

2.11. Semiconductor thermodynamics

Thermodynamics can be used to explain some characteristics of semiconductors and semiconductor devices, which cannot readily be explained based on the transport of single particles. One example is the fact that the Fermi energy is located within the energy gap where there are no energy levels and therefore also no electrons or holes. This is because the Fermi energy describes the energy of the particles in the distribution and the properties of the distribution can be markedly different from that of an individual particle. Thermodynamics can also be used to gain a completely different perspective. This section is therefore a worthwhile one to study as one can gain further insight into the field of semiconductors. However, it is not required to understand the following chapters.

2.11.1. Thermal equilibrium

A system is in thermal equilibrium if detailed balance is obtained. Detailed balance implies that every process in the system is exactly balanced by its inverse process. As a result, there is no net effect on the system.

This definition implies that in thermal equilibrium no energy (heat, work or particle energy) is exchanged between the parts within the system and between the system and the environment. Thermal equilibrium is obtained by isolating a system from its environment, removing any internal sources of energy, and waiting for a long enough time until the system does not change any more.

The concept of thermal equilibrium is of interest since a variety of thermodynamic results assume that the system under consideration is in thermal equilibrium. Few systems of interest rigorously satisfy this condition so that we often apply the thermodynamical results to systems, which are "close" to thermal equilibrium. Agreement between theories based on this assumption and experiments justifies this approach.

2.11.2. Thermodynamic identity

The thermodynamic identity simply states that adding heat, work or particles can cause a change in energy. Mathematically this is expressed by:

$$dU = dQ + dW + \mu dN \quad (2.11.1)$$

where U is the energy, Q is the heat and W is the work. μ is the energy added to a system when adding one particle without adding either heat or work. The amount of exchanged heat depends on the temperature, T , and the entropy, S , while the amount of work delivered to a system depends on the pressure, p , and the volume, V , or:

$$dQ = TdS \quad (2.11.2)$$

and

$$dW = -pdV \quad (2.11.3)$$

yielding:

$$dU = TdS - pdV + \mu dN \quad (2.11.4)$$

2.11.3. The Fermi energy

The Fermi energy, E_F , is the energy associated with a particle, which is in thermal equilibrium with the system of interest. The energy is strictly associated with the particle and does not consist even in part of heat or work. This same quantity is called the electro-chemical potential, μ , in most thermodynamics texts.

2.11.4. Example: an ideal electron gas

To illustrate the difference between the average energy of particles in a system and the Fermi energy, we now consider an ideal electron gas. The term ideal refers to the fact that the gas obeys the ideal gas law. To be "ideal" the gas must consist of particles, which do not interact with each other.

The total energy of the non-degenerate electron gas containing N particles equals:

$$U = \frac{3}{2} NkT + NE_c \quad (2.11.5)$$

as each non-relativistic electron has a thermal energy of $kT/2$ for each degree of freedom in addition to its minimum energy, E_c . The product of the pressure and volume is given by the ideal gas law:

$$pV = NkT \quad (2.11.6)$$

While the Fermi energy is given by equation (2.6.14):

$$E_F = E_c + kT \ln \frac{n}{N_c} \quad (2.11.7)$$

The thermodynamic identity can now be used to find the entropy from:

$$S = \frac{U - \mu N + pV}{T} \quad (2.11.8)$$

yielding:

$$S = \frac{5}{2} Nk - Nk \ln \frac{n}{N_c} \quad (2.11.9)$$

This relation can be visualized on an energy band diagram when one considers the energy, work and entropy per electron and compares it to the electro-chemical potential as shown in Figure 2.11.1.

