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Supplement I
Intrinsic and Extrinsic Semiconductors,
Fermi-Dirac Distribution Function,
the Fermi level and carrier concentrations
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This is a supplement on the concepts of charge carriers, intrinsic and extrinsic semiconductors, carrier concentrations, the Fermi-Dirac distribution function and the Fermi level, density of states and the effective density of states.

1 Review: Charge Carriers in Semiconductors

Remember the energy band diagram of a semiconductor, shown in Figure 1, displaying the conduction and valence bands and the bandgap.

The electrons in the valence band are bound to the atoms of the crystal. They need to have enough extra energy to go across the forbidden bandgap to get into the energy levels of the conduction band.

To quantify electron concentration ¹ we count the number of electrons in the conduction band per a

¹This is a short way of saying "conduction band electron concentration", since only the electrons in the conduction band contribute to conductivity as electrons.

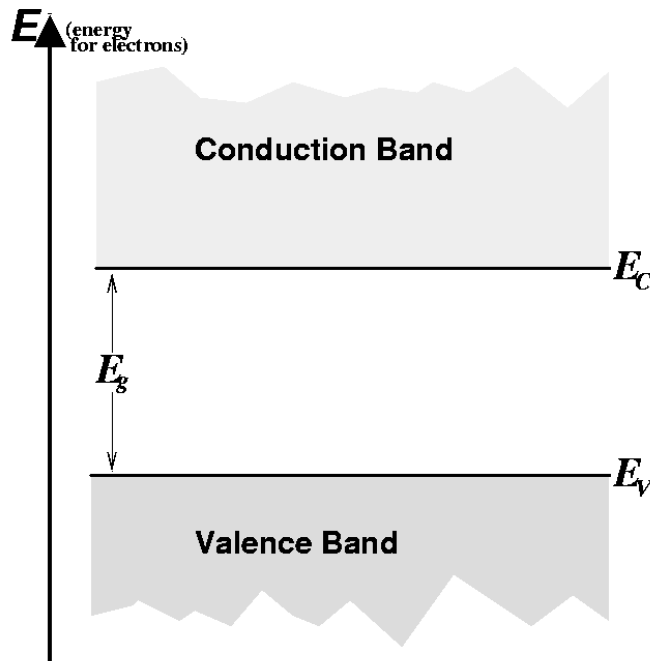


Figure 1:

unit volume, typically a cm^3 . This is shown by the symbol n . When the system is in equilibrium, it is shown by n_0 .

When an electron leaves the valence band to go to the conduction band, it is essentially breaking free of its bond, leaving behind an empty state available for another electron in the valence band energy levels. This empty state is called a "hole" and effectively behaves like a positively charged particle. The number of holes in the valence band per unit volume is called "hole concentration" and shown by the symbol p . In equilibrium, we use p_0 .

If, for instance, an external electric field is applied to the material, the electrons in the conduction band are free to move in the *opposite* direction of the field², because there are many states available around them at their energy level. Under the influence of the same field, electrons in the valence band can also move, but *only* if there are available states at their energy level, i.e. available states in the valence band—therefore, there is a contribution to the conduction in the valence band only if there are holes. Instead of monitoring the motion of many electrons in the valence band, we consider the effective motion of holes, which is in the *same* direction as the electric field, as shown in Figure 2.

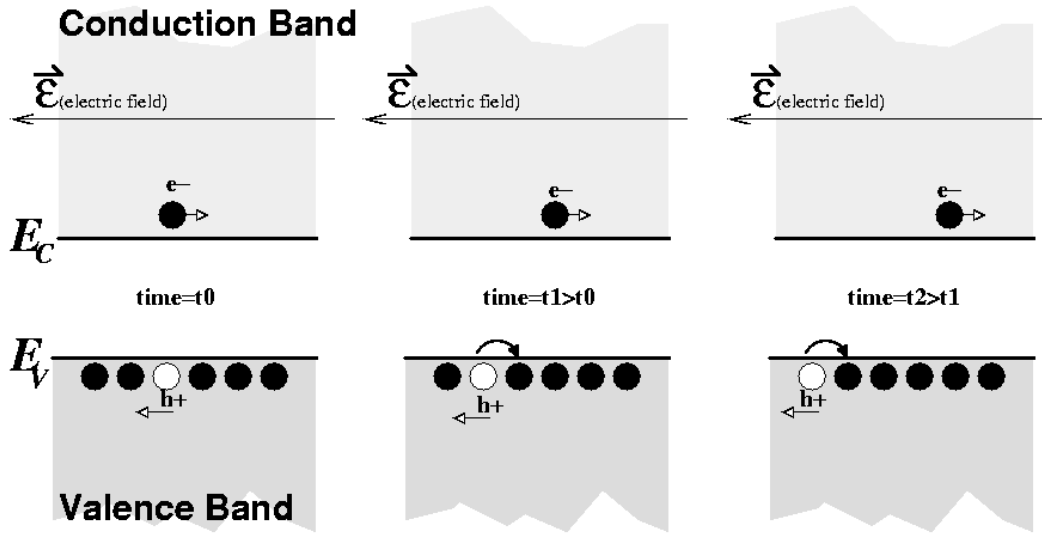


Figure 2:

2 Intrinsic and Extrinsic Materials

An *intrinsic* semiconductor is ideally a perfect crystal. When an electron in an intrinsic semiconductor gets enough energy, it can go to the conduction band and leave behind a hole. This process is called "electron-hole pair (EHP) creation". For the intrinsic material, since electrons and holes are always created in pairs,

$$n = p = n_i \quad (1)$$

where n_i is the symbol for "intrinsic carrier concentration."

²Responding to the force applied on them by the field.

At room temperature, relatively few electrons have enough thermal energy to make this jump. In fact, approximately one electron per 6.9×10^{12} silicon atoms does. So the intrinsic carrier concentration in silicon at room temperature is approximately

$$n_i = 1.45 \times 10^{10} \left[\frac{1}{\text{cm}^3} \right] \text{ silicon, } 300^\circ \text{K} \quad (2)$$

Extrinsic semiconductors are made by introducing different atoms, called *dopant* atoms, into the crystal. We can get two types of extrinsic material:

1. **n-type.** The dopant atoms added to the semiconductor crystal in this case are *donor* atoms.

For silicon, we can use phosphorus (P), arsenic (As) or antimony (Sb) as donors. These are column V elements, with five electrons in their outermost shell. When these atoms are included in the silicon crystal, one of the electrons in this shell can easily jump to the conduction band, leaving a positively charged atom behind. This process is sometimes called “activation” or “ionization” of the donor atoms. Figure 3 shows the required “activation” energies for these atoms in silicon; you can see that these are very small compared to the silicon bandgap.

The positively charged donor atom that is left behind after ionization is immobile and does not contribute to conduction. The electron leaving the atom by ionization does, and is counted in the electron concentration n . Because the activation energy is low, at room temperature almost all of the donor atoms included in the crystal will give an electron to the conduction band. So if N_D is the donor concentration, for an n-type material at equilibrium:

$$n_0 \approx N_D \left[\frac{1}{\text{cm}^3} \right] \quad (3)$$

2. **p-type.** The dopant atoms in this case are *acceptor* atoms.

For silicon, we can use boron (B), Aluminum (Al) and Gallium (Ga) as acceptors. These are column III elements, with three electrons in their outermost shell. When these atoms are included in the silicon crystal, one of the electrons in the silicon valence band can easily jump to the valence shell of one of the acceptor atoms, leaving a hole behind and making the acceptor atom negatively charged. Figure 3 shows where the valence shell energy level is for these atoms relative to the silicon valence band.

The negatively charged acceptor atom after an electron joins its valence shell is immobile and does not contribute to conduction. The hole left behind by that electron does, and is counted in the hole concentration p . Because the activation energy is low, at room temperature almost all of the acceptor atoms included in the crystal will accept an electron from the valence band. So if N_A is the acceptor concentration, for a p-type material at equilibrium:

$$p_0 \approx N_A \left[\frac{1}{\text{cm}^3} \right] \quad (4)$$

3 Law of Mass Action

For both intrinsic and extrinsic materials, at equilibrium:

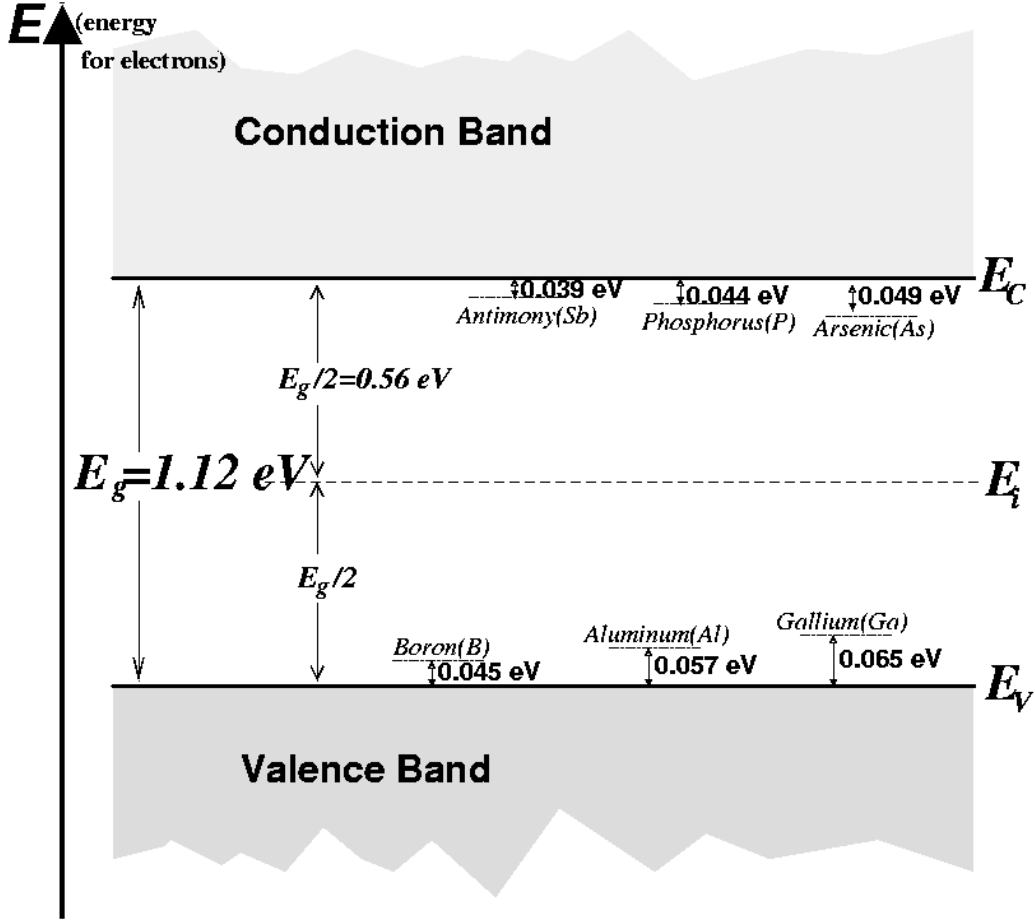


Figure 3: Donor and acceptor ionization energy levels. Adapted from Muller & Kamins 1986, not to scale.

$$n_0 p_0 = n_i^2 \Rightarrow n_0 = \frac{n_i^2}{p_0}, p_0 = \frac{n_i^2}{n_0} \quad (5)$$

So for an n-type material with only donor atoms³:

$$n_0 = N_D, p_0 = \frac{n_i^2}{n_0} = \frac{n_i^2}{N_D} \quad (6)$$

And for a p-type material with only acceptor atoms:

$$p_0 = N_A, n_0 = \frac{n_i^2}{p_0} = \frac{n_i^2}{N_A} \quad (7)$$

³Assuming complete ionization—unless stated otherwise, we will always be making this assumption from now on.

4 Impurity Compensation

Due to fabrication constraints, in many cases there are both donor and acceptor atoms present in a piece of semiconductor crystal. The eventual type of material and electron/hole concentrations depend on which type of dopant atom is more populous. The behavior is detailed in Table 1.

	If $N_D > N_A...$	If $N_A > N_D$
Material	n-type	p-type
Electron concentration at equilibrium	$n_0 = N_D - N_A$	$n_0 = \frac{n_i^2}{p_0}$
Hole concentration at equilibrium	$p_0 = \frac{n_i^2}{n_0}$	$p_0 = N_A - N_D$

Table 1:

5 The Fermi-Dirac Distribution Function and Fermi Level

The conduction band in a piece of semiconductor consists of many available, allowed, empty energy levels. When calculating how many electrons will fill these levels and thus be counted in n , contributing to conductivity, we consider two factors:

- How many energy levels are there within a given range of energy, in our case the conduction band, and
- How likely is it that each level will be populated by an electron.

The likelihood in the second item is given by a probability function called the *Fermi-Dirac distribution function*. $f(E)$ is the probability that a level with energy E will be filled by an electron, and the expression is:

$$f(E) = \frac{1}{1 + \exp((E - E_F)/(k_B T))} \quad (8)$$

where k_B is Boltzmann's constant, 8.62×10^{-5} [eV/K], and T is the temperature in degrees Kelvin.

E_F is called the *Fermi energy* or *Fermi level*. It is determined as the energy point where the probability of occupancy by an electron is exactly 50%, or 0.5:

$$f(E_F) = \frac{1}{1 + \exp((E_F - E_F)/(k_B T))} = \frac{1}{1 + \exp(0)} = \frac{1}{2} \quad (9)$$

5.1 Meaning of $(1 - f(E))$

Since f_{E_1} is the probability that the energy level E_1 *will be filled* by an electron, $(1 - f_{E_1})$ is the probability that the energy level E *will be empty*. Or, equivalently, if E_1 is in the valence band, $(1 - f(E_1))$ is the probability that the energy level E_1 will have a hole.

