

ME 432 Fundamentals of Modern Photovoltaics  
Homework Assignment #4, Fall 2023  
Due Monday October 16

Please note: You may attach Excel spreadsheets, Matlab code, Mathematica, etc. However, if you use external software, please write out the formulas or methodology you used to calculate your answer. Your logic flow/thought process should be described clearly.

**Question #1: Fermi energy and semiconductor statistics**

An allowed state for an electron in a semiconductor lies at an energy equal to 0.4 eV above the Fermi level. What probability has this state of being occupied by an electron under thermal equilibrium conditions at 300K?

This question is a straightforward application of the Fermi-Dirac distribution, which tells us the occupation probability as a function of temperature and deviation from the Fermi energy. Note that we need no material specific information (band gap, etc).

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} = \frac{1}{1 + \exp\left(\frac{0.4 \text{ eV}}{0.026 \text{ eV}}\right)} = 2.082(10^{-7})$$

I have used the fact that  $E - E_f = 0.4 \text{ eV}$  (as given in the problem statement), and that at room temperature  $kT = 0.026 \text{ eV}$ . We see that the probability is tiny – only about 1 out of  $10^7$ .

**Question #2: Effective density of states in silicon.**

Assuming that the effective masses of electrons and holes are equal to the free electron mass, calculate the effective density of states in the conduction and valence bands for silicon at 300K. Assuming a band gap of 1.1 eV, find the intrinsic concentration in silicon at this temperature.

First, we calculate the effective density of states. Note that in this class, we have defined three different types of “density of states”: available, occupied, and effective. Make sure you know the difference between these three! Since we are assuming that the effective mass for both electrons and holes are equal to the free electron mass, then the effective density of states at the conduction band  $N_c$  is equal to the effective density of states at the valence band  $N_v$ , and is given by:

$$n = 2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} \exp\left[ -\frac{E_C - E_F}{kT} \right] = N_c \exp\left[ -\frac{E_C - E_F}{kT} \right]$$

$$N_c = 2 \left( \frac{2\pi m_e^* kT}{h^2} \right)^{3/2} = 2 \left( \frac{2\pi \times 9.1094(10^{-31}) \text{ kg} \times 4.11(10^{-21}) \text{ J}}{(6.6261(10^{-34}) \text{ J-s})^2} \right)^{3/2} = 2.48(10^{25}) m^{-3}$$

I have used the fact that at room temperature,  $kT = 0.026 \text{ eV} = 4.11(10^{-21}) \text{ J}$ . Be sure that you are clear on how the units work out ( $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$ ). Note that the approximation that the effective masses are equal to the free electron mass is actually a pretty good one for silicon.

Finally, the intrinsic carrier concentration is

$$\begin{aligned} n_i &= (N_c N_v)^{1/2} \exp\left[-\frac{E_G}{2kT}\right] \\ &= (N_c) \exp\left[-\frac{E_G}{2kT}\right] \\ &= 2.48(10^{25}) \exp\left[-\frac{1.1 \text{ eV}}{2(0.026) \text{ eV}}\right] \\ &= 1.61(10^{16}) \text{ m}^{-3} \end{aligned}$$

**Question #3: Extrinsic doping of silicon with phosphorus atoms.**

- (a) Silicon is uniformly doped with  $10^{22}$  phosphorus atoms/ $\text{m}^3$ . Assuming that all these donor impurities are ionized, estimate the concentration of electrons and holes in this material under thermal equilibrium at 300K. Hence, calculate the energy of the Fermi level in this material below the conduction band edge.
- (b) Given that the donor level for phosphorus lies 0.045 eV below the conduction band edge, calculate the probability that this level is occupied by an electron at 300K and hence check on the assumption above that all donors are ionized. Use  $N_c = 3(10^{25}) \text{ m}^{-3}$ ,  $N_v = 1(10^{25}) \text{ m}^{-3}$ , and  $n_i = 1.5(10^{16}) \text{ m}^{-3}$ .

