EE113FZ
Solid State Electronics
Lecture 10: Doping & The Creation of Semiconductors

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What is to be Discussed Today?

- Effective mass;
- Silicon – an intrinsic semiconductor;
- How doping affect semiconductor materials;
- Some terminology that is needed;
- Fermi level and where it comes from;
- Carriers, carrier concentration, the Einstein relation;
- Basically getting into the detail of how charges move, and why, in a semiconductor material;
- HOWEVER – these concepts form the basis of how nearly all electronic devices operate and so it is important to understand them.

Effective Mass

- What is the mass of an electron in a semiconductor crystal?
- Surely, the mass is the same as that of a free electron.
- However, certain experiments suggest that the electrons in a semiconductor behave as though they have a quite different mass to that of a free electron.

Cyclotron Frequency of Electrons

- Question: By considering the forces acting on an electron in uniform magnetic field *B*, show that the electron moves in circular orbits with a frequency of

$$f_c = \frac{Be}{2\pi m_e}$$

- Solution: The magnitude of the magnetic force on an electron due to a magnetic filed *B* is $F_{mag} = Bev$, where *v* is the velocity of the electron. The centripetal force for the uniform circular motion, $F_{cen} = \frac{m_e v^2}{r}$ is provided by the magnetic force. Hence, $F_{mag} = F_{cen}$.
- This gives the speed of the electron as $v = Ber/m_e$ and the circumference of the trajectory is $2\pi r$. Hence, the frequency is $f_c = Be/(2\pi m_e)$. We call f_c the cyclotron frequency.

Cyclotron Frequency of Electrons

- By measuring the cyclotron frequency, and from the magnetic field B, we can obtain the mass of electron m_e;
- Surprisingly, the mass of electrons in the crystal obtained by the cyclotron frequency is different from that of a free electron;
- What is wrong?
- The problem is that an electron in a solid experience other forces, e.g., due to the ions and other valence electrons, and so it does not respond in the same way as a free electron.
- However, we can obtain agreement with $f_c = \frac{Be}{2\pi m_e}$ if we assume that the mass of an electron in a crystal is somehow different from the mass of a free electron, i.e., replace m_e with m_e^*, here m_e^* is the effective mass of an electron in the crystal.

Equation of Motion for an Electron in a Crystal

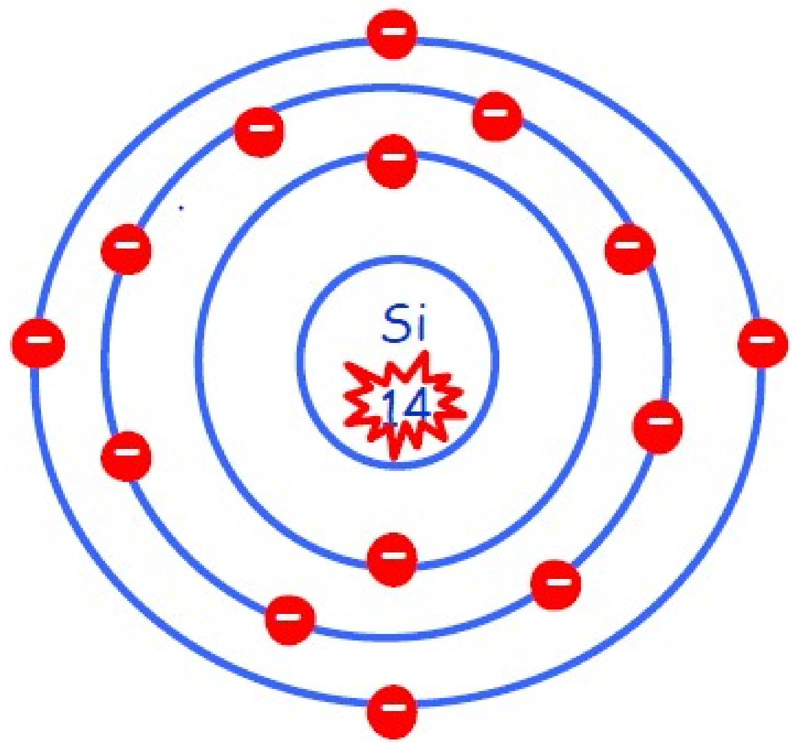
$$\vec{a} = \frac{1}{m_e}(\vec{F} + \vec{F}_l)$$

