Chem 584
Introduction to Materials Chemistry
Homework #8

Due at the beginning of lecture, Wednesday December 10. (Show work)

Callister Problems: 18.9, 18.10, 18.25, 18.43, 18.59

1) Semiconductors in single crystal form are usually produced by solidification of melts. To achieve extrinsic semiconductivity, it is customary to add to the melt "doping elements" that are substitutionally incorporated (i.e., they replace a silicon atom in the crystal). If the doping element is P, which has 5 valence electrons, and it replaces a Si atom (whose 4 valence electrons are normally immobilized because of bond formation), each P atom will be able to contribute one electron to conduction; its other four valence electrons take part in bond formation. Assume you add 3 mg P to 50 g Si and form a crystal in which the P atoms are uniformly distributed. What is the number of conduction elctrons/cm^3 in the doped crystal? (You may neglect the volume of the substitutionally replaced Si atoms and assume that only electrons from P atoms contribute to conduction.)

2) The number of electron-hole pairs in intrinsic Ge is given by:

$$n_i = 9.7\text{x}10^{15}\ T^{3/2}\ e^{\frac{-E_g}{2kT}}\ [\text{cm}^3] \qquad (E_g = 0.72\text{ eV})$$

a) What is the density of pairs at T=20°C?

b) Will (undoped) Ge be a good conductor at 200°C? (If so, why?)

3) a) How do you expect the conductivity to vary in an intrinsic semiconductor with increasing temperature? (Explain you answer.)

b) How do you expect the conductivity to vary in a metallic conductor with increasing temperature? (Explain in terms of Matthiessen's rule.)

4) Into 110 g Ge you substitutionally incorporate 27 mg of Sb.

a) Will the conductivity of the Ge be p-type or n-type?

b) What will be the number of free charge carriers/cm^3 in the conduction band of the material?

c) What is the room temperature conductivity?

5) Read the following article and answer the questions below:

> Chung, D.; Hogan, T.; Brazis, P.; Rocci-Lane, M.; Kannewurf, C.; Bastea, M.; Uher, C.; Kanatzidis, M. G. $CsBi_4Te_6$: A High-Performance Thermoelectric Material for Low-Temperature Applications; *Science* **287**, 1024-1027, (2000)

a) Define what a phonon is and how it effects thermal conductivity.

b) Describe how a thermoelectric material works.

c) In the context of the previous two questions, explain how $CsBi_4Te_6$ makes a good thermoelectric material.

d) Suggest a reason why the best thermoelectric behavior is seen along the b-axis of the crystal.

1) $MW_{Si} = 28.08$

$MW_P = 30.97$

$\rho_{Si} = 2.33\,g/cm^3$

1 valence e^- / P

~~3.0·10~~ $\dfrac{3.0\cdot10^{-3}\,g\ P}{50\,g\ Si}\cdot\dfrac{1\,mol\ P}{30.97\,g\ P}\cdot\dfrac{1\,mol\ e^-}{mol\ P}\cdot\dfrac{6.02\cdot10^{23}\,e}{mol\ e^-}$

$\cdot\dfrac{2.33\,g\ Si}{cm^3} = 2.7\cdot10^{18}\ e^-/cm^3$

2) $n_i = 9.7\cdot10^{15}\,T^{3/2}\,e^{-0.72\,eV/2kT}$

$k = 8.62\cdot10^{-5}\ eV/atom\ K$

a) $T = 20°C = 293\ K$

$n_i = 9.7\cdot10^{15}\,(293)^{3/2}\,e^{-0.72/2(8.62\cdot10^{-5})\cdot293}$

$\boxed{= 3.14\cdot10^{13}\ /cm^3}$

b) $\sigma = n_i|e|(\mu_e + \mu_h)$

$T = 200°C = 473\ K$

$n_i = 9.7\cdot10^{15}\,(473)^{3/2}\,e^{-0.72/2(8.62\cdot10^{-5})\cdot473}$

$= 1.46\cdot10^{16}\ /cm^3$

$\sigma = 1.46\cdot10^{16}/cm^3\cdot1.602\cdot10^{-19}\,C\,(\mu_e + \mu_h) = 1.46\cdot10^{\overset{22}{\cancel{16}}}\cdot1.602\cdot10^{-19}(0.38 + 0.18)$