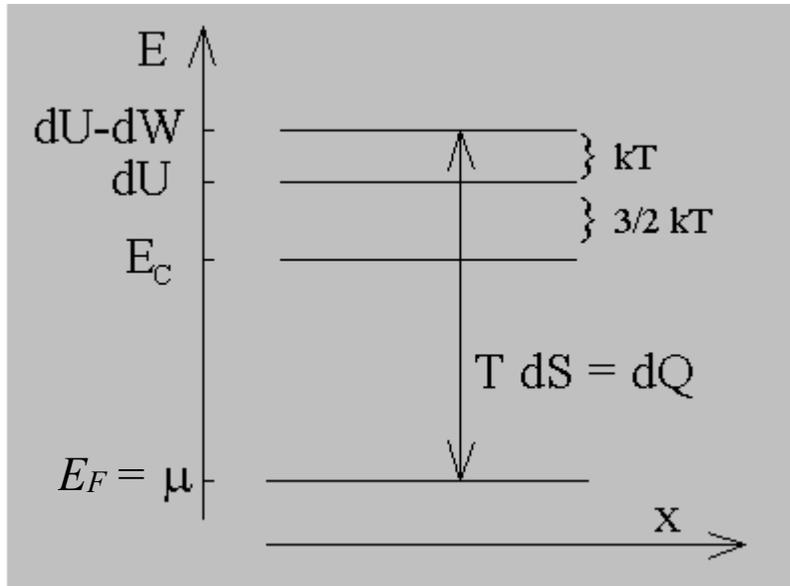


Figure 2.11.1 Energy, work and heat per electron in an ideal electron gas visualized on an energy band diagram.

The distinction between the energy and the electro-chemical potential also leads to the following observations: Adding more electrons to an ideal electron gas with an energy which equals the average energy of the electrons in the gas increases both the particle energy and the entropy as heat is added in addition to particles. On the other hand, when bringing in electrons through an electrical contact whose voltage equals the Fermi energy (in electron volts) one does not add heat and the energy increase equals the Fermi energy times the number of electrons added.

Therefore, when analyzing the behavior of electrons and holes on an energy band diagram, one should be aware of the fact that the total energy of an electron is given by its position on the diagram, but that the particle energy is given by the Fermi energy. The difference is the heat minus the work per electron or $dQ - dW = T dS + p dV$.

2.11.5. Quasi-Fermi energies

Quasi-Fermi energies are introduced when the electrons and holes are clearly not in thermal equilibrium with each other. This occurs when an external voltage is applied to the device of interest. The quasi-Fermi energies are introduced based on the notion that even though the electrons and holes are not in thermal equilibrium with each other, they still are in thermal equilibrium with themselves and can still be described by a Fermi energy which is now different for the electrons and the holes. These Fermi energies are referred to as the electron and hole quasi-Fermi energies, F_n and F_p . For non-degenerate densities one can still relate the electron and hole densities to the two quasi-Fermi energies by the following equations:

$$n = n_i \exp \frac{F_n - E_i}{kT} = N_c \exp \frac{F_n - E_c}{kT} \quad (2.11.10)$$

$$p = n_i \exp \frac{E_i - F_p}{kT} = N_v \exp \frac{E_v - F_n}{kT} \quad (2.11.11)$$

2.11.6. Energy loss in recombination processes

The energy loss in a recombination process equals the difference between the electron and hole quasi-Fermi energies as the energy loss is only due to the energy of the particles, which are lost:

$$\Delta U = F_n - F_p \quad (2.11.12)$$

No heat or work is removed from the system, just the energy associated with the particles. The energy lost in the recombination process can be converted in heat or light depending on the details of the process.

2.11.7. Thermo-electric effects in semiconductors

The temperature dependence of the current in a semiconductor can be included by generalizing the drift-diffusion current equation. The proportionality constant between the current density and the temperature gradient is the product of the conductivity, σ , and the thermo-electric power, \mathcal{P} .