- $\vec{a}$ is the acceleration of the electron in a crystal;
- $\vec{F}$ is the external force applied on the electron in a crystal, such as the force due to the electric field or magnetic field;
- $\vec{F}_l$ is the force applied to the electron from the lattice, such as the ions and bonding interaction.
- It is very difficult to know how large $\vec{F}_l$ is. Thus, if the influence of the lattice force on the electron is incorporated into the mass of the electron in a crystal, i.e., effective mass, we have:

$$\vec{a} = \frac{1}{m_e^*}\vec{F}$$

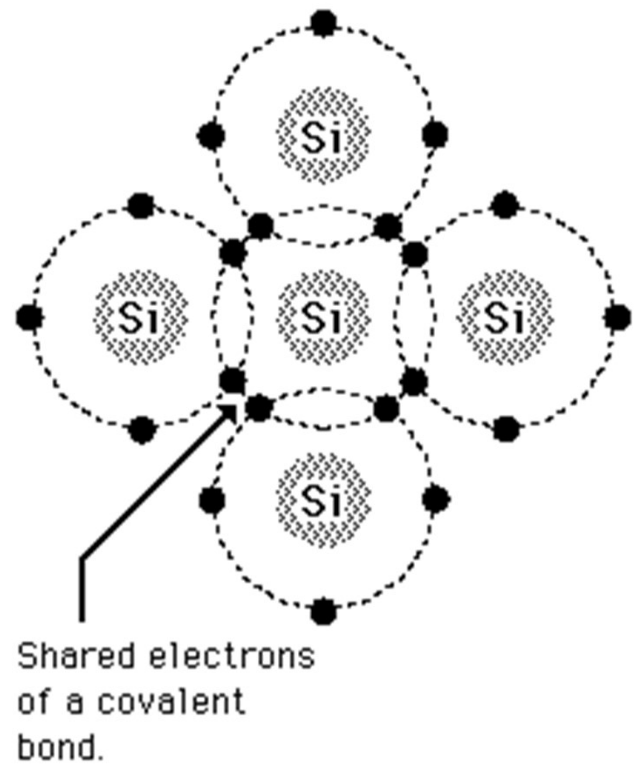
A Reminder: Silicon Atom

14 electrons, 2,8,4 in the 3 electron shells.



