

Lecture 7: Extrinsic semiconductors - Fermi level

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1 Dopant materials

Typical doping concentrations in semiconductors are in ppm (10^{-6}) and ppb (10^{-9}). This small addition of ‘impurities’ can cause orders of magnitude increase in conductivity. The impurity has to be of the right kind. For Si, n -type impurities are P, As, and Sb while p -type impurities are B, Al, Ga, and In. These form energy states close to the conduction and valence band and the ionization energies are a few tens of meV . Ge lies the same group IV as Si so that these elements are also used as impurities for Ge. The ionization energy data n -type impurities for Si and Ge are summarized in table 1. The ionization energy data for p -type impurities for Si and Ge is summarized in table 2. The dopant ionization energies for Ge are lower than Si. Ge has a lower band gap (0.67 eV) compared to Si (1.10 eV). Also, the

Table 1: Ionization energies in meV for n -type impurities for Si and Ge. Typical values are close to room temperature thermal energy.

Material	P	As	Sb
Si	45	54	39
Ge	12	12.7	9.6

Table 2: Ionization energies in meV for p -type impurities. Typical values are comparable to room temperature thermal energy.

Material	B	Al	Ga	In
Si	45	57	65	157
Ge	10.4	10.2	10.8	11.2

relative permittivity for Ge is higher ($\epsilon_r = 16$) compared to Si ($\epsilon_r = 11.9$) and the effective masses for electron and holes are also different. The ionization energies for dopants in Si and Ge are represented in the band diagram schematically in figure 1.

GaAs is a commonly used compound semiconductor. It is a III-V semiconductor with predominantly covalent bonding, with some ionic character. Doping is done by substitution and there are a number of possibilities for GaAs, as seen from the periodic table shown in figure 2. For n type doping As (group V) can be replaced by elements from group VI. These have an extra electron and can act as *donors*. Similarly, for p type doping Ga (group III) can be replaced by group II elements, which act as *acceptors*. Si in group IV can act as both donor and acceptor, depending on where the Si atom is substituted. This is called **amphoteric doping**. It is hard to control the location of Si in the lattice to get a specific type of doping. Ionization energies of some common dopants in GaAs are shown in figure 3. Donors are located close to the conduction band and acceptors close to the valence band. Si impurity levels can be close to either, depending on whether it is substituted for Ga or As.

Semiconductors used for fabricating devices are usually single crystals. This is because polycrystalline materials have defect states due to presence of grain boundaries. These defects states are located in the band gap and can modify the conductivity. There are two types of defect states

1. *Shallow states* - these are located close the band edges and can act as sources of electrons and holes. Common example is the dopants.
2. *Deep states* - these are located close to the center of the band gap, see figures 1 and 3 for examples of both. Deep states can act as traps for charge carriers and reduce the conductivity.

Film growth techniques can also introduce defects in a material, which can affect the conductivity. ZnO is a wide band gap semiconductor with E_g of 3.4 eV . Thin films of ZnO growth by conventional vapor deposition or solution growth techniques are n -type because of the presence of Zn interstitials and O vacancies. Thus, it is very hard to get p -type ZnO because of the presence of these defects.