The derivation starts by generalizing the diffusion current to include a possible variation of the diffusion constant with position, yielding:

$$J_n = q\mu_n n \mathcal{E} + q \frac{d(D_n n)}{dx} \quad (2.11.13)$$

If the semiconductor is non-degenerate the electron density can be related to the effective density of states and the difference between the Fermi energy and the conduction band edge (equation 2.6.12):

$$n = N_c \exp \frac{E_F - E_c}{kT} \quad (2.11.14)$$

yielding:

$$J_n = \mu_n n \left(\frac{dE_c}{dx} + k \frac{dT}{dx} + \frac{kT}{\mu_n} \frac{d\mu_n}{dx} + \frac{kT}{N_c} \frac{dN_c}{dx} + kT \frac{d\left(\frac{E_F - E_c}{kT}\right)}{dx} \right) \quad (2.11.15)$$

For the case where the material properties do not change with position, all the spatial variations except for the gradient of the Fermi energy are caused by a temperature variation. We postulate

that the current can be written in the following form:

$$J_n = \mu_n n \left(\frac{dE_F}{dx} - q P_n \frac{dT}{dx} \right) \quad (2.11.16)$$

and \mathcal{P}_n is the thermo-electric power in Volt/Kelvin. From both equations one then obtains the thermo-electric power:

$$\mathcal{P}_n = -\frac{k}{q} \left(\frac{5}{2} + \frac{T}{\mu_n} \frac{d\mu_n}{dT} + \ln \frac{N_c}{n} \right) \quad (2.11.17)$$

If the temperature dependence of the mobility can be expressed as a simple power law:

$$\mu_n \propto T^{-s} \quad (2.11.18)$$

the thermo-electric power becomes:

$$\mathcal{P}_n = -\frac{k}{q} \left(\frac{5}{2} - s + \ln \frac{N_c}{n} \right) \quad (2.11.19)$$

for n -type material and similarly for p -type material:

$$\mathcal{P}_p = \frac{k}{q} \left(\frac{5}{2} - s + \ln \frac{N_v}{p} \right) \quad (2.11.20)$$

The Peltier coefficient, Π , is related to the thermo-electric power by:

$$\Pi = \mathcal{P}T \quad (2.11.21)$$

If electrons and holes are present in the semiconductor one has to include the effect of both when calculating the Peltier coefficient:

$$\Pi_{total} = \frac{\sigma_n \Pi_n + \sigma_p \Pi_p}{\sigma_n + \sigma_p} \quad (2.11.22)$$

The resulting Peltier coefficient as a function of temperature for silicon is shown in the figure below:

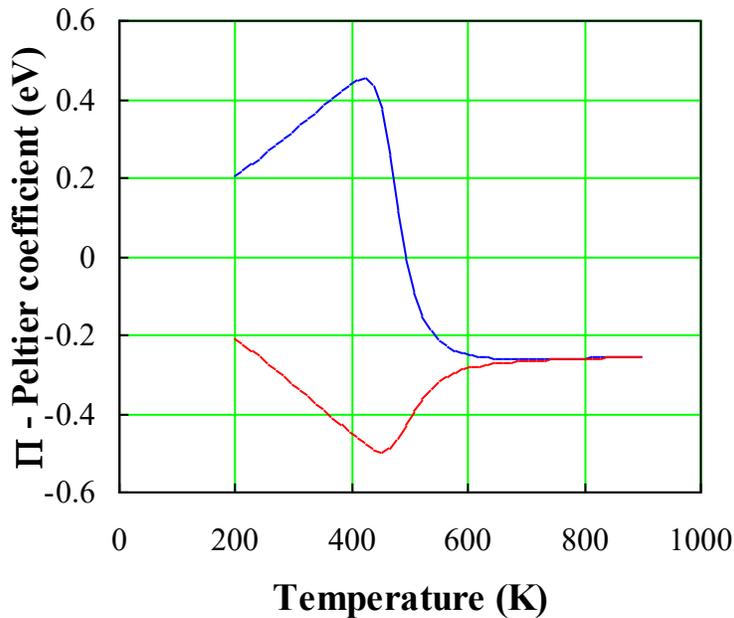


Figure 2.11.2 Peltier coefficient for *p*-type (top curve) and *n*-type (bottom curve) silicon as a function of temperature. The doping density equals 10^{14} cm^{-3} . 