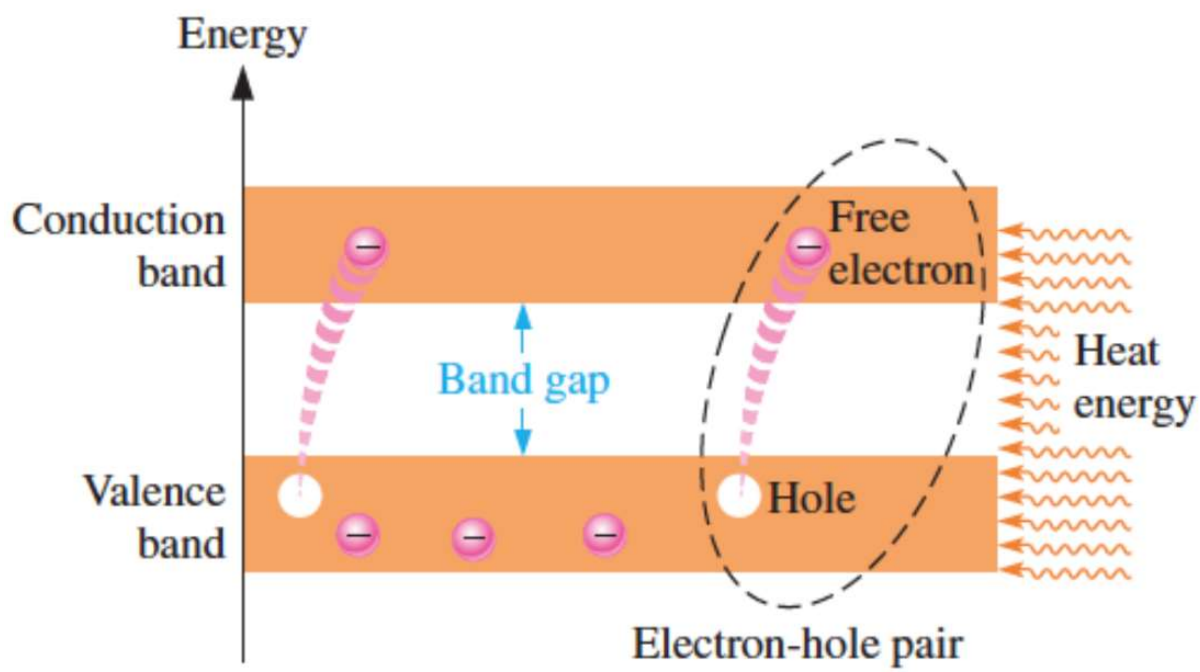
Intrinsic Semiconductor

- Let's look at the most popular semiconductor material, silicon (Si), in a bit more detail.
- In its natural state, it is called an 'intrinsic semiconductor' and will not, normally, conduct any charge (at low temperatures).
- As you can see from the image, there are no 'free' electrons or protons to move around. There is a small chance that with enough energy an electron can break its bond. This tends to leave behind a 'hole' in the silicon lattice. This hole is positive as the overall charge on the silicon is still zero.
- The free electron and free hole are now considered an electron-hole pair (EHP). The rate of generation of these EHP's is dependant on temperature but the net charge is still zero.



Electron-Hole Pair (EHP)

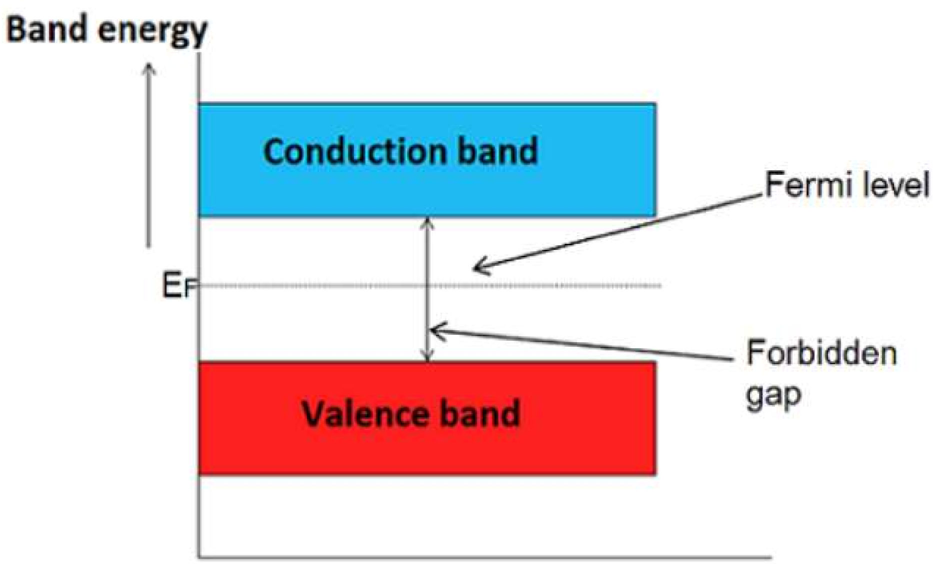
- An EHP is formed when an electron moves from the valence band to the conduction band, thus leaving a vacancy or ‘hole’ behind.



Energy diagram

Intrinsic Semiconductor

- An intrinsic (pure) semiconductor, also called an undoped semiconductor or i-type semiconductor, is a pure semiconductor without any significant dopant species present. The number of charge carriers is therefore determined by the properties of the material itself instead of the amount of impurities.



Fermi level in the middle of bandgap indicates equal concentration of free electrons and holes.

Hole/Electron Concentration

- The hole concentration in the valence band:

$$p = N_{\mathrm{V}} e^{\frac{-(E_{\mathrm{F}} - E_{\mathrm{V}})}{k_{\mathrm{B}} T}}$$

- The electron concentration in the conduction band:

$$n = N_{\mathrm{C}} e^{\frac{-(E_{\mathrm{C}} - E_{\mathrm{F}})}{k_{\mathrm{B}} T}}$$

- The parameters are:
  - k_B = 1.38 × 10^{-23} J/K, is the Boltzmann constant;
  - T is the absolute temperature in kelvin (K);
  - E_C: bottom edge of the conduction band;
  - E_V: top edge of the valence band;
  - N_C: effective density of states in the conduction band (m^{-3});
  - N_V: effective density of states in the valence band (m^{-3}).

