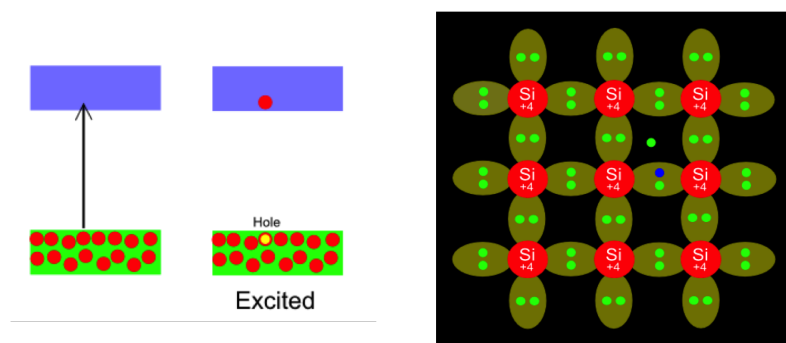


Section 2: Conduction properties of Semiconductors

Electrons and holes

We know that current is caused by moving electrons, it can also be caused by the absence of electrons moving. We call these absences holes, and they act as positive charges moving through solid.

In the case of semiconductors we call the full lower band the valence band, and the empty upper band the conduction band. When an electron is excited into the conduction band, it leaves behind a hole in the valence band, effectively creating two free charges at the same time.



We can treat the electron in the conduction band as a “free” particle. These electrons move through the crystal lattice by filling a hole, moving back into the conduction band, then filling a different hole. The “positively” charged holes can therefore be equivalently viewed as moving through the solid.

The average thermal energy of an electron is approximately $kT = 0.026$ eV at room temperature. By contrast, the bandgap in Silicon is 1.1 eV; not many electrons make it to the conduction band. At room temperature Silicon has about 10^{10} electron-hole pairs per cubic-centimetre (EHP cm^{-3}). This seems like a lot but there are 5×10^{22} atoms cm^{-3} in Silicon. Pure silicon is not a very good conductor.

Charge carrier concentration

Determining the concentration of charge carriers at different energies or temperatures is vital to understanding the conduction properties of semiconductors. There are two parts to the calculation:

- 1) Finding which energies correspond to an allowable energy state.
- 2) Determining which states the electrons are in (statistically speaking).

Density of states

Energy states are not uniformly distributed throughout the conduction and valence bands. The precise density of the states can be determined from quantum mechanics, but we only need an approximation here. The number density of electrons and holes $g(E)$ at energy E is found to have the form:

$$g(E) \propto \begin{cases} \sqrt{E - E_c} & E > E_c \\ 0 & E_v < E < E_c \\ \sqrt{E_v - E} & E < E_v \end{cases}$$

where E_c is the lowest energy level of the conduction band and E_v is the highest energy level of the valence band. But to find the total number of free electrons in the conduction band, we need to

multiply $g(E)$ by the probability of finding an electron at each energy level.

Fermi - Dirac distribution

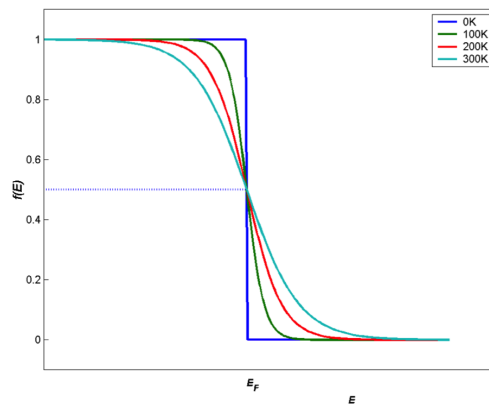
The probability that an energy level (E) will be filled by an electron is given by the Fermi-Dirac distribution from statistical mechanics. The filling of all available states up to the Fermi level, and then no electrons above that, only applies at zero kelvin. To model electrons at temperatures above absolute zero we need to make use of the full equation:

$$f(E) = \frac{1}{1 + e^{(E-E_f)/k T}}$$

k is Boltzmann's constant, 8.62×10^{-5} eV/K

T is the temperature in Kelvin

E_f is the Fermi level, note that $f(E_f) = \frac{1}{2}$



Because holes and free electrons are created in pairs, we expect that $E_f \approx (E_c + E_v)/2$, where again E_c is the lowest energy of the conduction band and E_v is the highest energy of the valence band.

