

How do we make semiconductors conductive?

As discussed so far this week, we need to excite electrons from the valence band to the conduction band to make semiconductors conductive.

This can be achieved by several different routes.

First, we can excite charge carriers using thermal energy.

Secondly, we can use impurities in the semiconductor material.

This is what we call doping.

The third option, which is very important to solar cells, is to use the energy in light to excite electrons from the valence band to the conduction band.

Before I will discuss these various routes to excite charge carriers, I will first discuss the important concept of the Fermi level.

Lets consider a metal.

Electrons are filling the electronic band of a metal.

The electronic band is a band of continuous energy levels.

This band is not fully filled by electrons.

The probability to find an electron is not the same at all energy levels.

At low energy levels you will have a probability of 100% that electrons fill this level, while at high levels this probability is close to zero.

The probability to find an electron can be expressed by the Fermi-Dirac distribution function.

This function reflects the probability that an electron will occupy a state at an energy E .

Low in the valence band this function is equal to 1, whereas high in the conduction band this function is equal to 0.

Note, that this equation is only valid for a material that is at thermal equilibrium, which means that no additional energy is coupled into the system by electrical biasing, light absorption or heat conductivity.

The Fermi level represents the energy level at which the electrons have a 50% change to occupy the energy level at any given time.

For a metal it easy to see where the Fermi level is positioned.

Physicists use in general the term Fermi level.

Chemists might use a different term, they might call this level the total chemical potential of an electron.

The shape of the Fermi-Dirac distribution does change with temperature.

At absolute zero, which means a temperature of 0 K (or minus 273 degree Celsius), the function looks like a step function.

The probability to occupy a state below the Fermi level is 100%, whereas the probability above the Fermi level is 0%.

For higher temperatures, this distribution starts to broaden around the Fermi level.

Around the Fermi level the energy is distributed over values between 0 and 1.

The higher the temperature the broader the distribution around the Fermi level will be.

As you can see, a metal has only one electronic band.

However, for semiconductors this situation is different.

The valence band is almost fully filled with electrons, whereas the conduction band only has a very few electrons.

The Fermi level is positioned in the forbidden band gap, between the valence and conduction band.

According to the Fermi-Dirac function electrons have a 50% probability to occupy the electronic states at the Fermi level.

Since no electronic band exists at this level in the forbidden band gap, no electrons can occupy this level.

So the real distribution of electrons over the two electronic bands becomes more complicated.

In general the Fermi Dirac function shows that the energy levels in the conduction band have a low probability to be occupied, while the energy levels in the valence band have a high probability to be occupied.

At absolute 0, a temperature of 0K (or minus 273 degree Celsius), all electrons fully occupy the valence band.

The semiconductor material is not conductive.

If we increase the temperature, the shape of the Fermi-Dirac function broadens around the Fermi level and some electrons have the change to occupy the conduction band as well.

The higher the temperature, the more electrons can occupy the conduction band. This demonstrates the physical principle that if you heat up a semiconductor material, it becomes more conductive.

Using the Fermi Dirac function you can tell something about the distributions of holes in the conduction band.

The positions in the valence band at which the electrons are missing are the locations at which the holes are present indicated by the blue dots again.

So if we remove the fixed electrons in the valence band, we are left with only the mobile charge carriers, the free electrons and free holes.

One minus the Fermi Dirac function, shows for a semiconductor the probability that you will find a hole at certain energy level.

This week we will focus on the behavior of the charge carriers, electrons and holes in a semiconductor.

We will use the semiconductor material silicon again as an example.

And again I will make a drastic simplification.

The silicon network is a 3-dimensional network as you can see in this animation.

The blue spheres represent the silicon atoms and the red dots represent the valence electrons in the molecular orbitals which are forming the bonds with the neighboring atoms.

To illustrate the behavior of charge carriers in the silicon lattice, I will flatten the material and consider the silicon lattice to be a 2-dimensional squared lattice.

In this 2-dimensional network, every silicon atom has four bonds with its neighboring silicon atom, like it has in a 3-dimensional network.

In this schematic silicon network we put some charge carriers.

The animation shows the mobile electrons, which again are indicated with the red dots.

Secondly, we show the holes, which are in this illustration indicated by the black dots.

They are part of a molecular bond in which one of the two valence electrons is missing.