N_C and N_V are related to the effective masses m_n^* and m_p^*, respectively.

Intrinsic Semiconductor: *p*/*n* Concentration

- The product of hole and electron concentrations is always a constant:

$$pn = N_\mathrm{V} N_\mathrm{C} e^{\frac{-(E_\mathrm{C}-E_\mathrm{V})}{k_\mathrm{B}T}}$$

- In an intrinsic semiconductor, electrons and holes have to be created in pairs:

$$p = n = n_\mathrm{i} = p_\mathrm{i} = \sqrt{N_\mathrm{V} N_\mathrm{C} e^{\frac{-(E_\mathrm{C}-E_\mathrm{V})}{2k_\mathrm{B}T}}} = \sqrt{N_\mathrm{V} N_\mathrm{C} e^{\frac{-E_\mathrm{g}}{2k_\mathrm{B}T}}}$$

in which n_i is the intrinsic carrier concentration.

- Assuming that holes and electrons have the same effective mass, $m_\mathrm{p}^* = m_\mathrm{n}^*$, we have

$$N_\mathrm{V} = N_\mathrm{C} \text{ and } E_\mathrm{F} = \frac{E_\mathrm{C}+E_\mathrm{V}}{2}$$

Fermi level lies exactly in the middle of the bandgap.

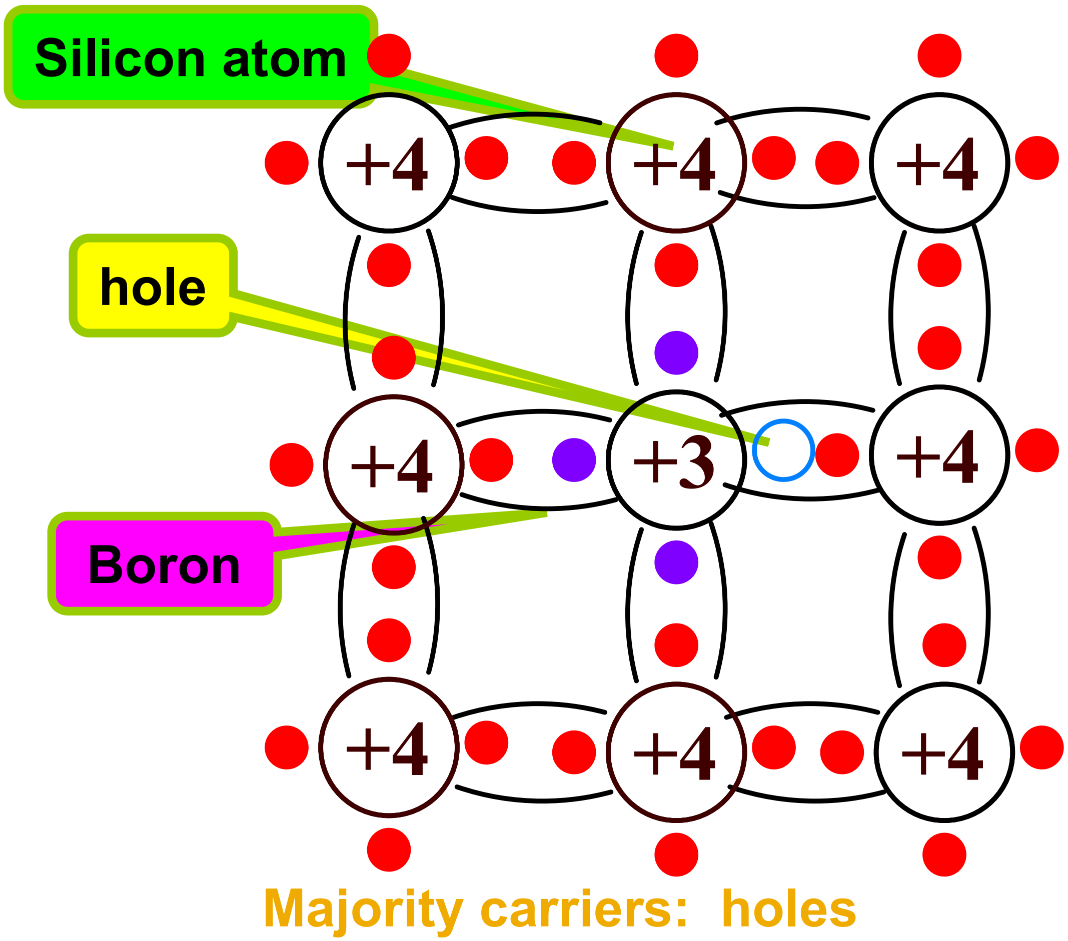
Doping

- Doping is the process of introducing another element into the silicon matrix;
- For silicon doping, the process allows the use of either group III or group V elements. The former is called p-type doping while the later is called n-type doping.

p-Type Doping