If $E - E_f \gg k T$ then we can approximate $f(E) \approx e^{-(E-E_f)/k T}$. At room temperature of 300 K, $k T = 0.026$ eV so this is usually the case, as band-gap energies are on the order of ~ 1 eV. We call this the Boltzmann approximation.

Number density of electrons/holes

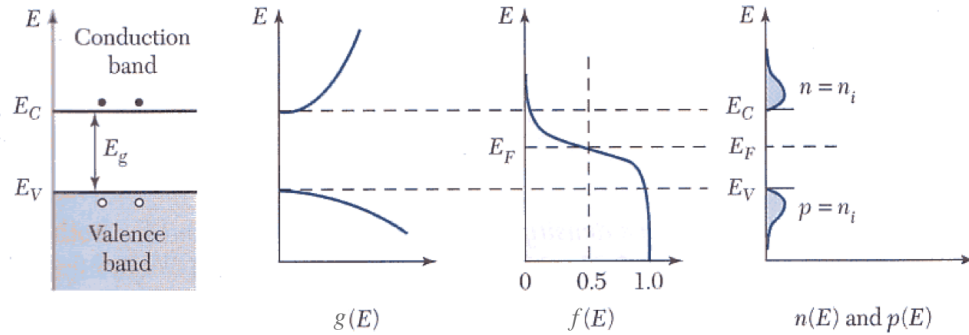
The number density of charge carriers is calculated by multiplying the density of states $g(E)$ by the probability of finding electrons in those states $f(E)$, then integrating with respect to the energy E . So the number density of free electrons n in the conduction band, where n stands for negative charge carrier is:

$$n = \int_{E_c}^{\infty} f(E)g(E) dE \approx N_c e^{-(E_c-E_f)/k T}$$

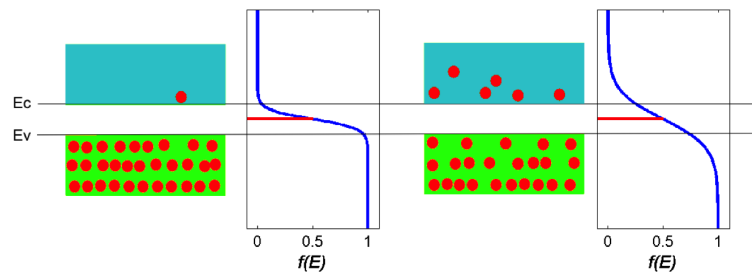
where N_c is the effective density of states in the conduction band. Similarly we can do this for holes, to get the number density of positive charge carriers p in the valence band :

$$p = \int_0^{E_v} (1-f(E))g(E) dE \approx N_v e^{-(E_f-E_v)/k T}$$

where N_v is the effective density of states in the valence band. Why do we write $1-f(E)$ here?



The Fermi-Dirac distribution has more higher energy states for electrons at higher temperatures; this leads to the production of more electron-hole pairs. We would therefore expect more conduction at higher temperatures.



Fermi level in intrinsic semiconductors

For pure semiconductors, electrons get into the conduction band via pair production. This means there are an equal number of holes p and free electrons n produced.

$$n = p = n_i$$

We call semiconductors like this intrinsic semiconductors, and n_i is the number density of intrinsic charge carriers. We then make use of an important relationship: the np product:

$$np = n_i^2$$

This may seem trivial, however it turns out to be a quite general relationship, even when we are not dealing with an intrinsic semiconductor. From this we get:

$$n_i = \sqrt{N_c N_v} e^{-E_g/2kT}$$

where $E_g = E_c - E_v$ is the band gap energy.