The Peltier coefficient is positive for *p*-type silicon and negative for *n*-type silicon at low temperature. The semiconductor becomes intrinsic at high temperature. Given that the mobility of electrons is higher than that of holes, the Peltier coefficient of intrinsic silicon is negative.

2.11.8. The Thermo-electric cooler

Thermo-electric effects in semiconductors cause carriers to flow due to temperature gradients but also cause temperature gradients when an electrical current is applied. The thermo-electric cooler is a practical device in which a current is applied to a semiconductor causing a temperature reduction and cooling.

Such thermo-electric cooler consists of multiple semiconductor elements, which are connected in series as shown in Figure 2.11.3. The doping density in the semiconductor elements is graded with the highest density at the high temperature end and the low density at the low temperature end. An electrical current is applied to the series connection of these elements. Alternating *n*-type and *p*-type elements are used to ensure that the carriers flow in the same direction. While in principle a single piece of semiconducting material could have been used, the series connection is typically chosen to avoid the high current requirement of the single element.

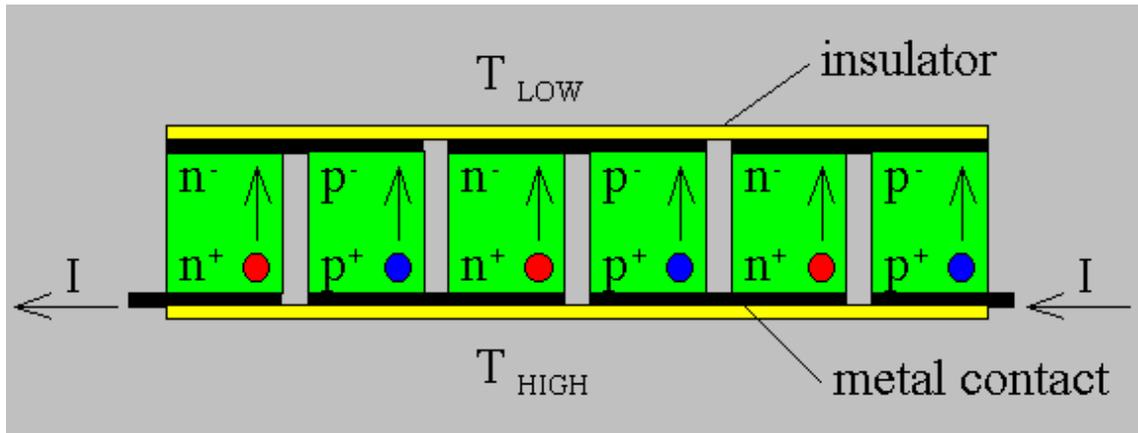


Figure 2.11.3 Cross-section of a thermo-electric cooler showing the alternating n -type and p -type sections described in the text.

The operation of the thermo-electric cooler is similar to that of a Joule-Thomson refrigerator in that an expansion of a gas is used to cool it down. While heating of a gas can be obtained by compressing it as is the case in a bicycle pump (where some of the heating is due to friction), a gas can also be cooled by expanding it into a larger volume. This process is most efficient if no heat is exchanged with the environment. This is also referred to as an isentropic expansion since the entropy remains constant if no heat is exchanged.