Assuming that all donors are ionized, we have

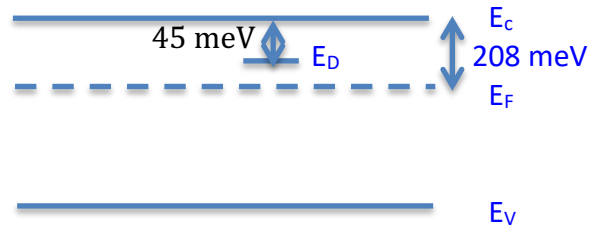
$$n = N_D = 10^{22} \text{ m}^{-3}$$

$$p = \frac{n_i^2}{n} = \frac{(1.5(10^{16}))^2}{(10^{22})} = 2.25(10^{10}) \text{ m}^{-3}$$

Then if the doping concentration is  $n = N_D$  and we assume that all dopants are ionized, we can determine the offset between the Fermi energy, and the conduction band edge:

$$\begin{aligned} n &= N_c \exp\left(-\frac{E_C - E_F}{kT}\right) \\ E_C - E_F &= kT \ln\left(\frac{N_c}{n}\right) = 0.026 \ln\left(\frac{3(10^{25})}{10^{22}}\right) = 0.208 \text{ eV} \end{aligned}$$

This tells us that the Fermi level is 208 meV below the CB edge. Note that the defect level itself is 45 meV below the conduction band edge. So the overall picture is (not to scale):



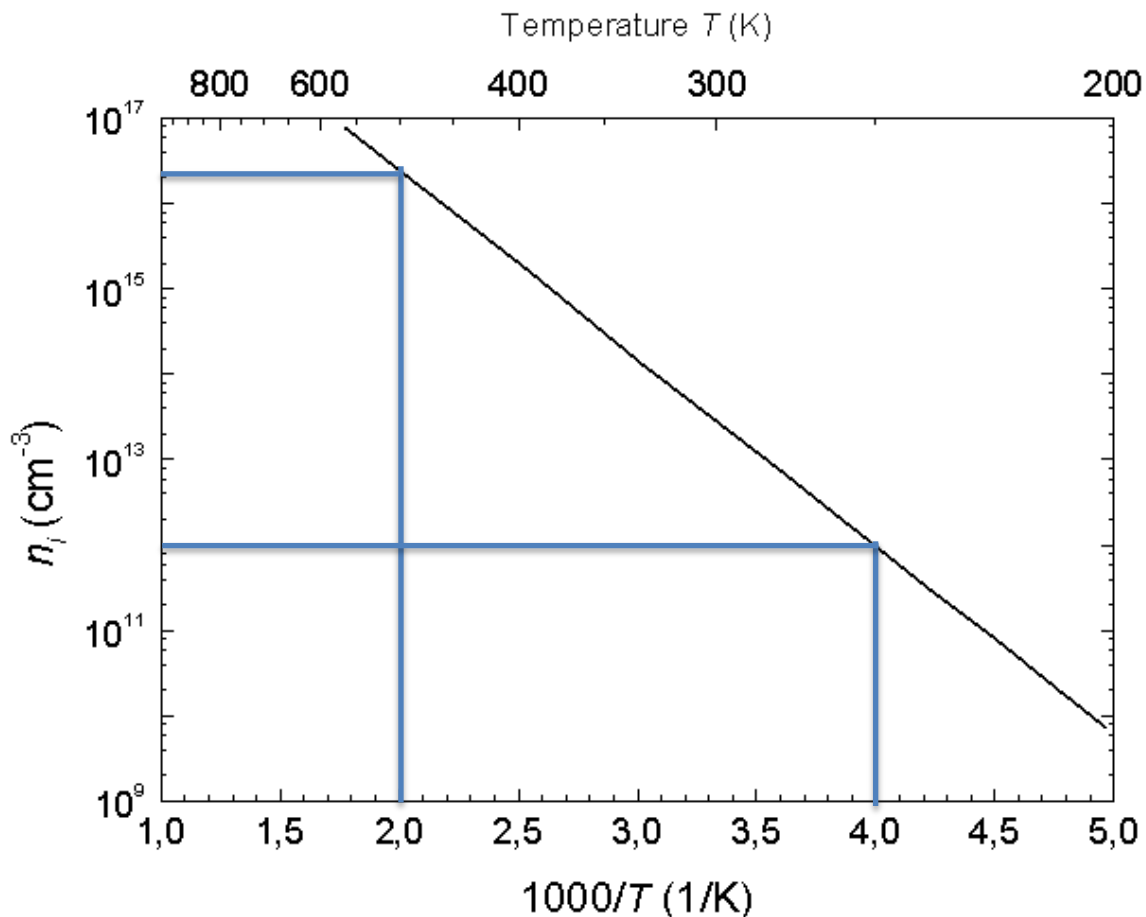
Since the Fermi level is actually quite close the defect level (only 208-45 meV away), we intuitively should expect that at room temperature where there is a reasonable amount of thermal energy available, the defect level is more likely to be unoccupied (i.e. the defect has lost its electron, and is ionized). To formally check the assumption that all donors are ionized, we use the Fermi-Dirac distribution. This tell us the probability that the defect state is occupied.