Example: Calculate the number density of charge carriers in a Silicon crystal lattice. At 300K the band gap energy is $E_g = 1.12$ eV, and the effective density of states in the conduction and valence bands are $N_c = 2.82 \times 10^{19} \text{ cm}^{-3}$, $N_v = 1.83 \times 10^{19} \text{ cm}^{-3}$ respectively.

At room temperature (300K),

$$\begin{aligned} kT &= (1.38 \times 10^{-23} \text{ J/K})(300\text{K}) \\ &= 4.14 \times 10^{-21} \text{ J} \\ &= 0.026 \text{ eV} \end{aligned}$$

The number of electron-hole pairs is therefore:

$$\begin{aligned} n_i &= \sqrt{(2.82 \times 10^{19} \text{ cm}^{-3})(1.83 \times 10^{19} \text{ cm}^{-3})} e^{-1.12 \text{ eV}/(2 \times 0.026 \text{ eV})} \\ n_i &= 10^{10} \text{ cm}^{-3} \end{aligned}$$

Equating the number density of holes p and free electrons n it is also possible to calculate the intrinsic Fermi level:

$$E_f = \frac{E_c + E_v}{2} + \frac{kT}{2} \ln\left(\frac{N_v}{N_c}\right)$$

The second term in this expression is much smaller than the first at room temperature, i.e. $E_f \approx (E_c + E_v)/2$. The Fermi Level is therefore very close to the centre of the band gap.

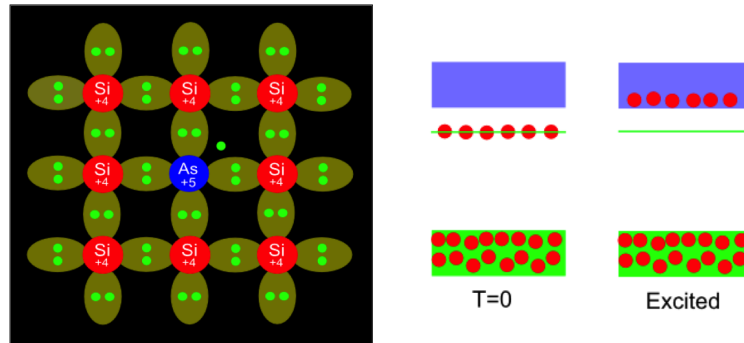
Doping

The carrier concentration in intrinsic semiconductors at room temperature is lower than we would like for device fabrication. If we wish to improve or control the conduction properties of our semiconductors, we can include dopants to change the number of free charge carriers. A group III element (B, Al, Ga, In) will act as an acceptor of electrons and produce a hole, a group V element (N, P, As, Sb) will act as a donor and produce a free electron.

These donor atoms take the place of one of the group IV atoms in our semiconductor, and either provide an extra hole or electron. These extra electrons or holes are very weakly bound to the donor or acceptor atoms and so an extra energy level is introduced, but very close to the conduction or valence band energies.

n-type semiconductors

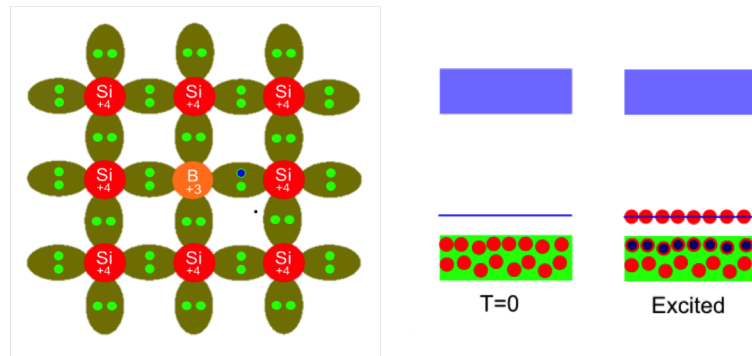
The Group V elements have an extra electron in their outer shell (than C, Si etc), creating extra negative carriers (hence n-type semiconductor). The extra electrons create extra energy levels near the top of the band gap. These levels are filled at zero temperature. These energy levels are close to the conduction band and thus the electrons easily move to the conduction band.