Both electrons and holes can move freely around.

So far we have discussed that we can manipulate the density of the free charge carriers using temperature.

The higher the temperature, the more free electrons and free holes can be excited.

Another approach to increase the density of the charge carriers is using doping.

Up to now we have considered pure semiconductor materials without any impurities.

These semiconductor materials are called intrinsic.

It means that the density of mobile electrons and holes are the same in the material.

We can intentionally incorporate impurities in the material.

This is called doping.

Doping can have a significant effect on the charge carrier density.

Which I will explain now.

As example we take again silicon, silicon is a material, which has four valence electrons.

In the periodic system Silicon is part of the column with atoms having only four valence electrons.

At the left side of the column with IV-valence elements we see that we have materials with only three valence electrons, like Boron, Aluminum, and Gallium.

On the right side of silicon in the periodic table we have atoms which have five valence electrons, like nitrogen and phosphorous.

First, we are going to intentionally put Phosphorous impurities in the silicon network.

Phosphorous has five valence electrons.

The Phosphorous atom will make molecular bonds with its four neighboring silicon atoms.

Since the Phosphorous atom has five valence electrons, it has one electron left.

This extra electron is easily excited to a free mobile state.

The Phosphorous atom left behind is not neutral anymore and becomes a positively charged entity.

This positive charge is fixed to the position where the Phosphorous atom is residing in the lattice.

The result is that by adding an impurity we have one extra free mobile electron and a fixed positive charge in the background.

This is called n-doping.

For n-doped semiconductors, the electrons are called the majority charge carriers, as the density of electrons is much higher than that of the holes.

The holes are called the minority charge carriers in a n-doped semiconductor.

n-doping of silicon can also be illustrated by an electronic band diagram.

The Phosphorous atoms are represented as donor states.

These donor states have an energy level within the forbidden band gap of the silicon matrix, which can be occupied by electrons.

The energy level of the donor states is closer to the conduction band than to the valence band.

This means it requires much less energy for an electron to jump from the donor state to the conduction band than for an electron from the valence to the conduction band.

At typical room temperatures many to all of the electrons in the donor states can be excited to the conduction band.

As a result we have more free mobile electrons than mobile holes in an n-type semiconductor.

We call the states donor states, because they donate an electron to the conduction band.

The electrons are the majority charge carriers, the hole are the minority charge carriers.

As the electrons are the majority charge carriers, the Fermi level will be closer to the conduction band than to the valence band.

Secondly, we are going to intentionally put Boron impurities in the silicon network.

Since the Boron atom has only three valence electrons, it is missing one electron to make a molecular bond with its four neighboring Silicon atoms.

As a consequence one molecular bond is filled with only one electron.

This entity is the same as the hole.

This extra hole is easily excited to a free mobile state as well.

The Boron atom left behind is not neutral anymore, but becomes negatively charged.

This negative charge is fixed to the position where the Boron atom is residing in the lattice.

The result is that by adding a Boron impurity we have one extra free mobile hole available and one fixed negative charge.

This is called p-doping.

The state is called acceptor as it accepts one electron from the valence band.

For p-doped semiconductors, the electrons are called the minority charge carriers as the density of electrons is much smaller than the density of the holes.

The holes are the majority charge carrier in p-doped material.

p-doping of silicon can be illustrated by an electronic band diagram as well.

The Boron atoms result in acceptor states.

These acceptor states have an energy level within the forbidden band gap of the silicon matrix and the acceptor states can be occupied by electrons.

The energy level of the acceptor states is closer to the valence band than to the conduction band.

This means that it requires much less energy for an electron to jump from the valence band to the acceptor state than to the conduction band.

For silicon at room temperature many electrons of the valence band can be excited to the acceptor states.

As a result we have more free mobile holes than mobile electrons in a p-type semiconductor.

The electrons are the minority charge carriers, the holes are the majority charge carriers.

As the holes are the majority charge carriers the Fermi level will be closer to the valence band than to the conduction band.

Let's get a feeling for typical concentrations for majority and minority charge carriers in doped silicon networks in the dark.

Typical densities for majority charge carriers in silicon are 10^{16} per cubic centimeter, whereas the density of minority charge carriers in that case would be 10^4 per cubic centimeters.

This shows that the density of the majority charge carrier can be many orders of magnitude higher than that of the minority charge carrier.