- Group III elements, such as boron (B), will introduce extra ‘holes’ as boron only has 3 electrons in its outer shell;
- This is known as a p-type material. P is for positive, as the majority charge carriers are holes (in this case, minority charge carriers are electrons).

Boron-Doped Silicon Matrix



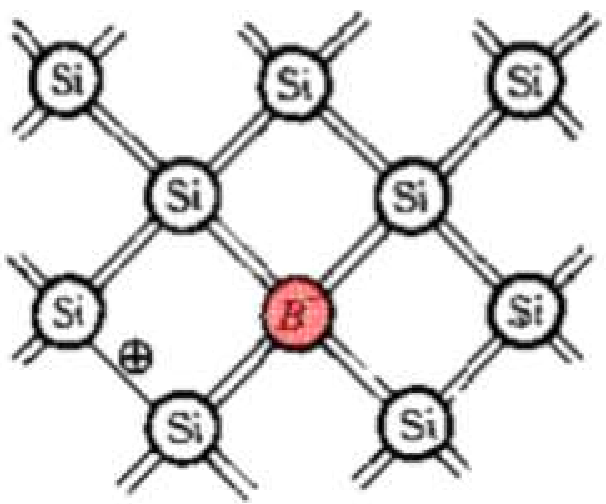
- p-type doping: Trivalent impurity elements, such as boron or gallium, are added to the intrinsic semiconductor;
- Boron is an acceptor impurity in silicon, because it has one fewer valence electron than the atom that it replaces. The acceptor impurity will provide holes as majority carriers;
- An increase in the number of holes, enough to allow current to flow easily and predictably!

p-Type Doping

- The hole concentration is

$$p_0 = N_V e^{\frac{-(E_F - E_V)}{k_B T}} = n_i e^{\frac{(E_i - E_F)}{k_B T}}$$

in which E_i represents the Fermi level of the intrinsic semiconductor without doping.



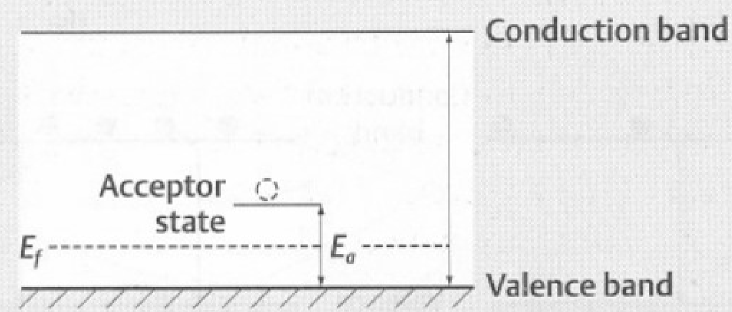


Figure 5.17 The energy band diagram for a p-type semiconductor. The acceptor state is at an energy E_a above the valence band edge, where $E_a \ll E_g$. At $T = 0$ K the Fermi energy is midway between the valence band edge and the acceptor state.