If we include a number density N_d donor atoms, where $N_d \gg n_i(T)$, and there is enough thermal energy to excite the donor electrons into the conduction band, then $n \approx N_d$. This is called an extrinsic semiconductor. We can find the number of holes by using $np = n_i^2$, i.e. $p = n_i^2 / N_d$. The electrons are called the majority charge carriers, the holes are the minority charge carriers.

p-type semiconductors

We could instead include a number density N_a of group III acceptor atoms, adding holes and creating extra positive carriers (hence p-type semiconductor). Extra energy levels near the bottom of the band gap. These are empty at zero temperature. These energy levels are close to the valence band and thus the electrons easily move to them and leave behind holes.



Similar to before we have $p \approx N_a$ and $n = n_i^2 / N_a$. The holes are the majority charge carriers and the electrons are the minority charge carriers.

If we add both N_a group III atoms and N_d group V atoms, what we end up with depends on the relative values of N_a and N_d . If $N_a > N_d$ then we have a p-type semiconductor with $p = N_a - N_d$. Alternatively if $N_d > N_a$ then we have an n-type semiconductor with $n = N_d - N_a$. These relations both assume that $(N_a - N_d)^2 \gg n_i^2$.

Fermi level and temperature dependence

n-type semiconductors

The Fermi level is adjusted by the doping of the semiconductor crystal. If there is sufficient thermal energy to excite all the donated electrons in an n-type semiconductor then we have $n \approx N_d$. Also recall that $n = N_c e^{-(E_c - E_f)/kT}$. Combining these the Fermi level for an n-type semiconductor is:

$$E_f = E_c - kT \ln\left(\frac{N_c}{N_d}\right)$$

Increasing the number of donor atoms therefore increases the Fermi level.

p-type semiconductors

If there is sufficient thermal energy to excite all the electrons out of the acceptor atoms in a p-type semiconductor then we have $p \approx N_a$. The Fermi level for a p-type semiconductor is thus:

$$E_f = E_v + kT \ln\left(\frac{N_v}{N_a}\right)$$

Increasing the number of acceptor atoms therefore decreases the Fermi level.

Temperature dependence and “Freeze out”

In assuming that $n = N_d$ for n-type semiconductor, we had to make two assumptions:

1. $N_d \gg n_i(T)$; this stops being true at higher temperatures when the number of intrinsic charge carriers becomes comparable to the number of donor atoms. Consider silicon doped with $N_d = 10^{17}$ atoms cm^{-3} donor atoms. We can roughly estimate the temperature at which the extrinsic region (where $n = N_d$) starts to give way to the intrinsic region, by calculating when n_i is say 10% of N_d . Now to do this we will assume that the effective density of states is constant (it actually has a $T^{3/2}$ dependence). So we have:

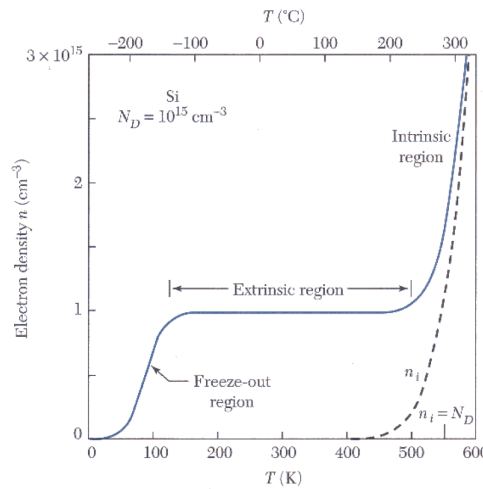
$$n_i = \sqrt{N_c N_v} e^{-E_g/2kT} = 0.1 N_d$$

Solving this with our values for silicon gives us $T \sim 840\text{K}$, which is very hot, but still well below the melting point of silicon (1,687 K). If we include the $T^{3/2}$ temperature dependence we get $T \sim 720\text{K}$, which is not too far off. These are rough estimates, as there are other factors involved but they give an idea of the temperatures.

