XII. ELECTRONIC PROPERTIES II (DRAFT)

12.1 Electron-hole equilibria

A quantitative description for the electronic properties of semiconductors demands that we know the density of charge carriers—holes and electrons—resulting from doping. This is just another example of a chemical equilibrium.

Holes and electrons will come to equilibrium when the number of electrons being excited to the conduction band is equal to the number of electrons and holes that recombine, i.e., when the rate of excitation is equal to the rate of recombination. The rate of excitation is given, of course, by the Boltzmann equation as,

$$\boldsymbol{p}_{\uparrow} = \boldsymbol{A} \; \boldsymbol{e}^{-\frac{E_g}{kT}}$$

where p_{\uparrow} is the probability of exciting a silicon electron across the energy gap of E_g . The rate at which this process will occur we denote as R_{\uparrow} and note that it will be proportional to the product of the number of Si electrons available for excitation, N_{Si} (usually expressed as the number per cubic centimeter) times the probability of an excitation. Hence,

$$R_{\uparrow} \propto N_{Si} p_{\uparrow} = N_{Si} A e^{-\frac{E_g}{kT}} = N_{Si} K'(T)$$

where K'(T) is a function that depends only on temperature.

The rate of recombination, R_{\downarrow} , will be proportional to the product of the number of electrons in the conduction band, N_e , with the number of hole carriers in the valence band, N_h , times the probability of recombination, p_{\downarrow} . This latter term is once again a constant function that depends only on temperature, which gives,

$$R_{\uparrow} \propto N_e N_h p_{\uparrow} = N_e N_h k'(T)$$

At equilibrium, the rate of excitation will equal the rate of recombination and hence it is easy to show that,

$$N_e N_h = \frac{N_{Si} K'(T)}{k'(T)} = K(T).$$

Note that because N_{Si} is a constant function that depends only on the element and its crystal structure, the product of the number of electron carriers with the number of hole carriers is a temperature dependent constant. For silicon at room temperature K(T) is equal to 10^{20} cm⁻⁶.

K(T) is the equilibrium constant discussed in Chapter 4. In fact, we could have come to the same conclusion by writing the excitation to create a hole and an electron pair as a chemical equation,

bond
$$\rightleftharpoons h + e$$

and then applying equation 4-8.

Nonetheless, we may now assess the effect of doping on the concentration of electron and hole carriers. In an intrinsic semiconductor, the concentration of holes and electrons must be equal, so $N_e = N_h = N = 10^{10} \text{ cm}^{-3}$. Though this may seem like a large number of carriers, there are 5 x 10^{22} silicon atoms per cm³ in crystalline silicon. So, an electron from approximately one in a trillion silicon atoms is excited and moving in the conduction band. If we were to dope the silicon to make it p-type by adding 10^{17} boron atom per cm³, every boron atom would produce one hole and hence the concentration of holes would be 10^{17} and the number of electron carriers is simply computed as 10^3 per cm³. Even at 10^{17} doping there would be a hole on fewer than one in 10,000 silicon atoms and less than one in 10^{19} silicon atoms would host a conduction electron.

12-2 THE FERMI ENERGY

All atoms, molecules and solids have a tendency to attract electrons and become charged. The property measuring this tendency is referred to as electronegativity or equivalently electron

chemical potential. You may have seen tabulated values for the electronegativity of the atoms of the period table. The electronegativity of molecules and solids is controlled by a weighted average of the occupied and unoccupied orbitals, or bands in the case of a solid. This weighted average is expressed as an energy called the Fermi energy, E_f. For



n-type semiconductor

example, Figure 12-1 shows the position of the Fermi energy in a metal as well as in an intrinsic,

p-type and n-type semiconductor. For the metal the E_f marks the dividing point between the occupied and unoccupied band states. For an intrinsic semiconductor where the number of thermally excited holes and electrons must be equal, the Fermi energy passes through the middle of the energy gap. As holes are added, which remove electrons from the conduction band, the Fermi energy falls toward the valence band edge. Conversely when doped n-type by adding more electrons to the conduction band the Fermi energy rises toward the conduction band edge. The important point here is that through doping we can control the position of the Fermi energy. Let's see why this is so important.

For two materials, the one with a lower Fermi energy attracts electrons more strongly, becoming negatively charged while leaving the other material with a positive charge. As electrons move between the materials, on the material losing electrons the bands shift down in energy along with the Fermi energy while the bands and Fermi energy of the material gaining electrons shift up in energy. When their Fermi energies become equal the electron transfer stops. Compared to the total number of electrons in these materials, the number of electrons transferred is very small.