The gas in a thermo-electric cooler is the electron or hole gas. As a current is applied such that carriers flow from the high density (high T) region to the low-density (low T) region, one can imagine that the volume around a fixed number of carriers must increase as the carriers move towards the lower doped region. A possible energy band diagram is shown below:

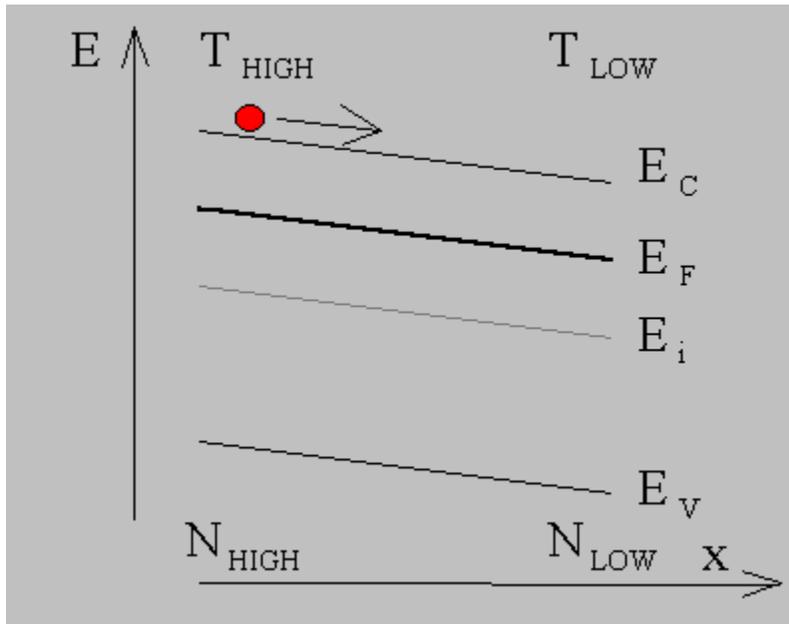


Figure 2.11.4 Energy band diagram of an *n*-type element of the thermo electric cooler of Figure 2.11.3

At constant temperature and in thermal equilibrium there is no current as the diffusion current is balanced by the drift current associated with the built-in electric field caused by the graded doping density. As a current is applied to the semiconductor the built-in field is reduced so that the carriers diffuse from the high to low doping density. This causes a temperature reduction on the low-doped side, which continues until the entropy is constant throughout the semiconductor. Since the entropy per electron equals the distance between the conduction band edge and the Fermi energy plus $5/2 kT$ one finds that the conduction band edge is almost parallel to the Fermi energy.

An ideal isentropic expansion is typically not obtained due to the Joule heating caused by the applied current and the thermal losses due to the thermal conductivity of the material. The need to remove heat at the low temperature further increases the lowest achievable temperature.

2.11.9. The "hot-probe" experiment

The "hot-probe" experiment provides a very simple way to distinguish between *n*-type and *p*-type semiconductors using a soldering iron and a standard multi-meter.

The experiment is performed by contacting a semiconductor wafer with a "hot" probe such as a heated soldering iron and a "cold" probe. Both probes are wired to a sensitive current meter. The hot probe is connected to the positive terminal of the meter while the cold probe is connected to the negative terminal. The experimental set-up is shown in Figure 2.11.5:

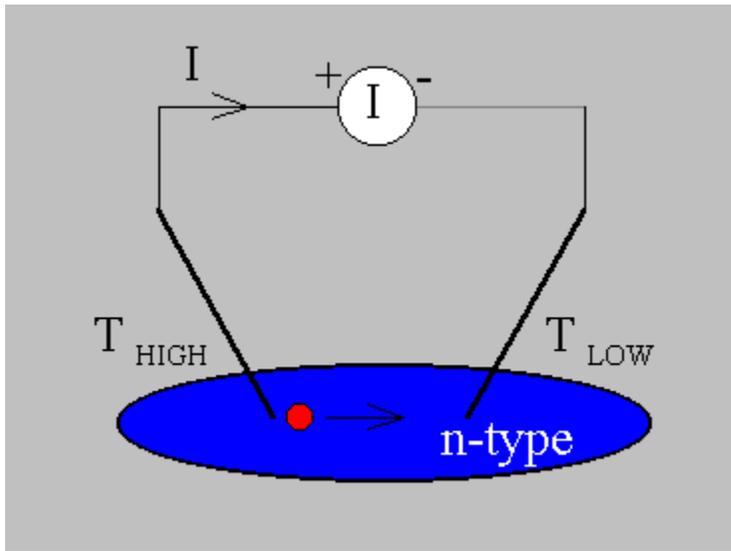


Figure 2.11.5 Experimental set-up of the "hot-probe" experiment.