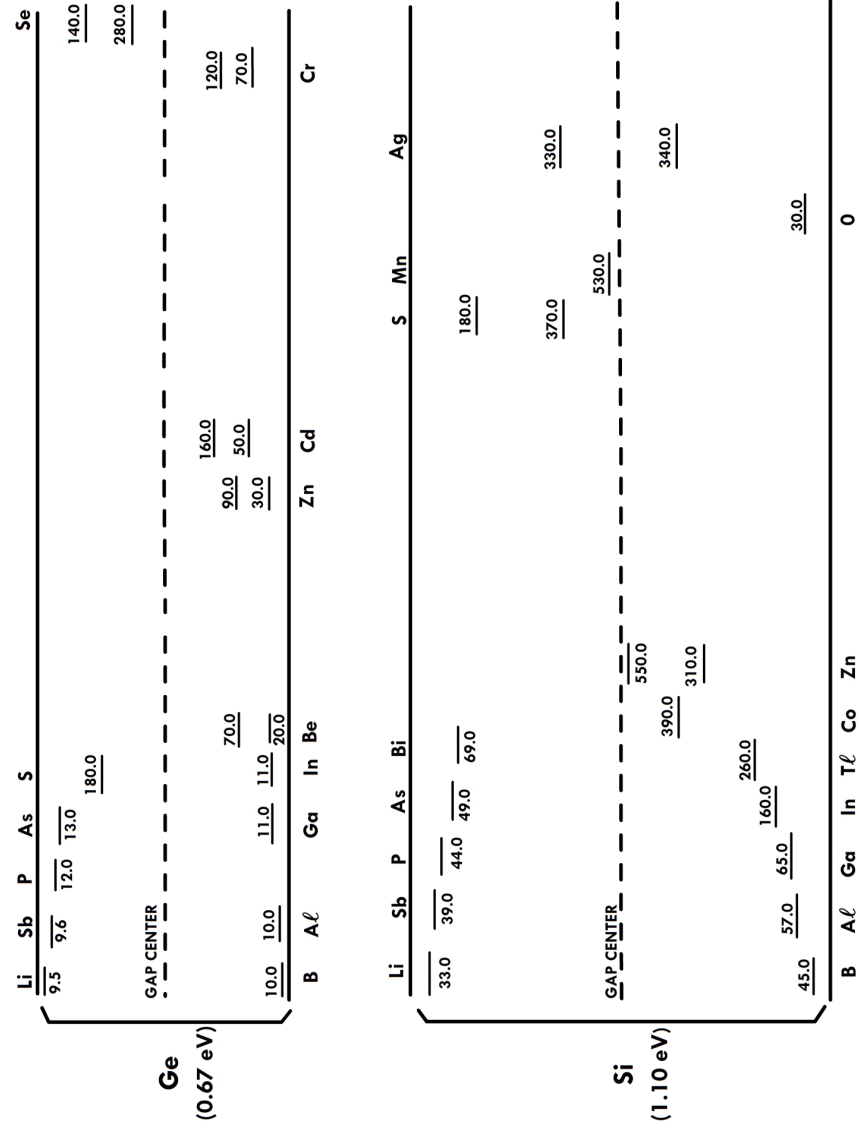


Figure 1: Ionization energies of dopants in Si and Ge. The gap center represents approximately the intrinsic Fermi level. Dopants located close to the band edges can be easily ionized and are called shallow states while those located closer to the gap center are called deep states. Adapted from *Physics of semiconductor devices* - S.M. Sze.

	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	
	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	
12 IIB 2B	13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	
30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	
48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	
80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	

Figure 2: Portion of the periodic table around Ga and As (groups III and V). Elements from groups II - VI, can act as dopants. Source <http://chemistry.about.com/od/periodictable/ss/How-To-Use-A-Periodic-Table.htm>