2. The other assumption is that there is enough energy to excite donor electrons into the conduction band. “Freeze out” occurs when there isn’t sufficient thermal energy to excite electrons out of this state into the conduction band. To get a rough estimate of the temperature freeze-out begins, let us say that we have a semiconductor with band gap 0.039 eV (i.e. the n-type dopant is Antimony). We want the temperature at which the number of free electrons for our tiny band gap semiconductor is equal to N_d . Assuming the Fermi level is halfway between the donor level and the conduction band we have:

$$n = N_c e^{-0.039 \text{ eV} / 2 k T} = N_d$$

Solving this gives $T \sim 40$ K, or with the $T^{3/2}$ temperature dependence in N_c a slightly hotter $T \sim 67$ K. These are very rough estimates, and only apply to lightly doped semiconductors. If the doping level is significant freeze-out effects can be eliminated, similarly if both n-type and p-type dopants are included this can compensate and also reduce the effects of freeze-out.



At room temperature, both of these assumptions are typically satisfied and we can take $n = N_d$. These same assumptions discussed for n-type semiconductors also apply for p-type semiconductors.

Currents and conductivity

Effective carrier mass

Electrons can effectively behave like free particles moving through the lattice. However the electron is *not* in free space, the lattice affects its behaviour. We can account for this difference by introducing a modified carrier mass m_n , where we find that usually $m_p < m_n < m_e$ (free). Strictly speaking m_n depends on the energy of the electron (i.e. position within the conduction band). However, we will assume that the electrons are all near the bottom of the conduction band so we can ignore this effect. This effective mass is a good way to hide many of the complications of the lattice structure.

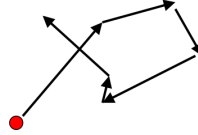
Charge transport in the valence band is also a result of electron motion. However, it is harder for valence band electrons to move around, so we expect a larger effective mass for electrons in the valence band. Thus, m_p is the effective mass of the positive charge carriers (or the effective mass of a hole).

Brownian motion

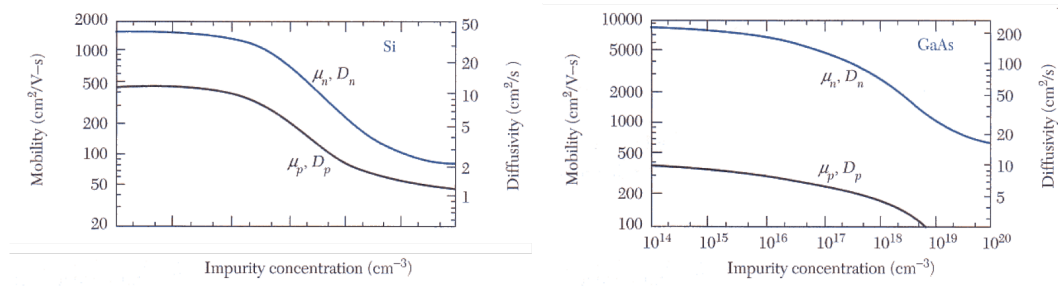
Free particles inside a semiconductor undergo random thermal motion at room temperature, known as Brownian motion. The kinetic energy is $E_K = \frac{1}{2} m_n v_{\text{th}}^2 = \frac{3}{2} k T$ leading to the "root-mean-squared"

speed of $v_{th} = \sqrt{3kT/m_n}$ for the electrons ($v_{th} \approx 10^5$ m/s in Si at 300K). This movement is not in one direction though, it is random; the electrons scatter off each other, impurities in the lattice or even thermal vibrations of the atoms. There is no mean distance travelled, i.e. thermal carrier motion produces to macroscopic current.

