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 $\Delta G$ is the change in the Gibbs Free Energy, $\Delta H$ is the change in the enthalpy, $\Delta S$ 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 $\Delta G^0$ is the standard state value of $\Delta G$. 
Example – Ellingham Diagrams

• Plots of $\Delta G^0$ 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:

\[ \frac{4}{3} Al + SiO_2 \rightarrow \frac{2}{3} Al_2O_3 + Si \quad \Delta G^0 = -55kcal \]
\[ 2Cu + SiO_2 \rightarrow 2CuO + Si \quad \Delta G^0 = +130kcal \]

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.

\[ D = D_0 \exp\left(-\frac{E_D}{k_B T}\right) \]

• 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:

\[
N = N^* A^* \omega
\]

where \(N^*\) is the equilibrium concentration of the stable nuclei, \(\omega\) 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 (Pᵥ/Pₛ). The density of SiO₂ is 2.63 g/cm³.

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

  \[ m_{\text{SiO}_2} = 60m_N = 9.96 \times 10^{-23} \text{ g} \quad \Omega_{\text{SiO}_2} = \frac{m_{\text{SiO}_2}}{\rho_{\text{SiO}_2}} = \frac{9.96 \times 10^{-24} \text{ g}}{2.63 \text{ g/cm}^3} = 3.79 \times 10^{-23} \text{ cm}^3 / \text{molecule} \]

  Nucleation will start at the equilibrium radius (r*)

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

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

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

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 \textit{viscous} (like a fluid).
If \(Kn > 1\), the flow is \textit{molecular and ballistic}. 
Example

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

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

• 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

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

  - Series connections:

\[ C_{sys} = \left( \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + ... \right)^{-1} \]

  - Parallel connections:

\[ C_{sys} = C_1 + C_2 + C_3 + ... \]

- 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 \( P_p \):
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.

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

with \( P \) expressed in Torrs

• The flux of molecules on the surface leads to deposition where the rate of film growth depends on the flux.

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

where \( M_{\text{film}} \) is the molar molecular mass (g/mol) and \( \rho_{\text{film}} \) 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 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.
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:
  \[ \Phi_e = 3.513 \times 10^{22} \frac{P_v}{\sqrt{MT}} \text{ molecules cm}^{-2}\text{s}^{-1} \]
  or
  \[ \Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{M}{T}} P_v \text{ gr cm}^{-2}\text{s}^{-1} \]

- The total mass evaporated from the source is:
  \[ M_e = \int_0^t \int_{A_e} \Gamma_e dA_e dt \]
  where \( A_e \) is the surface area of the source

- The deposited mass per substrate area is:
  \[ \frac{dM_s}{dA_s} = \frac{M_e \cos \theta}{4\pi r^2} \]
  or
  \[ \frac{dM_s}{dA_s} = \frac{M_e (n+1) \cos^n \phi \cos \theta}{2\pi r^2} \]
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.

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

- If we want to deposit Al at a 50 Å/s rate on a 1 cm² 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.)

\[
\frac{dM_s}{dA_s} = \frac{M_e}{4\pi r_0^2} = \frac{\int \int \Gamma_e dA_e dt}{4\pi (d/2)^2} = \frac{t\Gamma_e A_e}{4\pi (d/2)^2}
\]

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

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

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

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

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

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