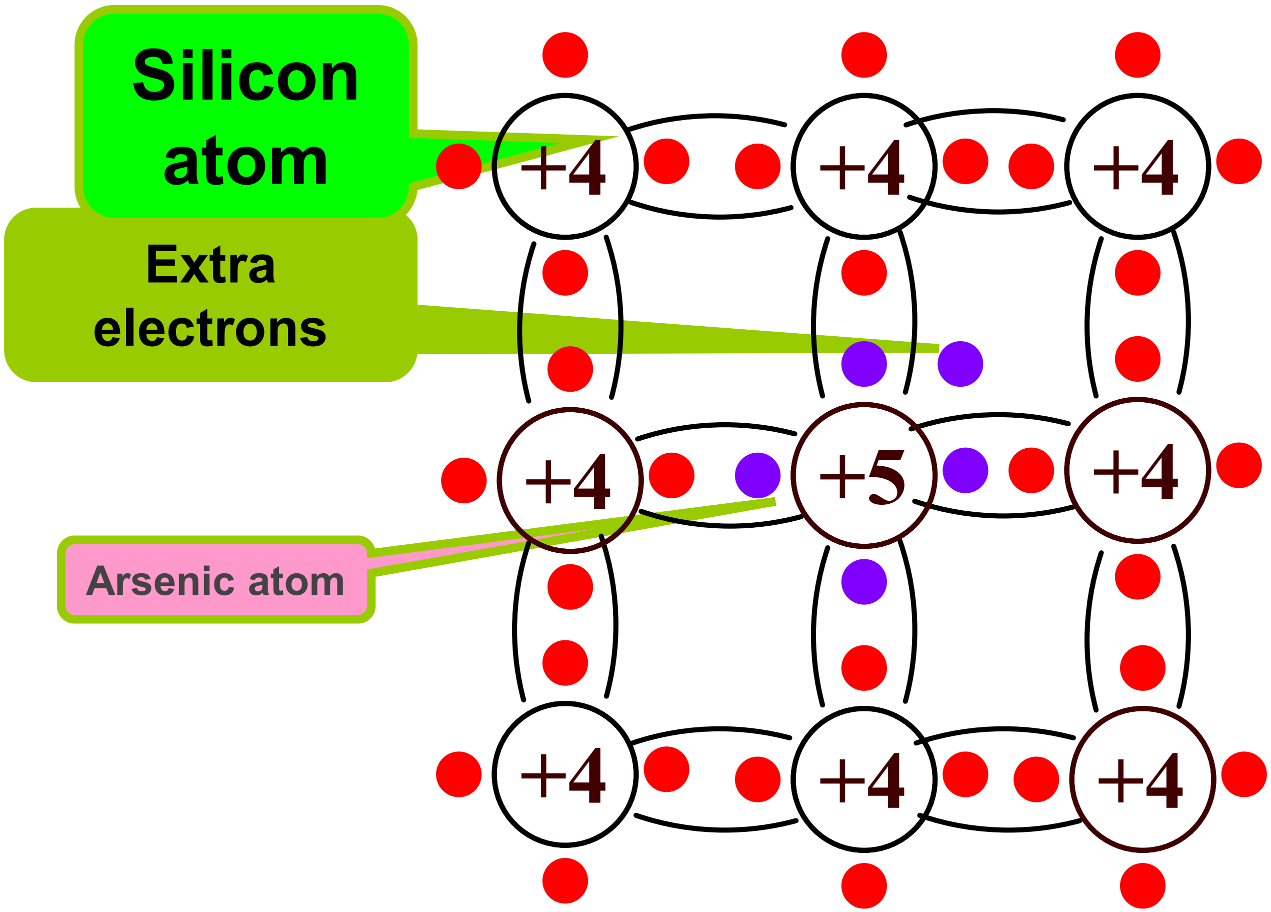
p_0 denotes the hole concentration at thermodynamic equilibrium.

n-Type Doping

- A donor impurity is an atom that has one more valence electron than the atom that it replaced;
- Group V elements, such as arsenic (As) will allow for extra electrons as arsenic has 5 electrons in its outer shell. Group V elements are donor impurities for silicon.
- This is known as n-type doping, n is for negative, as the majority charge carriers will be electrons.
- Finally, we should point out that although the addition of donor impurities leads to an increase in the number of conduction electrons, the semiconductor remains electrically neutral because the number of positively charged donor ions is exactly equal to the number of conduction electrons in the sample.