The average time between scattering events is τ_c , and so the average distance travelled, termed the mean free path, is $l_c = v_{th} \tau_c$. As an estimate, $\tau \sim 1$ ps and $l \sim 10^{-5}$ cm.



If we include an electric field ϵ there will be some net movement of the electrons, each electron will experience a force $F = -e\epsilon$ and will be accelerated in between each collisions. During this time the momentum gained is $F \tau_c = m_n v_n$. The average drift velocity of electrons is thus $v_n = -\frac{e \tau_c}{m_n} \epsilon = -\mu_n \epsilon$, where $\mu_n = \frac{e \tau_c}{m_n}$ is the electron mobility. Thus the electrons drift against the electric field with a velocity that is proportional to the strength of the field. Similarly for holes we have $v_p = \mu_p \epsilon$, where $\mu_p = \frac{e \tau_c}{m_p}$ is the hole mobility. p carriers are much less mobile than n carriers; atoms are much heavier than electrons.



The mobilities μ_n and μ_p depend on both the temperature and the level of doping; they are measured experimentally.

Lattice scattering: The carrier “collides” with vibration in the lattice. These vibrations increase with temperature decreasing the mobility as $\mu_{lattice} \propto T^{-3/2}$.

Impurity scattering: The carrier travels past an impurity in the lattice and is deflected. At higher temperature the carrier spends less time near the impurities increasing the mobility as $\mu_{impurity} \propto T^{3/2}$.

The total mobility is the found by summing the frequency of collisions, i.e. $f_{total} = f_{lattice} + f_{impurity}$ and so $1/\mu_{total} = 1/\mu_{lattice} + 1/\mu_{impurity}$.

Drift current

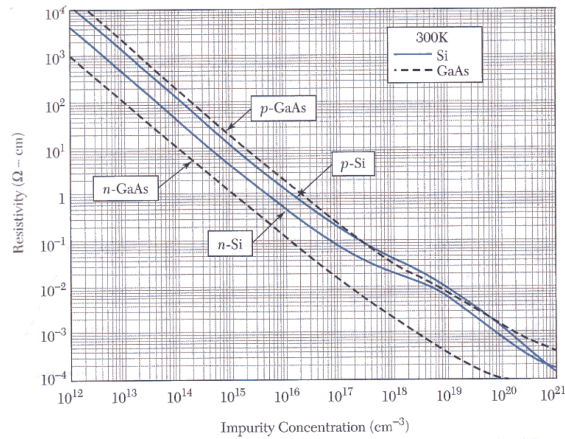
But we actually want to know the current due to a voltage applied across the semiconductor.

The current I passing through cross-sectional area A is $J = I/A = -e n v_n$ (i.e. the current density), with drift velocity $v_n = -\mu_n \epsilon$. This gives us drift current for electrons of $J_{n,drift} = n \mu_n e \epsilon$ and similarly for holes of $J_{p,drift} = p \mu_p e \epsilon$. The total drift current is the sum of the currents caused by the electrons and holes:

$$J_{drift} = J_{p,drift} + J_{n,drift} = e (\mu_p p + \mu_n n) \epsilon = \sigma \epsilon.$$

This is just Ohm's Law $J = \sigma \epsilon$, where $\sigma = e (\mu_p p + \mu_n n)$ is the conductivity. The resistivity $\rho = 1/\sigma$ is thus $\rho = 1/e (\mu_p p + \mu_n n)$ and the resistance $R = L/A \sigma$ is $R = L/A e (\mu_p p + \mu_n n)$. In p-type semiconductors we can neglect the contribution due to the electrons, similarly in n-type semiconductors we can

neglect the contribution due to holes.