When applying the probes to *n*-type material one obtains a positive current reading on the meter, while *p*-type material yields a negative current.

A simple explanation for this experiment is that the carriers move within the semiconductor from the hot probe to the cold probe. While diffusion seems to be a plausible mechanism to cause the carrier flow it is actually not the most important mechanism since the material is uniformly doped. However, as will be discussed below there is a substantial electric field in the semiconductor so that the drift current dominates the total current.

Starting from the assumption that the current meter has zero resistance, and ignoring the (small) thermoelectric effect in the metal wires one can justify that the Fermi energy does not vary throughout the material. A possible corresponding energy band diagram is shown below:

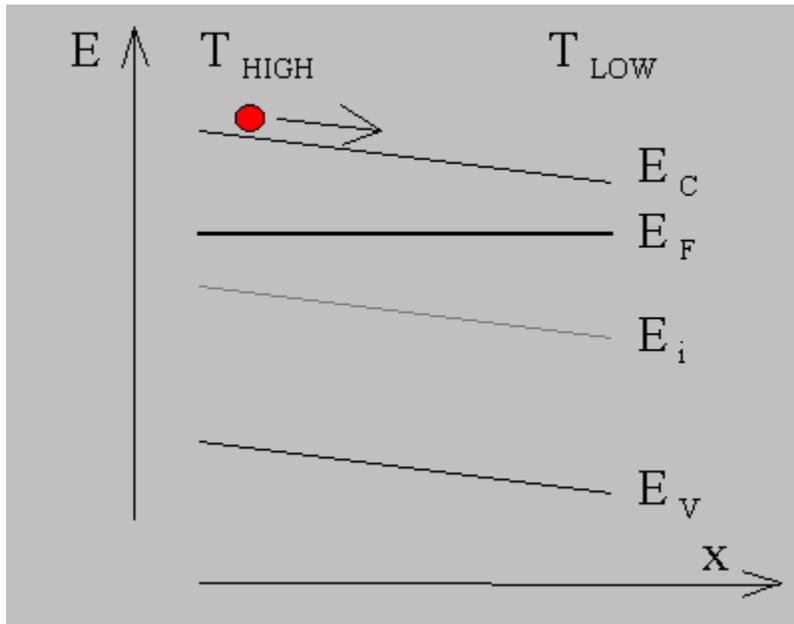


Figure 2.11.6 Energy band diagram corresponding to the "hot-probe" experiment illustrated by Figure 2.11.5.

This energy band diagram illustrates the specific case in which the temperature variation causes a linear change of the conduction band energy as measured relative to the Fermi energy, and also illustrates the trend in the general case. As the effective density of states decreases with decreasing temperature, one finds that the conduction band energy decreases with decreasing temperature yielding an electric field, which causes the electrons to flow from the high to the low temperature. The same reasoning reveals that holes in a p-type semiconductor will also flow from the higher to the lower temperature.

The current can be calculated from the general expression:

$$J_n = \mu_n n \left(\frac{dE_c}{dx} - q\mathcal{P} \frac{dT}{dx} \right) \quad (2.11.23)$$

where

$$q\mathcal{P}_n = -k \left(\frac{5}{2} + \frac{T}{\mu_n} \frac{d\mu_n}{dx} + \ln \frac{N_c}{n} \right) \quad (2.11.24)$$

The current will therefore increase with doping and with the applied temperature gradient as long as the semiconductor does not become degenerate or intrinsic within the applied temperature range.