Arsenic-Doped Silicon Matrix

Additional free electrons -> n-type material

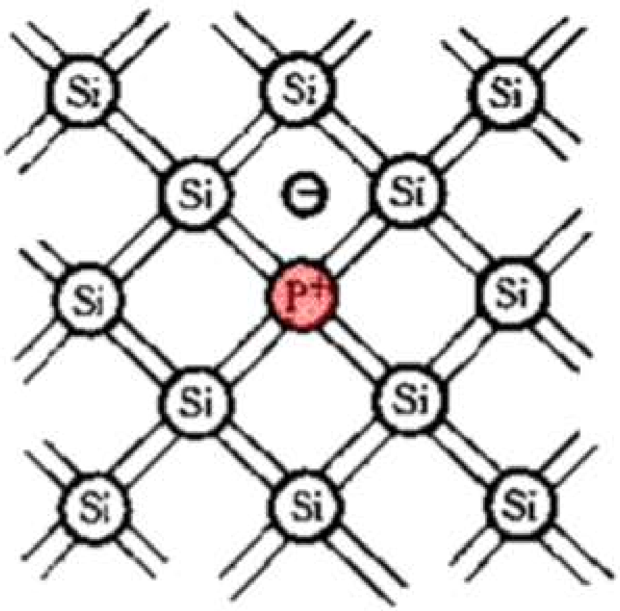


n-Type Doping

- The electron concentration is

$$n_0 = N_\mathrm{C} e^{\frac{-(E_\mathrm{C} - E_\mathrm{F})}{k_\mathrm{B} T}} = n_\mathrm{i} e^{\frac{(E_\mathrm{F} - E_\mathrm{i})}{k_\mathrm{B} T}}$$

in which E_i represents the Fermi level of the intrinsic semiconductor without doping.



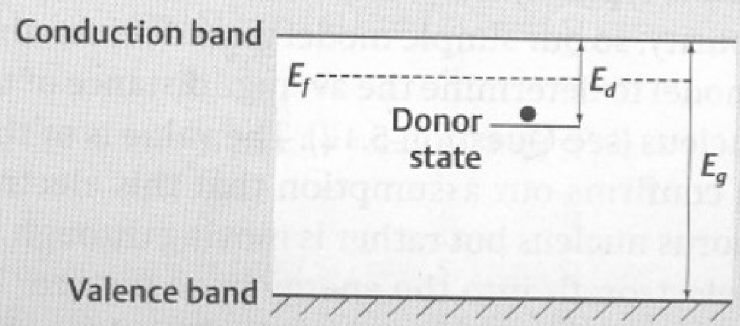


Figure 5.13 The energy band diagram for an n-type semiconductor. The donor state is at an energy E_d below the conduction band edge, where $E_d \ll E_g$. At $T = 0$ K the Fermi energy is midway between the donor state and the conduction band edge, i.e. typically about 20–30 meV below the conduction band edge.

n_0 denotes the electron concentration at thermodynamic equilibrium.

Dopant *vs*. Carrier Concentrations

- A small concentration of impurities can result in a large change in conductivity;
- In a sample of intrinsic silicon, the concentration of conduction electrons at room temperature is $\sim 1 \times 10^{16}\ \mathrm{cm}^{-3}$;
- If we replace one in every million silicon atom with a donor impurity and all of these impurities are ionised, then the concentration of conduction electrons is $\sim 5 \times 10^{22}\ \mathrm{cm}^{-3}$;
- In the semiconductor industry, the technology of producing ultra-pure silicon crystals with very few impurities is of critical importance. Impurity levels as low as only one atom in every hundred billion atoms have been reported.

Conductivity

- In both cases, n-type and p-type doping, there has been an increase in the number of ‘free’ charge carriers;
- By ‘free’ we mean that they are not bound to atoms;
- These free carriers can now move, either under the influence of an electric or magnetic field OR through kinetic motion;
- Directional movement of charge is current!
- Hence the ability to move charge, conductivity, has been increased!
- Its symbol is σ and is measured in $S{\cdot}m^{-1}$ (Siemens per metre).

