

**Ch/ChE 140a**  
**Problem Set #4**  
**2007/2008**  
**SHOW ALL OF YOUR WORK!**  
(100 Points Total)  
Due Thursday, March 13<sup>th</sup>, 2008

Please read chapter 5 (pp. 134-169) of Advanced Semiconductor Fundamentals by Pierret.

The open-circuit photovoltage of many efficient solar energy conversion devices is limited by the quality of the bulk semiconductor crystal of which the device is made rather than the nature and quality of the rectifying junction itself. Recall the dark (exchange) current,  $J_o$ , through a semiconductor device is the sum of all the contributing recombination mechanisms, but is usually dominated by only one of the several mechanisms:

$$J_o = J_{th} + J_{tb} + J_{ssr} + J_{drr} + J_{br} + J_{hv}$$

Where

- $J_o$  = the total dark (exchange) current through the interfacial region.
- $J_{th}$  = the exchange current due to thermionic emission: majority carriers surmounting the interfacial potential barrier  $V_{bi}$ .
- $J_{tb}$  = the exchange current due to majority carriers tunneling through the interfacial potential barrier.
- $J_{ssr}$  = the exchange current due to carrier recombination at surface states on the interface.
- $J_{drr}$  = the exchange current due to carrier recombination within the depletion region.
- $J_{br}$  = the exchange current due to non-radiative (trap mediated) recombination in the bulk.
- $J_{hv}$  = the exchange current due to radiative recombination in the bulk.

Whichever exchange current dominates this sum under a given set of conditions is the controlling factor in limiting the photovoltage of a given device. Improvements in the maximum photovoltage under these conditions can only be realized by reducing the magnitude of this dominant exchange current. The goal of this problem set is to familiarize you with how this interplay actually works.

When superposition holds, the net current through a device is

$$J = J_{ph} + J_{dark} = J_{ph} - J_o[\exp(-qV_{app}/AkT) - 1]$$

Where  $J_{ph}$  is the photocurrent, determined solely by the number of photons absorbed by the semiconductor per unit area per unit time. At open-circuit,  $V_{app} = V_{oc}$  and the net current flux through the device must be zero:

$$\text{At } V_{oc}: \quad J = 0 = J_{ph} + J_{dark} \quad \Rightarrow \quad J_{ph} = -J_{dark} = J_o[\exp(-qV_{app}/AkT) - 1]$$

Ideally, we expect  $J_{ph}$  to be independent of the potential difference across the device, whereas the dark current depends in a nearly exponential manner on this potential difference  $V_{app}$ . The open-circuit photovoltage ( $V_{oc}$ ) is simply the value of  $V_{app}$  when no current flows. For  $V_{oc}$  values greater than  $3kT/q$ , we can ignore the 1 and simplify the expression to:

$$J_{ph} \approx J_o \exp\left(\frac{-qV_{oc}}{AkT}\right) \quad \Rightarrow \quad -V_{oc} \approx \frac{AkT}{q} \ln\left(\frac{J_{ph}}{J_o}\right)$$

Let's consider a situation in which  $J_o$  is dominated by  $J_{th}$  and  $J_{br}$  in reasonably close competition, with all other exchange current contributions negligible. As described in section 4.2.2.4 of *Photocatalysts* (a.k.a. "Mary and Nate"), we can solve for the rate of trap-mediated bulk recombination  $J_{br}$  in an infinitely thick n-type semiconductor sample:

$$J_{br} = \frac{q D_p p_o}{L_p}$$

where  $p_o$  is the dark hole concentration and can be expressed as  $p_o = n_i^2/N_D$  since  $n_o p_o = n_i^2$ .  $L_p$  is the hole diffusion length,  $D_p$  is the hole diffusion coefficient, and  $\tau_p$  is the hole lifetime. The value of  $D_p$  is a property of the semiconductor, and may be calculated from the Einstein relationship:

$$D_p = \mu_p \frac{kT}{q} \quad \text{whereas } L_p \text{ is defined as: } L_p = \sqrt{D_p \tau_p}$$

The hole diffusion length,  $L_p$ , is a function of the quality of the semiconductor crystal and it describes how far a hole is likely to move by diffusion before it recombines with an electron. The larger  $L_p$  is, the fewer recombination centers (traps) in the bulk and the smaller the bulk recombination exchange current. Although the equation presented above for the bulk recombination exchange current is derived for an infinitely thick sample, the equation can be modified to approximate bulk recombination in a *finite* semiconductor sample if  $L_p$  is substituted with an effective  $L_p'$ , where  $L_p'$  is half the wafer thickness whenever the thickness is less than twice  $L_p$ . In other words, for a sample of thickness,  $t$ :

$$L_p' = \begin{cases} L_p & \text{when } t > 2L_p \\ \frac{t}{2} & \text{when } t < 2L_p \end{cases}$$