Diffusion current

If there is an uneven distribution of free electrons in the semiconductor material, then those carriers will tend to move apart over time. The flux of electrons is given by $F_n = -D_n \frac{dn}{dx}$, where $D_n = v_n l_c$ is called the diffusion constant and the minus sign means electrons flow out of areas with high electron density. These fluxes produce diffusion currents $J_{n,diff} = -e F_n = e D_n \frac{dn}{dx}$ and $J_{p,diff} = e F_p = -e D_p \frac{dp}{dx}$.

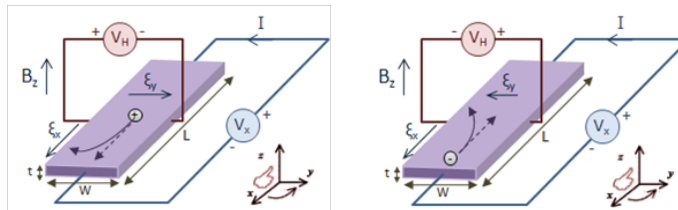
The total electron and hole currents in the semiconductor material are thus $J_n = J_{n,drift} + J_{n,diff}$ and $J_p = J_{p,drift} + J_{p,diff}$, and the total current is $J = J_n + J_p$.

The drift and diffusion currents are characterised by the mobilities μ and the diffusion constant D . These quantities are related by the Einstein relation:

$$\frac{D_n}{\mu_n} = \frac{D_p}{\mu_p} = \frac{kT}{e}$$

Hall effect and mobility

Carrier mobility is most commonly measured using the Hall effect. Consider a semiconductor of length L , width W and height t with a voltage V applied along its length producing current, and magnetic field B applied perpendicular to the current.



The moving charges will experience a force $\underline{F} = q \underline{v} \times \underline{B}$ (Lorentz force) producing an electric field ϵ_H across the width of the material. Electrons and holes end up moving the same direction ($-y$), which means the direction of the electric field will depend on whether the semiconductor is p-type or n-type. Intrinsic semiconductors will not produce an electric field since there is an equal number of holes and electrons.

In a p-type semiconductor the force on an electron in the y direction (width) is given by: $F_y = -e(-\epsilon_H + | \underline{v} \times \underline{B} |)$. In equilibrium we will have $F_y = 0$ and so $\epsilon_H = v_{drift} B$. Now in the x direction (length) we have $J = e p v_{drift}$. Eliminating v_{drift} gives us $\epsilon_H = JB / e p = R_{Hp} JB$ where $R_{Hp} = 1 / e p$ is called the Hall coefficient for holes. Similarly the Hall coefficient for electrons is $R_{Hn} = -1 / e n$.

We can measure these coefficients; $R_H = \varepsilon_H / JB = \frac{V_H W}{B I W t} = V_H t / I B$, where V_H is the voltage across the width of the material. This is very useful, since $R_{Hp} = 1 / e p$ we have $p = 1 / e R_{Hp} \approx N_a$, and similarly since $R_{Hn} = -1 / e n$ then $n = -1 / e R_{Hn} \approx N_d$. We can measure therefore measure dopant density! a very well controlled setup can measure densities down to $\sim 10^{12}$ atoms/cm³, i.e. 1 in 10^{10} atoms!

The mobilities and diffusion constants can then be calculated by measuring the resistance. $R = L / W t \sigma = L / W t \mu_p e p = L R_H / W t \mu_p$. We can then get the diffusion coefficient from the Einstein relations.

Direct and Indirect semiconductors

A direct semiconductor (i.e. GaAs) has the minimum energy of the conduction band at the same momentum as the valence band maximum energy. This allows free electrons to recombine with holes easily and produce photons. These photons will have energy equal to the band gap energy. This makes direct semiconductors good light emitting diodes.

Indirect semiconductors (i.e. Si) don't have the momentums coincide, it is more difficult then for electrons to drop down and recombine with holes as this requires a change in momentum. As a result indirect semiconductors make poor LEDs.