Note that the silicon density in crystalline silicon is 5×10^{22} per cubic cm.

This means that the total number of charge carriers is much lower than the typical density of silicon atoms, the ratio majority charge carriers to silicon atoms in this example is 1 to 5 million.

The densities of charge carriers can be described by the law of mass action.

What does this law mean for charge carriers in semiconductor materials?

This law tells us that at a given temperature the product of the electron density and hole density is constant, independent of the doping concentration.

If n corresponds to the electron density and p corresponds to the hole density, this law tells us that the product np is constant if we would manipulate either n or p . So let's consider intrinsic silicon.

This is silicon without any impurities.

At room temperature the electron density N and hole density P are equal.

For silicon the electron and hole density is in the order of 1.1×10^{10} per cubic centimeters at room temperature.

This means the product, $n \times p$, is equal to 1.21×10^{20} per squared cubic centimeters.

Now we consider a n-doped silicon material.

We incorporate a density of phosphorous atoms in the lattice, which we call N_D .

We assume that all donors give a free electron to the lattice.

So it means the electron density n_0 is equal to N_D .

Now we can calculate the hole density p_0 .

The law of mass action tells us at a given temperature the product of the electron density and hole density is constant independent of the doping.

So p_0 is equal to the square of the intrinsic charge carrier density divided by the electron density n_0 .

The same is valid for p-doped silicon material.

We incorporate Boron atoms with density of N_A in the silicon network.

We assume that all acceptor take one electron and therefore create hole density p_0 equal to the acceptor density N_A .

This means that the electron density n_0 is equal to the square of the intrinsic charge carrier density divided by the hole density p_0 .

Let's take an example.

We incorporate 10^{16} cubic centimeters phosphorous atoms in the lattice, or in other words:

we have a donor density N_D of 10^{16} per cubic centimeters.

As we assume that all donors give a free electron to the lattice the electron density n_0 is equal to donor density N_D .

Now we can calculate the hole density p_0 .

So p_0 is equal to the square of the intrinsic charge carrier density divided by the electron density n_0 .

So the hole density is given by 1.21×10^{20} divided by the number by 10^{16} we get the hole density of 1.12×10^4 per cubic centimeters.

Now we consider a third approach to excite charge carriers, which is by light absorption.

Let's consider the electronic band diagram again and photon with an energy equal to the band gap, indicated by the green arrow.

This photon can be absorbed in a semiconductor material and can be used to excite an electron from the valence band to the conduction band.

So, light can make a semiconductor material more conductive.

However, if we have a photon with an energy smaller than the band gap, this photon is lacking the energy to excite an electron from the valence band to the conduction band.

This photon cannot be absorbed by the semiconductor material.

Another situation is when the photon has an energy much larger than the band gap.

This photon can excite an electron at an energy level deeper in the valence band in to the conduction band.

Or an electron to higher energy levels in to the conduction band.

In these situations the hot electrons or holes very fast relax back to the lower energy positions.

For the electron this is the bottom of the conduction band and for the hole this would mean the top of the valence band.

This extra energy is released as heat and will and heat up the semiconductor material.

So the rest energy, which is the photon energy minus the band gap energy, ends up as heat.

Finally in this block I would like to discuss how light absorption affects the charge carrier density in doped materials.

Let's consider again the situation with a density of majority charge carriers of 10^{16} per cubic centimeters and density of minority charge carrier of 10^4 per cubic centimeters.

Now let's assume we generate electron-hole pairs by light absorption.

We generate 10^{11} electron-hole pairs per cubic centimeters.

What will happen to the density of the majority and minority charge carriers?

So we will simply add up the numbers.

What you see is that the majority charge carrier density is not affected by the light absorption.

10^{11} is much smaller than 10^{16} .

On the other hand the density of minority charge carriers is drastically affected.

10^{11} is much larger than 10^4 .

Its density is increased with 7 orders of magnitude.

This is an important conclusion, which we will need later to understand the working principle of solar cells.

In doped semiconductor materials, light absorption has only affect on the density of minority charge carriers.

Summarized, in this block we have discussed how to excite charge carriers in a semiconductor material, by temperature, doping and light absorption.

The next question is: how do those charge carriers move around and what makes them move around in a semiconductor material?

I will talk about that in the next block, where we are going to discuss transport of charge carriers.