For single-crystal Si,  $L_p$  is about 0.1 cm and  $L_p'$  must be used for samples thinner 0.2 cm. Polycrystalline Si, typically used for solar cell devices, has many crystalline grain boundaries within the bulk that can act as active sites for carrier recombination. These

active grain boundaries, since they decrease the mean diffusion length of excited carriers, significantly reduce the value of  $L_p$ .

We have discussed the mathematical form of the thermionic emission exchange current,  $J_{th}$ :

$$J_{th} = A^* T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \quad \text{Use } A^* \approx 120 \text{ A}/(\text{cm}^2 \text{ K}^2) \text{ for electrons in Si}$$

1.
  - a) Briefly describe superposition and the assumptions it requires. (15 points)
  - b) Discuss situations at a semiconductor-liquid or semiconductor-metal interface for which you would **not** expect superposition to hold rigorously. Include in your discussion the effects of the following things on the assumptions of superposition:
    - i) The insulating layer in an MIS diode. (5 points)
    - ii) The difference in electron transfer kinetics between semiconductor/solution and semiconductor/metal contacts. (See problem 2c) (5 points)
    - iii) Situations under low and high band-bending. (5 points)
    - iv) Surface or depletion-region recombination. (5 points)
  
2. Assuming superposition rigorously does hold, consider the following situation. You have a “magic”  $n$ -Si Schottky contact with a tunable barrier height ( $\phi_b$ ), no surface states, and negligible interfacial oxide. Electrons surmount the Si-metal barrier via thermionic emission at exactly the rate predicted by the equation presented above. The bulk hole diffusion length,  $L_p$ , in this sample of Si is 100 nm, and you are able to vary the thickness,  $t$ , of the Si at will. It has a dopant density of  $N_D = 1 \times 10^{16} \text{ cm}^{-3}$ .
  - a) For a given combination of  $t$  and  $\phi_b$ , describe how you would determine whether the open-circuit photovoltage at a given light intensity is controlled by bulk recombination rather than thermionic emission. (For example, what plots would you make? [There are a couple ways to do this problem, so be creative.]) (You are not allowed to vary  $\phi_b$  or  $t$  in this experiment!) NOTE:  $\mu_p \propto T^{-2.42}$ . (15 points)
  
  - b) Given complete freedom to modify  $t$  or  $\phi_b$  to any physically realistic values, what would be the maximum photovoltage you could generate using a sample of this  $n$ -Si at 300 K and under an illumination intensity of  $J_{ph} = 20 \text{ mA}/\text{cm}^2$ ? (Remember in these problems  $J_o = J_{br} + J_{th}$ )
    - i) How do we maximize the photovoltage at a given illumination intensity? (5 points)
    - ii) What value for  $t$  would be ideal? Why? (5 points)
    - iii) What value for  $\phi_b$  would be ideal **and also** possible? (5 points)

- iv) Compute the values of  $J_{th}$  and  $J_{br}$  for your values of  $t$  and  $\phi_b$ . (10 points)
- v) Calculate  $J_0$  and the max photovoltage,  $V_{oc}$ . (5 points)
- vi) Briefly discuss your answer to (v) in terms of the max  $V_{oc}$  (is it pretty big or pretty small) and in terms of solar energy conversion. (5 points)

c) Some of our semiconductor-liquid junctions have effective barrier heights as large as 0.93 V in  $n$ -Si. With a very rapid redox couple, the rate of electron transfer to solution might be  $10^{-5}$  times the thermionic emission rate at a metal.

(i.e.  $J_{th,E} = 10^{-5} J_{th,M}$ ) Assuming this to be a good approximation at 300 K:

i. What would the minimum hole diffusion length,  $L_p$ , have to be in an  $n$ -Si sample such that the photovoltage for a junction with  $\phi_b = 0.93$  V were not limited by bulk recombination? (i.e. at what point do  $J_{th}$  and  $J_{br}$  become equal?) (10 points)

ii. Suppose a Si sample of such quality could be made, how thick would the Si sample have to be in order to keep the *effective* hole diffusion length,  $L_p'$ , that long? What does this imply in terms of cost? Would it be worthwhile to make a sample of Si that thick in order to attain that photovoltage? (5 points)