Extrinsic Carrier Concentrations (due to doping)

For silicon and germanium (group IV elements), the crystal structure is that of diamond: each atom is bonded to four others via covalent bonding. If we deliberately introduce an impurity (another atom), the impurity may (depending on which atom it is) replace one of the silicon or germanium atoms in the lattice. This is **in contrast** to having the impurity atoms in the interstitial spaces.

If we **dope the group IV material** (Si or Ge) **with a Group V element** (such as P [phosphorus], As [arsenic], Sb [antimony]), then the doping atom can substitute for the regular group IV atom. But since it has an extra electron (group V has five valence electrons instead of the four that a group IV atom has), that extra electron is only weakly bound to the atom. [We show how weakly bound it is on the next page.] It has an energy level that is higher than the valence band, but still a little below that of the conduction band. If we are above a certain temperature (we'll see more about this on the page after next), the probability of exciting that electron up to the conduction band is very high since it is a lot closer to the conduction band than are the electrons in the valence band. Note that this energy level, called a **donor level**, is not part of the valence band! Thus if the temperature is high enough to excite the extra electron from its bound level up to the conduction band, we can **increase the conduction electrons while not adding any more holes**! This **will make the semiconductor an n-type material**: most of the electrical conductivity will be carried by the negative electrons.

If we **dope the group IV material** (Si or Ge) **with a Group III element** (such as B [boron], Al [aluminum], Ga [gallium], In [indium]), then the doping atom can again substitute for the regular group IV atom. But in this case the atom has one less electron. This causes a place (an energy level not in the regular band structure) that is a little higher than the valence band, but still well below that of the conduction band. This is called an **acceptor level**. If the temperature is high enough (again we will consider this on the page after next), we can have electrons in the valence band jump up to this acceptor level. Thus we can **increase the number of holes in the valence band without increasing the number of electrons in the conduction band**. This **will make the semiconductor a p-type material**: most of the electrical conductivity will be carried by the positive holes.

If we have a **compound semiconductor** (such as a III-V or II-VI), we can have a **deficit of one of the materials**. This will also cause a shift in the n and p values. This is called a **deficit semiconductor**.

Donor Impurities

These impurity atoms substitute for normal atoms. They are NOT in interstitial sites!
These impurity atoms **create donor energy levels** which are filled at T=0 but the electrons may jump up to the conduction band from these levels adding to the n at higher T's, but not adding to the p.

To get an idea of what energy levels these donor atoms provide, let's use the Bohr theory idea:

E_{total} = KE + PE = $\frac{1}{2}mv^2 + -ke^2/r$

(but m becomes m^*, and $k = 1/4\pi\varepsilon_o$ which becomes $1/4\pi\varepsilon = k^*$)

thus $E_{total} = \frac{1}{2}m^*v^2 - k^*e^2/r$ (1)

$\Sigma \mathbf{F} = m\mathbf{a}$ leads to $k^*e^2/r^2 = m^*v^2/r$ or re-writing $m^*v^2 = k^*e^2/r$ (2)

$L = m^*vr = \#\hbar$ (here # refers to a quantum number) (3)

(recall that L is angular momentum and h has units of angular momentum)

Multiplying both sides of (2) by m^*r^2 gives $m^{*2}v^2r^2 = m^*k^*e^2r$ (4)

And squaring (3) gives $m^{*2}v^2r^2 = \#^2\hbar^2$ (5).

Combining (4) and (5) gives: $r = \#^2\hbar^2/m^*k^*e^2$ (6).

Using (2) in (1) gives:

$E_{total} = \frac{1}{2}k^*e^2/r - k^*e^2/r$ or $E_{total} = -k^*e^2/2r$ (7).

Now using (6) in (7) gives:

$E_{total} = -k^*e^2/2[\#^2\hbar^2/m^*k^*e^2] = -m^*k^{*2}(e^2)^2/2\hbar^2\#^2$ (8).

The minus sign in (8) indicates that the electron is bound (not free). It is really a measure of how far below the conduction band the level is. Therefore, $E_{donor} = -E_{total\ from\ 8}$.

We can relate (6) and (8) to the hydrogen values:

$E_{donor} = (m^*/m)(k^*/k)^2 E_{Hy} = (m^*/m)(k^*/k)^2\ 13.6\ eV$, and

$r_{donor} = (m/m^*)(k/k^*)\, r_{Hy} = (m/m^*)(k/k^*)\ .053\ nm.$

See Table 4 in Chapter 8 of Kittel 6th ed. for $k^*/k = \varepsilon/\varepsilon_o$. (Note Kittel's ε is my $k/k^* = \varepsilon_o/\varepsilon$)
The values range from 5.5 to 17.88. If we use $m^* = m/10$ and $k^* = k/10$, then we get energy levels in the 10 meV range.