$$f(E) = \frac{1}{1 + \exp\left(\frac{E_D - E_f}{kT}\right)} = \frac{1}{1 + \exp\left(\frac{(0.208 - 0.045) \text{ eV}}{0.026 \text{ eV}}\right)} = 0.00189$$

Since we want the probability that the defect state is not occupied (is ionized), it is given by  $1 - f(E) = 0.998$ . Hence, yes, it is a reasonably good assumption (although there will certainly be some unionized donors).

#### Question #4: A solar cell success story?

After years of working at the university, your professor (who usually does computational work, but has recently started dabbling in experiments) has synthesized a new semiconducting material, which she calls *unobtainium*. She claims that unobtainium will revolutionize photovoltaics technology, and invites you to invest in her new start-up company that will commercialize the new unobtainium cells. When you ask for some data on the material, she provides you with the following measurements on carrier concentration vs. temperature for intrinsic unobtainium. Find the band gap of unobtainium. Based on its gap, what is its maximum possible efficiency? Do you invest? *Hint: Write down the expression for intrinsic carrier concentration vs. temperature. Based on this expression, you can relate the slope of the curve to the band gap of the material.*



This is a useful approach to estimating the band gap of a material, given an experimental measurement of carrier concentration vs. temperature. We start with the expression for the intrinsic carrier concentration, and do some manipulation:

$$n_i = (N_c N_v)^{1/2} \exp\left[-\frac{E_G}{2kT}\right]$$

$$\ln(n_i) = \ln\left((N_c N_v)^{1/2} \exp\left[-\frac{E_G}{2kT}\right]\right)$$

$$\ln(n_i) = \ln\left((N_c N_v)^{1/2}\right) + \ln\left(\exp\left[-\frac{E_G}{2kT}\right]\right)$$

$$\ln(n_i) = \ln\left((N_c N_v)^{1/2}\right) - \frac{E_G}{2kT}$$

$$\ln(n_i) = -\frac{E_G}{2kT} + \ln\left((N_c N_v)^{1/2}\right)$$

$$\ln(n_i) = -\frac{E_G}{2k(1000)}\left(\frac{1000}{T}\right) + \ln\left((N_c N_v)^{1/2}\right)$$

The final expression here looks like the equation for a line “ $y = m x + b$ ”, with

$$y = \ln(n_i)$$

$$m = -E_G/2000k$$

$$x = (1000/T)$$

$$b = \ln((N_c N_v)^{1/2})$$

It is useful to us, because it tells us that if we plot  $y$  vs.  $x$  ( $\ln(n_i)$  vs.  $(1000/T)$ ), the slope of the line should be exactly  $m = -E_G/2000k$ .

From the graph provided, we can estimate the slope of the line. You can pick any two points, I have selected the two indicated on the chart. Be careful here! On the chart, the  $y$ -axis is  $n_i$ , rather than  $\ln(n_i)$ . We need to take the natural log to put the  $y$ -axis in the correct form. Thus in my case, the data points are roughly  $(x,y)=(2,\ln(2(10)^{16}))$  and  $(x,y)=(4,\ln(1(10)^{12}))$ . The slope then is

$$m = \frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\ln(2 \times 10^{16}) - \ln(10^{12})}{2 - 4} = -4.95 \text{ K}$$

and the units of  $m$  are ( $y/x = \text{temp in Kelvin K}$ ). Now we can find the band gap directly:

$$E_g = -2000km = -2000(8.6173(10^{-5}) \text{ (eV/K)})(-4.95\text{K}) = 0.85 \text{ eV}$$

Not bad! At least in terms of the potential efficiency achievable according to our analysis above. Of course, in reality there are several materials that have good band gaps – but are still not widely used as photovoltaic absorbers. They may have poor mobilities (like many of the oxides and oxy-sulfides), or just be too expensive to manufacture (GaAs).