$\cancel{= 1.3\cdot10^{-3}\ \Omega\ m}$

$= \boxed{1.3\cdot10^{3}(\Omega\,m)^{-1}}$

$\mu_e = 0.38\ m^2/V\cdot s$

$\mu_h = 0.18\ m^2/V\cdot s$

$1.46\cdot\dfrac{10^{16}}{cm^3}\cdot\left(\dfrac{100\,cm}{m}\right)^3 = 1.46\cdot10^{22}/m^3$

→ Good semiconductor σ,

but still less than good metals (20°C)

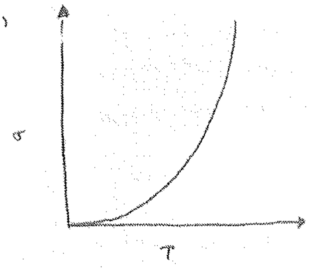
$\sigma_{Al} = 3.57\cdot10^{7}\ (\Omega\,m)^{-1}$

$\sigma_{Cu} = 5.68\cdot10^{7}\ (\Omega\,m)^{-1}$

σ_{Si} (intrisic) $= 4\cdot10^{-4}\ (\Omega\,m)^{-1}$

σ_{InSb} (intrinsic) $= 2\cdot10^{4}\ (\Omega\,m)^{-1}$

3 a)

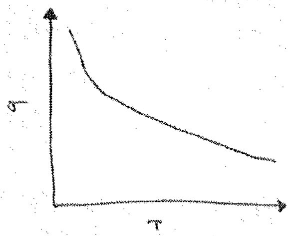


Increasing temperature will increase the conductivity by thermally populating the conduction band will e⁻ and leaving holes in the valence band. There will be a Boltzmann type distribution, which will increase carrier density exponentially with temperature

b) Matthiessen's rule: resistivity = resistivity of thermal vibrations + resistivity defects + resistivity impurity

$$\frac{1}{\sigma} = \rho_{(tot)} = \rho_{therm} + \rho_{def} + \rho_{impur}$$

Increasing temperature will increase the thermal motion of lattice atoms, increasing electron scattering, lowering conductivity. Increasing temperature will also increase the number of lattice defects lowering the conductivity. The number of impurities should stay constant.



4 a) Ge - 4 valence e⁻

Sb - 5 valence e⁻ $\Rightarrow$ n-type conductivity

b) $$n = \frac{0.027\text{ g Sb}}{110\text{ g Ge}} \cdot \frac{\text{mol Sb}}{121.76\text{ g Sb}} \cdot \frac{1\text{ mol e}^-}{\text{mol Sb}} \cdot \frac{6.02\cdot10^{23}\text{ e}^-}{\text{mol e}^-} \cdot \frac{5.32\text{ g Ge}}{\text{cm}^3}$$

$$\boxed{= 6.46\cdot10^{18}\text{ e}^-/\text{cm}^3}$$

c) $$\sigma = n|e|\mu_e = 6.46\cdot10^{18}\,\text{e}^-/\text{cm}^3 \cdot \left(\frac{100\text{ cm}}{\text{m}}\right)^3 \cdot 1.6\cdot10^{-19}\text{ C/e}^- \cdot (0.38\text{ m}^2/\text{V}\cdot\text{s})$$

$$\boxed{= 3.93\cdot10^{5}\ (\Omega\text{ m})^{-1}}$$

5 a) A phonon is the cooperative vibrations of atoms in a lattice. It can be compared to a wave in water. Phonons are a major contributor to the total thermal conductivity, K

$$K = K_{elec} + K_{lattice}$$

Increasing the ability of phonons to propagate through a material will increase the thermal conductivity of the material

b) Thermoelectrics work by having two different materials in contact with each other, but both at different temperatures. Heat will flow from the hot material to the cold material. Heat can flow in two ways, electronically + by phonons. By limiting the heat conduction by phonons, thermoelectrics ~~creating~~ create a current by only the e^- moving from the hot material to the cold material.