See Tables 5 & 6 in Chapter 8 of Kittel 6th ed. for E_{donor} and $E_{acceptor}$ ionization energies.
The values range from 9.6 to 57 meV.
Recall that the band gap energies for semiconductors are around 1 eV = 1,000 meV.

Note that the radius of the donor atoms should a lot larger than the radius of the hydrogen atom, and so these electrons should start to overlap at higher donor concentrations, and may even form energy bands at sufficiently high donor atom concentrations. We'll see (and use) this in later sections.

Thermal Ionization of Donors and Acceptors

According to the Boltzmann Distribution, the probability of having an energy, ε, is related to the energy and the temperature by:

$$\text{Prob}(E) = A\, e^{-E/kT} .$$

From the **law of mass action**, the probability of an electron jumping up from the valence band to the conduction band is (with $n = p = (np)^{1/2}$)

$$\mathbf{n_{intrinsic} = n_o e^{-Egap/2kT}} \quad \text{where} \quad n_o = 2[m_e^* k_B T/2\pi\hbar^2]^{3/2} .$$

Likewise, from a consideration of the statistics involved, the electron density from donor atoms is related to temperature **at low temperatures** (that is, for $E_{donor} \gg k_B T$): by the following:

$$\mathbf{n_{e\ from\ donor} = (n_o n_{donor\ atom})^{1/2} e^{-Edonor/2kT}} ,$$

where $n_{donor\ atom}$ is the donor atom density and n_o is defined above.
Note the similarity of this to the Law of Mass Action. Recall that only the electrons in the semiconductor near the top of the valence band will have a reasonable probability of jumping up while all of the electrons in the donor atoms will have a very good probability of jumping up.

At high temperature: $n_{e\ from\ donor} \approx n_{donor\ atoms}$. Actually, $n_e \approx \frac{1}{2} n_{donor\ atoms}$ since the probability of rising up and falling down will be about the same. Otherwise we would have a population inversion – more in the higher state than in the lower state. At this point we are worried more about order of magnitude so we neglect the ½ factor. Note that for $E_{donor} \ll k_B T$, we get a big increase in n_{donor} as T increases, but as $E_{donor} \gtrsim k_B T$, $n_{donor} \approx$ constant! And since $E_{donor} < E_{gap}$, the donor electrons will greatly surpass the regular semiconductor electrons for some intermediate temperatures - even if the donor atom concentration is relatively low! This temperature range is called the **extrinsic temperature range**, and in this range the electron density is approximately constant. Most all of the donor electrons have been excited; and while the number of regular valence electrons jumping up are still increasing with temperature, they are such a small fraction of the donor electrons that their contribution can be neglected. Of course at higher temperatures, the sheer number of regular electrons jumping from the valence to the conduction band will take over and we will then be in the intrinsic temperature range.

As an **example**, consider silicon doped with 20 parts per billion Arsenic:

silicon: $\mathbf{n_{si}} = (2.3\,\text{gm/cm}^3)(6\times10^{23}\,\text{atoms/mole})/(28\,\text{gm/mole}) = 5\times10^{22}\,\text{cm}^{-3} = \mathbf{5\times10^{28}\,m^{-3}}$, $\mathbf{E_{gap\text{-}Si} = 1.11\,eV}$.

arsenic: $20 \times 10^{-9} * 5\times10^{28}\,\text{m}^{-3} = \mathbf{n_{dope} = 1\times10^{21}\,m^{-3}}$, $\mathbf{E_{donor\text{-}As}} = 49\,\text{meV} = \mathbf{.049\,eV}$;

Let's now compute the intrinsic electron density for silicon excited at various temperatures (with $m^* = m_e$):

$$n_{intrinsic\text{-}Si} = n_o e^{-Egap/2kT} ,$$

where $n_o = 2[(m_e k_B T)/(2\pi\hbar^2)]^{3/2} = 2[(m_e k_B)/(2\pi\hbar^2)]^{3/2} T^{3/2}$

$= 2[(9.1\times10^{-31}\text{kg}\ 1.38\times10^{-23}\text{J/K})/(2\,\pi\,(6.63\times10^{-34}\text{Js}/2\pi)^2)]^{3/2} T^{3/2}$

$= (4.81\times10^{21}\,\text{m}^{-3}\text{K}^{-3/2})\,T^{3/2}$.

Also for silicon, the exponent becomes: $E_{gap}/2k_BT = (E_{gap}/2k_B)(1/T)$

$= [1.11\,\text{eV}/(2\times1.38^{-23}\text{J/K})(1\,\text{eV}/1.6\times10^{-19}\text{J})](1/T) = (6435\,\text{K})(1/T).$

Therefore, $n_{intrinsic\text{-}Si}(T) = (4.81\times10^{21}\,\text{m}^{-3}\text{K}^{-3/2})\,T^{3/2}\,e^{-6435\text{K}/T}$.

