.
- Using separate sources or depositing under partial gas pressures are possible solutions.