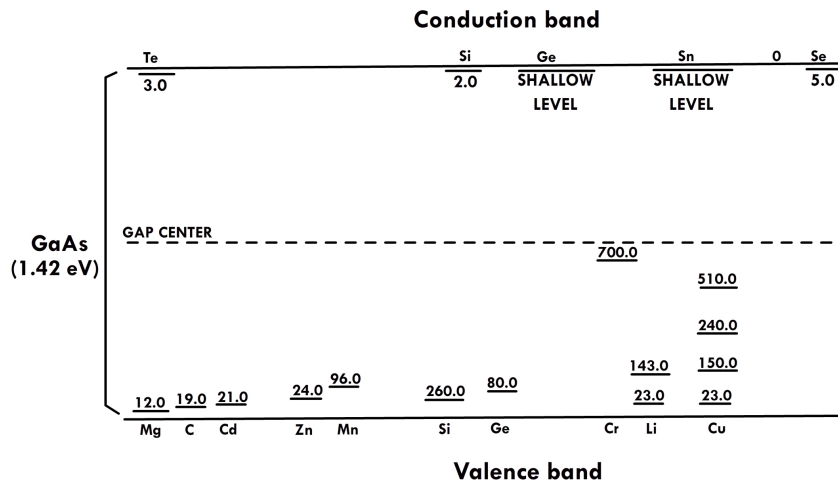


Figure 3: Ionization energies of dopants in GaAs. Group II elements act as acceptors and group VI elements act as donors. Si can substitute in either Ga or As site, though Si as a *n*-type dopant (Ga substitution) has a lower energy. Adapted from *Physics of semiconductor devices* - S.M. Sze.

2 E_F in extrinsic semiconductors

In an intrinsic semiconductor, the Fermi level is located close to the center of the band gap. Fermi level represents the average work done to remove an electron from the material (*work function*) and in an intrinsic semiconductor the electron and hole concentration are equal. In an extrinsic semiconductor, with the dopants fully ionized, there is an imbalance in the electron and hole concentration. This in turn is reflected in the Fermi level position being shifted from the center of the band gap towards either the conduction band or valence band depending on the type of dopant.

In an n -type semiconductor the electron concentration (n) is related to the position of the Fermi level (E_{Fn}) by

$$n = N_c \exp\left[-\frac{(E_c - E_{Fn})}{k_B T}\right] \quad (1)$$

Equation 1 can be modified for an intrinsic semiconductor, where the Fermi level is close to center of the band gap (E_{Fi}).

$$n_i = N_c \exp\left[-\frac{(E_c - E_{Fi})}{k_B T}\right] \quad (2)$$

Manipulating equations 1 and 2, gives the Fermi level position in the n -type extrinsic semiconductor with respect to the intrinsic Fermi level

$$\boxed{E_{Fn} - E_{Fi} = k_B T \ln\left(\frac{n}{n_i}\right)} \quad (3)$$

For an n -type semiconductor with N_d donors which are fully ionized, $n = N_d$ when $N_d \gg n_i$, so that the Fermi level is shifted above the center of the band gap, closer to the conduction band. For Si with $N_d = 10^{15} \text{ cm}^{-3}$ and $n_i = 10^{10} \text{ cm}^{-3}$, using equation 3, E_{Fn} is 0.25 eV above E_{Fi} .

A similar argument can be used for p -type semiconductors, where the hole concentration is higher than the electron concentration. The Fermi level position (E_{Fp}) is given by

$$\boxed{E_{Fp} - E_{Fi} = -k_B T \ln\left(\frac{p}{n_i}\right)} \quad (4)$$

For a p -type semiconductor with N_a donors which are fully ionized, $p = N_a$ when $N_a \gg n_i$, so that the Fermi level is shifted below the center of the band gap, closer to the valence band. The Fermi level position with carrier type and concentration for Si is summarized in figure 4.

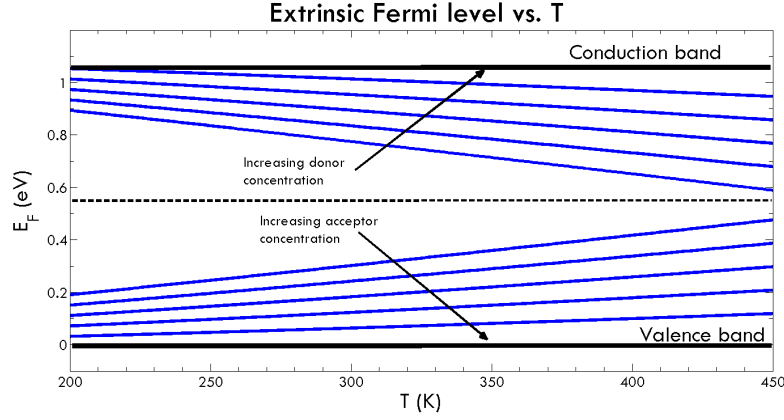


Figure 4: E_F position in Si, with doping type and concentration. The donor and acceptor concentration was varied from 10^{14} to 10^{18} cm^{-3} in steps of 10 and the temperature was varied from 200 to 450 K. The dotted line in the center represents E_{Fi} , which is approximately $E_g/2$ at room temperature. For the calculation the variation of E_{Fi} with temperature was also considered. The plot was generated using MATLAB.