You have probably experienced the results of this electron transfer in the form of a shock when touching someone or something after shuffling your feet along a carpeted floor. Electrons are transferred from the carpet to you and then to the person or thing you touch. The driving force here is that your Fermi energy is lower than that of the carpet. You become negatively charged, raising your Fermi energy and upon touching someone with a lower Fermi energy those electrons are discharged. This is the same process that drives lightning strikes and despite being a common phenomenon is poorly understood.

We can control charge transfer between two semiconductors at their interface by adjusting

their relative Fermi energies as is shown in Figure 12-2. We imagine producing an interface by bringing a p-and n-type material into contact (this is not how it is actually done). A very small number of electrons will be transferred a short distance across the interface from the n-type to the p-type material. As the electrons are transferred the bands of the n-type material will shift down



Fig 12-2 *The flat band diagram at resulting at the interface between a p- and n-type semiconductor*

relative to the p-type semiconductor until their Fermi energies are equal, at which point there will be no further charge transfer across the interface.

The diagram on the right of Figure 12-2 represents the distribution and the energies of the electrons and holes near a p-n junction. Note that for electrons to move from right to left in the conduction band they must overcome a small step in potential denoted as V_S , which is typically reported in volts. Though there is no barrier for the movement of electrons from left to right, there are very few electrons to the left of the barrier. This barrier is the key to rectification. The energy required for one electron to overcome this barrier is eV_S where e is of course the charge on an electron.

12-3 THE EFFECT OF BIASING A P-N JUNCTION

Now consider what happens to the barrier to electron motion when the junction is biased by

imposing an electric potential difference at its two ends, i.e., hooking it up to a battery. The possibilities are picture in Figure 12-3. Shown at the center of this figure is the neutral situation in which there is no voltage across the p-n junction and the barrier energy is simply eV_S . On the left is shown the situation of



Fig. 12-3 The change in the barrier to electron motion due to bias. Note that Eg is not changed by the bias

a reverse bias where electrons may lower their potential by flowing to the right of the junction. In this case, the barrier increases due to the loss of a tiny number of electrons to the right. If the bias voltage is V_B then the potential barrier due to the bias is now $V_S + |V_b|$ and the energy required for one electron to climb this barrier is $e(V_S + |V_b|)$. Pictured to the right is the forward bias situation. Here higher potential electrons are injected from the right and as a consequence the barrier height decreases. Now the potential barrier due to the bias is $V_S - |V_b|$ and the energy required for one electron to climb this barrier is $e(V_S - |V_b|)$. Define the reverse bias as a negative voltage then for both forward and reverse bias the energy to surmount the barrier will be given by $e(V_S - V_b)$.

12-3 THE CURRENT ACROSS A P-N JUNCTION

All that remains to do is to calculate the probability that an electron can get over the barrier in the neutral, forward and revers bias directions. Let's begin with the neutral case. Figure 12-4 depicts the flat band diagram for an unbiased p-n junction along with arrows indicating the directions and magnitudes of the hole and electron currents. We will consider only the electron current, though what follows pertains equally to the hole current.)

Because there is some probability that a conduction electron may surmount the barrier, there must be an electron current to the left, I_L . At the same time, there is some probability that electron carriers from the p-side (left) of the





junction will descend the barrier and hence there is an electron current to the right, I_R . However, there can be no net current and hence $|I_L| = |I_R|$, which we will designate as I_0 .

It is straightforward to compute I_0 . The number of electrons surmounting the barrier is just the product of the number of conduction elections in the n-type material (a number of the order of 10^{17} cm⁻³) with the probability of a transition over the barrier as given by Boltzmann's equation, i.e.

$$I_0 = N_e A e^{-\frac{eVs}{kT}}$$

When biased, the barrier to electron motion changes as depicted in Figure 12-5, with the barrier to electron motion increasing for reveres bias and decreasing for forward bias. The magnitudes of I_L changes correspondingly, increasing for forward bias and decreasing for revers bias. Recalling that the reverse bias voltage is taken as negative, for both cases the current is given as,



Fig. 12-5

$$I_L = N_e A e^{-\frac{e(Vs-Vb)}{kT}} = N_e A e^{-\frac{eVs}{kT}} e^{\frac{eVb}{kT}} = I_0 e^{\frac{eVb}{kT}}$$

While I_L is dependent on the bias, because there is no change in the barrier to I_R , its value remains unchanged at I_o . Thus, the total measurable current is,

$$I_T = I_L - I_0 = I_0 e^{\frac{eVb}{kT}} - I_0.$$

Leading to our desired result,

$$I_T = I_0 \left(e^{\frac{eVb}{kT}} \cdot 1 \right).$$

Note that for a large reverse bias ($V_b \ll 0$) I_T asymptotically approaches I_0 . Under forward bias the current increases exponentially. This is exactly the current as a function of voltage behavior of a rectifier picture in Figure 11-1.

12-4 LEDs revisited