Thus, $n_{intrinsic\text{-}Si}(T= 300K) = (4.81\times10^{21})(300)^{3/2}\, e^{-6435/300}\, m^{-3} = 1.21\times10^{16}\, m^{-3}$;

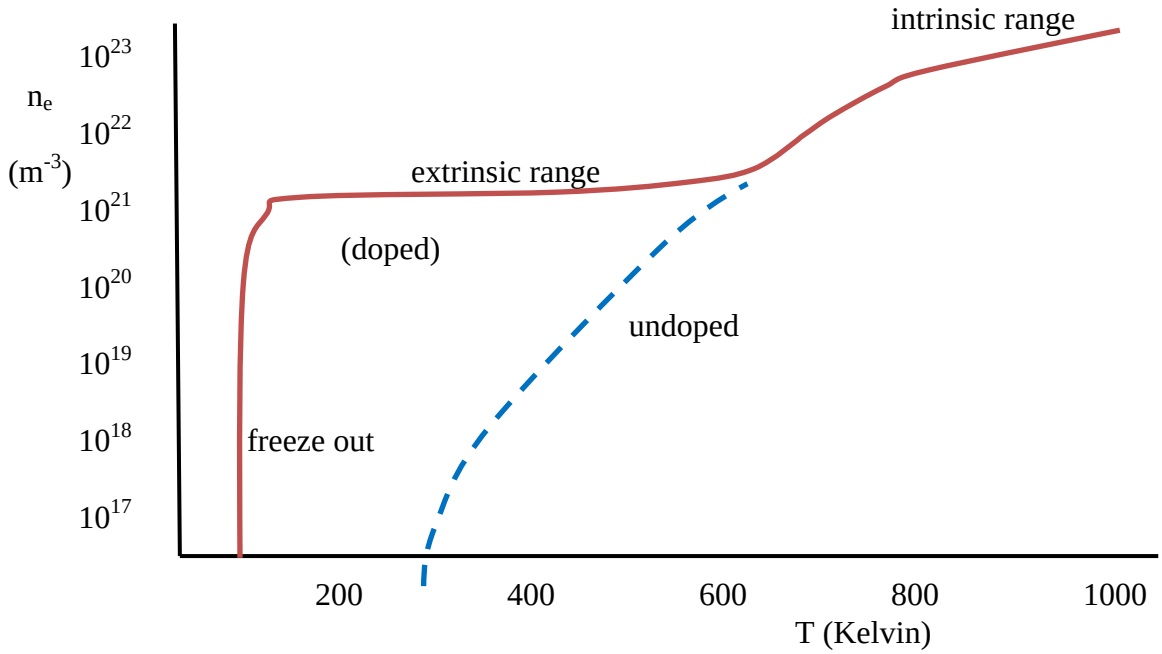
$n_{intrinsic\text{-}Si}(T= 500K) = (4.81\times10^{21})(500)^{3/2}\, e^{-6435/500}\, m^{-3} = 1.38\times10^{20}\, m^{-3}$;

$n_{intrinsic\text{-}Si}(T=1000K) = (4.81\times10^{21})(1000)^{3/2}\, e^{-6435/1000}\, m^{-3} = 2.44\times10^{23}\, m^{-3}$;

The electron density due to the Arsenic is since $E_{donor\text{-}As} = .049\,eV$ and $2k_BT$ (at T=300K) = .052 eV [so $E_{donor\text{-}As} \approx 2k_BT$].

$$n_{e \text{ due to donor}} \approx n_{donor\ atoms} \approx 10^{21}\, m^{-3},$$

For Silicon, you can see from the above values for electron densities that the intrinsic range is above 500 K and the extrinsic range is below 500 K.



See the excel spreadsheet Extrinsic.

In the **intrinsic** range, the **conductivity ($\sigma=ne^2\tau/m$) increases as the temperature** increases since the electron density (n) increases with temperature as an exponential while the collision time (τ) decreases with temperature since the phonon density increases as the temperature increases but only as a power law.

In the **extrinsic** range**, σ decreases as the temperature increases** since n remains essentially constant while τ decreases as the temperature increases.

The following values should help with understanding the above:

T	k_BT (ev)	E_{gap} (eV)	$e^{-Egap/2kT}$	E_{donor}(eV)	$e^{-Edonor/2kT}$
30	0.00259	1.11	8.6×10^{-94}	0.049	7.8×10^{-5}
100	0.00863	1.11	1.2×10^{-28}	0.049	5.6×10^{-2}
300	0.0259	1.11	4.9×10^{-10}	0.049	3.9×10^{-1}
1,000	0.0863	1.11	1.6×10^{-3}	0.049	7.5×10^{-1}
3,000	0.259	1.11	1.2×10^{-1}	0.049	9.1×10^{-1}