**Solid State, Semiconductors, Electrochemistry, and Nanowires for Solar Cells: Discuss!**

***Please read the following article before class***

**Hernandez-Pagan, L.; Wang, W.; Mallouk, T. E. “Template Electrodeposition of Single-Phase p- and n-Type Copper Indium Diselenide (CuInSe2) Nanowire Arrays,” *ACS Nano* 2011, *5*, 3237-3241. DOI: 10.1021/nn200373k.**

**In order to prepare for class, answer the following questions. During discussion add notes/corrections in a different color. You may want to leave room for notes/corrections in your answers. You will be asked to turn in your answers and added notes/corrections at the end of class to be graded.**

**Electrochemistry:**

1. Calculate the concentration of each ion in solution. (Look in the materials and methods fabrication section for electrolyte details.)
2. Which ion is easier to reduce, copper or indium? (Look up standard reduction potentials.)
3. Based on your answer to the previous question, why does the deposition voltage at -700 mV result in Cu-rich nanowires, and the deposition voltage at -750 mV result in In-rich nanowires?
4. How many electrons does it take to reduce the necessary ions and make one formula unit of CuInSe2? (*Hint: Use the Table of Standard Reduction Potentials to write a balanced reduction reaction.*)

**Nanowires:**

1. Consult Figure 2 in the paper. All of the images are of the same nanowire. What is the diameter of the nanowire? What is the length of the nanowire?
2. Define the phrase “orthogonal direction” as used in the third sentence of the first paragraph.
3. Two things must happen in a semiconductor for it to be a useful solar cell: light must be absorbed, and an electron must be separated from its hole. Of these two processes, which would occur better in a thinner layer of material? Which would occur better in a thicker layer of material?
4. Why is it a good idea to fabricate semiconductors for solar energy in the shape of a nanowire?
5. Equation 1 on page 3238, known as the Scherrer Equation, is used to calculate the crystalline grain size from X-ray diffraction data. Define the variables in this equation, including units.
6. The lowest angle peak in the XRD pattern for CuInSe2 occurs at 2$θ\_{β}$ = 26.59°. For a sample containing 2 nm particles, calculate the $β$ value of this peak at half-height in radians (Hint: Remember to use $θ\_{β}$ in your calculation, not 2$θ\_{β}$).
7. Compare Figure 1a and 1b. What is the relative grain size of the particles in these XRD patterns? (Hint: Consult Equation 1)
8. Define the term “annealing” as used in the last sentence of the first paragraph in Results and Discussion. (Hint: See the last sentence of the “Fabrication” section in Methods and Materials).
9. What happens to the 2 nm particles when they are annealed? Describe how and why the XRD pattern changed between the as-deposited and annealed nanowires.

**Semiconductors:**

1. Explain the difference between an indirect and a direct gap semiconductor. How does the band gap of CuInSe2 compare to the band gap of Si?
2. Which doping type is expected for Cu-rich nanowires? For In-rich wires? Your answer must explain why.
3. The colors of solids relate to their band gap energy. For example, pure Si has a band gap of 1.1 eV and is black, while Fe2O3 has a band gap of 2.2 eV and is rust red. Calculate the wavelength and color of the lowest energy light that can be absorbed by Fe2O3 and use this information to explain the color of rust. Explain why pure Si is black..
4. A *p-n* junction is formed at the interface between *p*-type and *n*-type semiconductors. Explain what happens to the electrons at a *p-n* junction. Describe a unique property of a *p*-*n* junction.
5. Describe the experimental set-up of the four-probe method. How does the four-probe method determine resistance? What information is needed to convert resistance into resistivity?

**Solid State:**

1. Consider the unit cell of the sphalerite (zinc blende) structure. CuInSe2 adopts the chalcopyrite structure (shown below), which can be derived from the sphalerite structure. Describe how these two structures are related. Is the unit cell symmetry of chalcopyrite the same as sphalerite? Explain why or why not.
2. What are the coordination environments of the Cu, In and Se? (refer to unit cell figure)
3. Define Miller Indices. The (112) plane has the strongest peak in the XRD. Draw a (112) plane on the unit cell of CuInSe2 below (hint: ‘c’ is the longest axis). What atoms lie in this plane? Explain how this would result in the strongest XRD peak.
4. What does the ICP analysis tell you about the solid state compound?
5. Where do the extra atoms substitute in the (a) Cu-rich, and (b) In-rich compounds? Look up ion sizes.
6. Recalculate element ratios of the compounds in Table 1 assuming Se = 2.00. How could you use a density measurement to determine which element ratio is true?

Unit cell of CuInSe2