c) $CsBi_4Te_6$ is a good thermoelectric material because it consists of ribbons of Cs^+ ions in between Bi-Te sections. These Cs^+ ions undergo thermal "rattling" motions, which scatters phonons + stops their propagation through the crystal. Electrons can still move quickly through the crystalline Bi-Te sections to conduct heat. By limiting the phonon propagation, $CsBi_4Te_6$ can only equalize the heat by movement of e^-, creating a current

d) It was found that the Cs^+ ribbons run parallel to the b-axis. Electrons trying to flow along the c-axis, $\perp$ to the ribbons, must flow the regions of different densities + will become scattered ~~to~~ at the interface between Cs^+ + Bi-Te sections. Along the b-axis, e^- can run through the Bi-Te sections + minimize scattering while phonons are too large to propagate in these sections

18.9) - Drift velocity is the averge velocity of a charge carrier in the direction on an applied electric field.

- Mobility of a charge carrier is a measure of the number of scattering events. It can also be seen as the mean free path of a carrier in an electric field

18.10) a) $T = 298 K$ in Si
$E = 500 V/m$
$\mu_e = 0.14 m^2/V \cdot s$

$V_d = \mu_e E = 0.14 \frac{m^2}{Vs} \cdot 500 \frac{V}{m} = \boxed{70 m/s}$

b) time for 25 mm?

$25 mm \cdot \frac{1m}{1000mm} \cdot \frac{1\cancel{70}s}{70m} = \boxed{3.57 \cdot 10^{-4} s}$

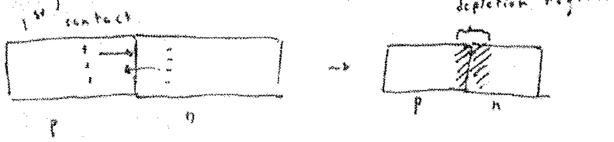
18.25) $n = 5 \cdot 10^{17} m^{-3}$
$V_d = 350 m/s$
$E = 1000 V/m$

$V_d = \mu_e E$ $\quad 350 m/s = \mu_e \, 1000 V/m$ $\quad \mu_e = 0.35 m^2/Vs$

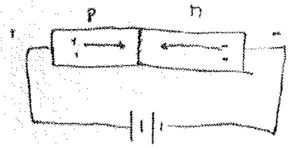
$\sigma = n |e| \mu_e$

$= \frac{5 \cdot 10^{17}}{m^3} (1.6 \cdot 10^{19} c)(0.35 m^2/Vs) = 0.028 (\Omega m)^{-1}$

18.43) p-n junction

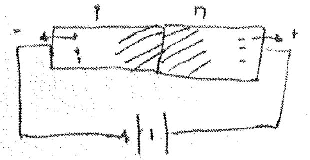


Foward bias



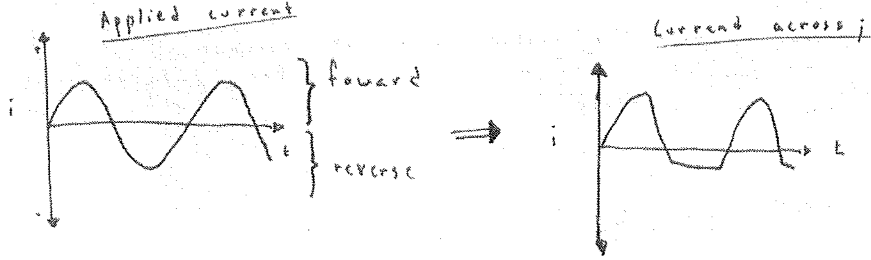
- Under foward bias (+ to p & - to n) e⁻ and holes are pushed to depletion region & make it smaller & allows current to flow across the junction

Reverse Bias



- Reverse bias attracts the majority carriers in both materials to the voltage source, making the depletion region larger, allowing little current to flow.

Under alternating current (AC), current will flow under forward bias but little current can flow under the reverse bias.



Applied current

Current across junction

Small currents still flow under reverse bias due to leakage current from the minority carriers

18.59) $BaTiO_3$ is a perovskite material. At low temperatures the Ti^{4+} ion can be displaced slightly from the center of the unit cell, leaving the cell with a net polarization. Above it's Curie temperature, the Ti^{4+} atom will have enough thermal energy to move between the two possible sites it can occupy, leading to an average of no net dipole.