5.2 Symmetry of $f(E)$ around E_F

It can easily be shown that

$$f(E_F + E) = 1 - f(E_F - E) \quad (10)$$

5.3 Fermi Level in Intrinsic and Extrinsic Semiconductors

In an intrinsic semiconductor, $n = p$. If we use the band-symmetry approximation, which assumes that there are equal number of states in equal-sized energy bands at the edges of the conduction and valence bands, $n = p$ implies that there is an equal chance of finding an electron at the conduction band edge as there is of finding a hole at the valence band edge:

shouldn't it be finding e- in the valence band ?

$$f(E_C) = 1 - f(E_V) \quad (11)$$

From Eqn. 10 we can deduce that the Fermi level E_F must be in the middle of the bandgap for an intrinsic semiconductor, as seen in Figure 4. In fact, this level is called the “intrinsic Fermi level” and shown by E_i :

$$E_i = E_C - E_g/2 = E_V + E_g/2 \quad (12)$$

where E_g is the bandgap energy.

For an *n-type* semiconductor, there are more electrons in the conduction band than there are holes in the valence band. This also implies that the probability of finding an electron near the conduction band edge is larger than the probability of finding a hole at the valence band edge. Therefore, the Fermi level is closer to the conduction band in an n-type semiconductor:

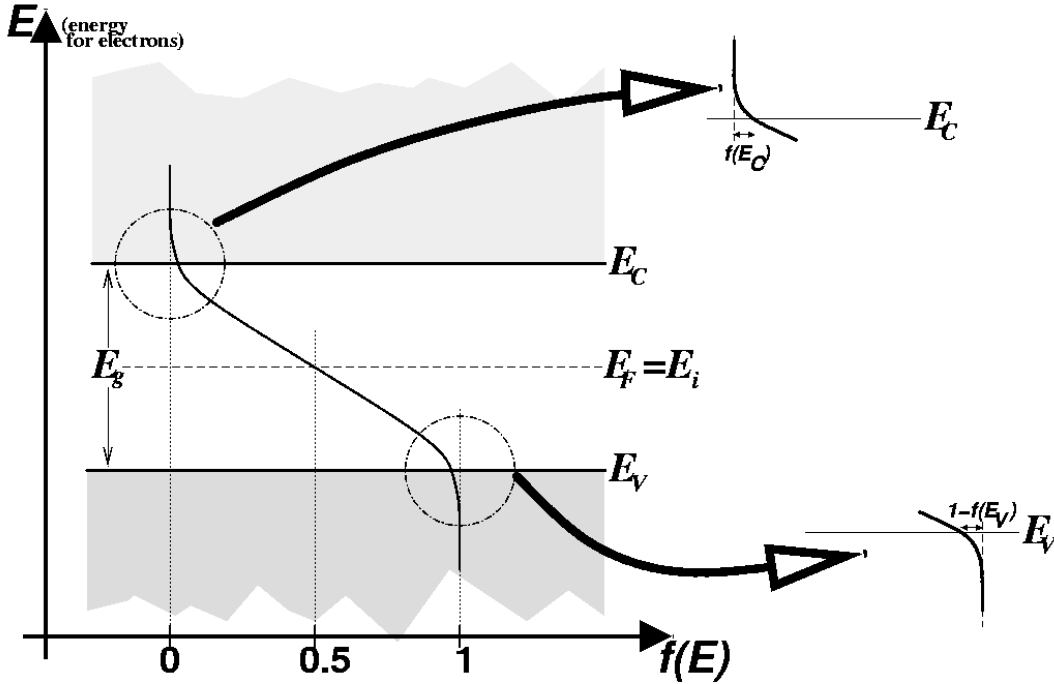


Figure 4:

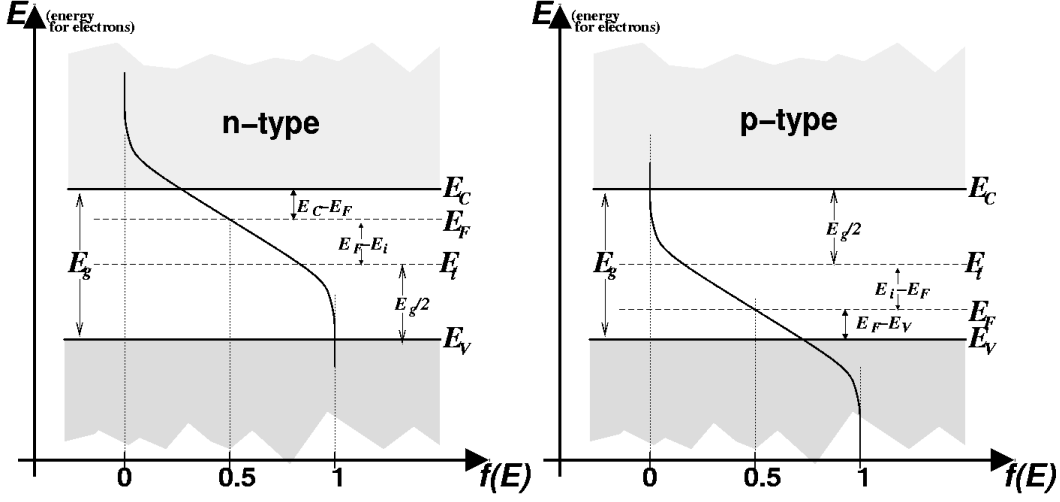


Figure 5: The extrinsic Fermi levels. The curvature of the Fermi-Dirac distribution function is exaggerated to emphasize the difference between $f(E_C)$ and $1 - f(E_V)$ in the n-type and p-type materials.

Material type	Relationships
n-type	$E_F > E_i$ $E_C - E_F = \frac{E_g}{2} - (E_F - E_i)$
p-type	$E_F < E_i$ $E_F - E_V = \frac{E_g}{2} - (E_i - E_F)$

Table 2:

For a *p-type* semiconductor, there are more holes in the valence band than there are electrons in the conduction band. This also implies that the probability of finding an electron near the conduction band edge is smaller than the probability of finding a hole at the valence band edge. Therefore, the Fermi level is closer to the valence band in an n-type semiconductor.

The following relationships summarize these last points:

$$n - type : f(E_C) > (1 - f(E_V)) \Rightarrow |E_C - E_F| < |E_F - E_V| \Rightarrow E_F > E_i \quad (13)$$

$$p - type : f(E_C) < (1 - f(E_V)) \Rightarrow |E_C - E_F| > |E_F - E_V| \Rightarrow E_F < E_i \quad (14)$$

Figure 5 shows the situation for extrinsic materials.

Finally, since the bandgap energy is a constant, with $E_g = E_C - E_V$, the relationship between E_g , E_i , E_C , E_V and E_F can be deduced also by looking at Figure 5. Table 2 summarizes these relationships.

6 Effective Density of States and the Carrier Concentrations

The first factor mentioned in Section 5, how many energy states are there available for electrons in the conduction band⁴, is described by a *density-of-states* function, $N(E)$. The expression $N(E)dE$ gives the number of states in the energy range $[E, E + dE]$. To find the total number of electrons in the conduction band, we multiply this density of states with the probability that each energy level will have an electron occupying it ($f(E)$) and integrate across the conduction band.

However, assuming that the Fermi level is far away enough from the conduction band edge ($|E_C - E_F| > 4k_B T$), we can consider all the available energy levels in the conduction band to be gathered right at the band edge. In doing so, we are defining an *effective density of states*, shown with N_C for the conduction band and N_V for the valence band. Then, in the conduction band, all we have to do to find the number of electrons per unit volume is to count this number of states at the band edge per unit volume (N_C) and multiply it with the probability that a state at that level will be filled ($f(E_C)$):

$$n_0 = N_C f(E_C) = N_C \frac{1}{1 + \exp((E_C - E_F)/(k_B T))} \quad (15)$$

If the assumption $|E_C - E_F| > 4k_B T$ holds, we can also approximate the Fermi-Dirac distribution function with the Boltzmann distribution function:

$$f(E_C) = \frac{1}{1 + \exp((E_C - E_F)/(k_B T))} \approx \exp(-(E_C - E_F)/(k_B T)) \quad (16)$$

In an n-type semiconductor, if we know the doping level N_D , we know we can say $n_0 = N_D$; therefore, using the Boltzmann approximation:

$$n_0 = N_D = N_C \exp(-(E_C - E_F)/(k_B T)) \quad (17)$$

Similarly, for the holes in the valence band, we take the effective density of states (N_V) and multiply it with the probability that a state at that level will be empty ($1 - f(E_V)$):

$$p_0 = N_V (1 - f(E_V)) = N_V \exp(-(E_F - E_V)/(k_B T)) , \quad (18)$$

once again using the Boltzmann approximation for $f(E_V)$.

⁴We will later also look at how many states are there available for holes in the valence band.