3 Temperature dependence of carrier concentration

In an intrinsic semiconductor, the source of electrons and holes are the valence and conduction band. The carrier concentration depends exponentially on the band gap, given by

$$n_i = \sqrt{N_c N_v} \exp\left(-\frac{E_g}{2k_B T}\right) \quad (5)$$

A plot of n_i vs. T is shown in figure 5. The plot is approximately a straight line, with the slope depending on the band gap. In an extrinsic n type-semiconductor, there are two sources for the electrons (same arguments are valid for p -type semiconductors)

1. The *donor energy levels* close to conduction band. This has an ionization energy $\approx \text{meV}$.
2. The *valence band* of the semiconductor, with ionization energy $\approx \text{eV}$.

Because of the vast difference in the ionization energies for the two sources they operate in different temperature regimes, so that it is possible to understand the temperature behavior of the extrinsic semiconductors by dividing into different regimes

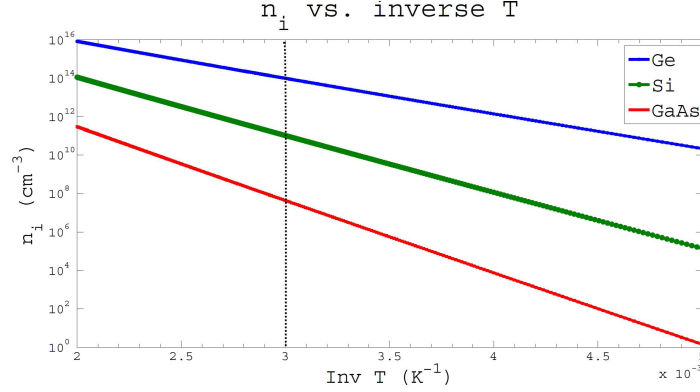


Figure 5: Carrier concentration vs. inverse temperature for three intrinsic semiconductors, Ge, Si, and GaAs. There is a single line with a constant slope, given by the band gap of the semiconductor. The plot was generated using MATLAB and the dotted line represents room temperature.

3.1 Low temperature regime ($T < T_s$)

At absolute zero there are no ionized carriers. Valence band is full and the donor level is full and conduction band is empty. As temperature is increased, electrons are excited from the valence band and the donor level to the conduction band. But since the valence band ionization energy is of the order of eV , at low temperature the number of electrons excited from it are negligible compared to the electrons from the donor level. So the valence band contribution can be ignored and only electrons from the donor level are excited to the CB. This regime is called **ionization regime** and extends up to a temperature until all the donor electrons are ionized. The electron concentration (in CB), in the ionization regime, is given by

$$n = \left(\frac{1}{2} N_c N_d \right) \exp\left(-\frac{\Delta E}{2k_B T}\right) \quad (6)$$

ΔE is the ionization energy of the donor level i.e. the energy difference between the donor level and the conduction band. The $\frac{1}{2}$ enters equation 6 because the donor levels are localized and can accommodate only one electron instead of two like a regular energy state.

It is possible to define a *saturation temperature* (T_s) based on equation 6. The saturation temperature is defined as the temperature where $n = 0.9N_d$ where N_d is the donor concentration. This corresponds to 90% ionization. Consider Si with N_d of 10^{15} cm^{-3} . Take N_c to be independent of temperature and equal to $2.8 \times 10^{19} \text{ cm}^{-3}$. For As, ΔE is 0.054 eV. Then, using

equation 6 the saturation temperature, T_s , is 32 K. The actual value (taking temperature dependence of N_c) is around 60 K, which is still much lower than room temperature. This means that the donor atoms (and similarly the acceptor atoms) are fully ionized at room temperature so that we are justified in equating the electron concentration (hole concentration) to the donor concentration (acceptor concentration).

3.2 Medium temperature regime ($T_s < T < T_i$)

Above the saturation temperature the donor levels are completely ionized so that $n = N_d$. As temperature keeps increasing there comes a temperature when the electrons from the valence band (intrinsic carriers) becomes comparable in concentration to N_d . This temperature is called the *intrinsic temperature*, T_i . Above this temperature the semiconductor behaves as intrinsic. T_i is defined as the temperature when $n = 1.1 N_d$. This corresponds to 110% ionization. Between T_s and T_i the majority carrier concentration changes from 90% to 110% N_d , so the variation in concentration is only 20% overall.

The intrinsic temperature for Si can be calculated using the equation for intrinsic semiconductors. When $n = 1.1 N_d$ the hole concentration, p , can be calculated using a charge balance equation.

$$n = p + N_d \quad (7)$$

So, $p = 0.1 N_d$. Using the law of mass action $n_i^2 = np$, the intrinsic carrier concentration is $0.33 N_d$. This corresponds to a temperature of 526 K, which is the intrinsic temperature.

Thus there is a temperature regime, from 60 K - 526 K, where the majority carrier concentration is nearly a constant. The majority carrier concentration vs. temperature is plotted in figure 6. There are 3 regions from the plot. A *ionization regime* at low temperature, a *saturation regime* where the electron concentration is nearly a constant, and a *intrinsic regime* where the semiconductor behaves like an intrinsic semiconductor. In Si, this saturation regime is around room temperature so that the carrier concentration is a constant and independent of temperature.

Thus doping in a semiconductor has 2 functions

1. It increases the conductivity by preferentially increasing either electron or hole concentration. The conductivity can be precisely tuned by controlling the type and amount of dopant.
2. The majority carrier concentration is a constant and temperature independent (near room temperature) so that small temperature variations

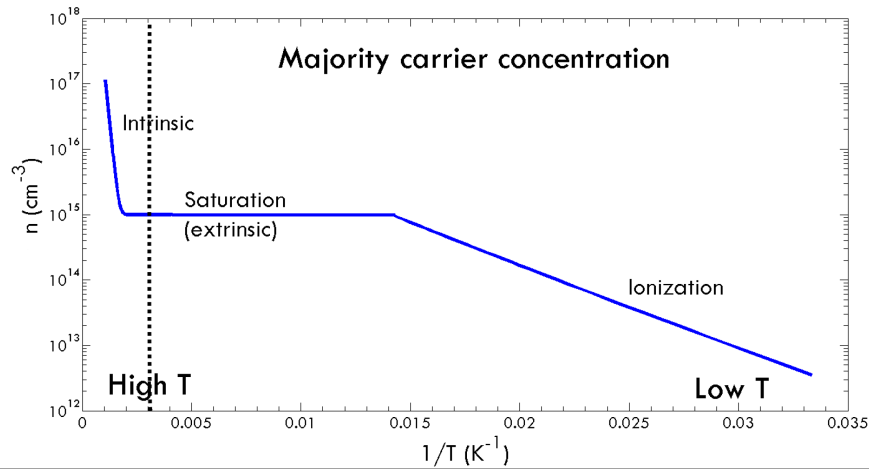


Figure 6: Majority carrier concentration vs. inverse temperature for an extrinsic semiconductor. In the ionization regime, donor atoms are partially ionized. Then in the saturation regime where donors are fully ionized and carrier concentration is a constant. Finally, at high temperatures there is the intrinsic regime where it behaves like an intrinsic semiconductor. The temperatures corresponding to these depend on the donor concentration. The plot was generated in MATLAB with a donor concentration of 10^{15} cm^{-3} . The vertical dotted line marks room temperature.

will not change the conductivity. Thus, electrical devices can be formed with very little variation in their electrical properties during normal operating temperatures.