Conductivity & Bandgap

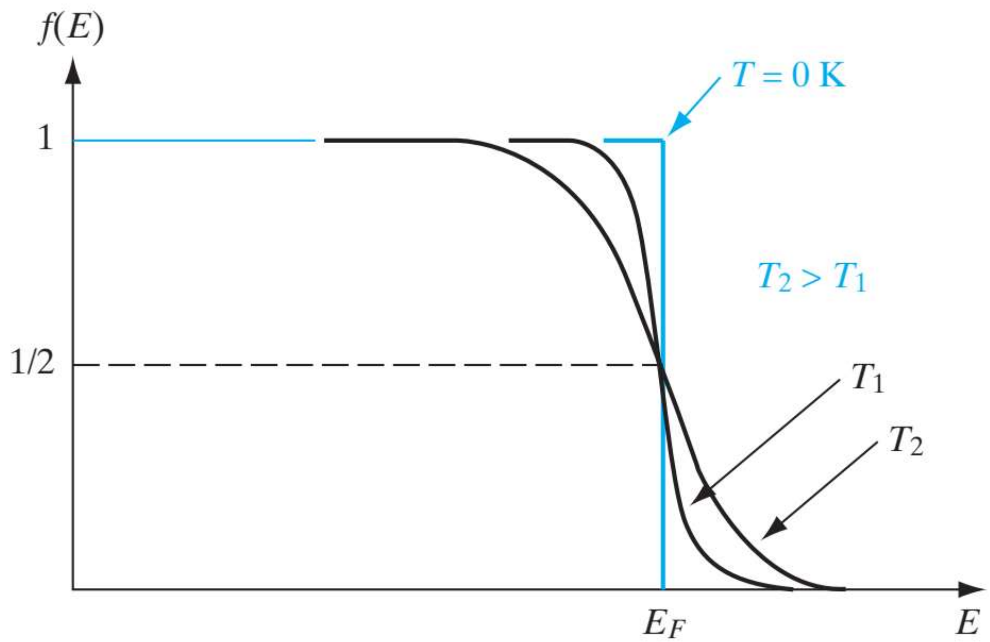
- Remember the term ‘bandgap’ that we spoke about in a previous lecture?
- So increased conduction means that more charge carriers are moving. One possible way to increase conductivity is to reduce the bandgap between the conduction and valence bands.
- The energy required to move across that bandgap has been reduced, which will increase the conductivity!
- Another way to increase conductivity is doping, which will introduce donor or acceptor levels into the bandgap.
- As a result, there are more carriers in the materials.

Fermi-Dirac Distribution & $f(E)$ Graph

- Electrons fill energy bands following the Fermi-Dirac distribution:

$$f(E) = \frac{1}{1 + e^{(E - E_{\mathrm{F}})/k_{\mathrm{B}}T}}$$

- It describes the probability of an energy level E being occupied by and electron at a temperature T under equilibrium.



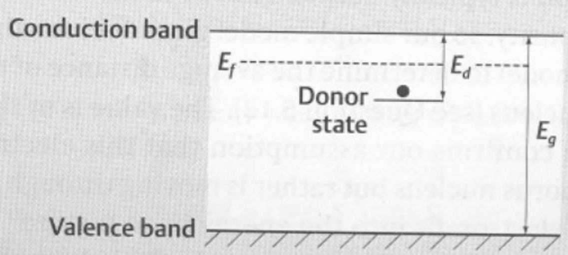
An energy state at the Fermi level, E_{F}, has a probability of 50% to be occupied by an electron.

$f(E)$ graph explanation

- At 0 K (-273.16°C) there is no thermal excitation. All the electrons are in the valence band;
- Above 0 K there is a small, but increasing, chance of electrons being excited into the conduction band and becoming a free carrier;
- To increase the likelihood of finding a free carrier you either need to increase the temperature OR otherwise create free carriers (through doping);
- The Fermi energy level, E_F, depends on the material used and also the dopant levels.

Effects of Doping on the Fermi Level

- To get more free electrons, dope with a group V element;
- This effectively moves the Fermi level, E_F, from the centre of the bandgap to a higher number, meaning that it is more likely to find an electron in the conduction band;
- To get more free holes, dope with a group III element;
- Again this means the Fermi level, E_F, changes and there is less chance of finding an electron in the conduction band.



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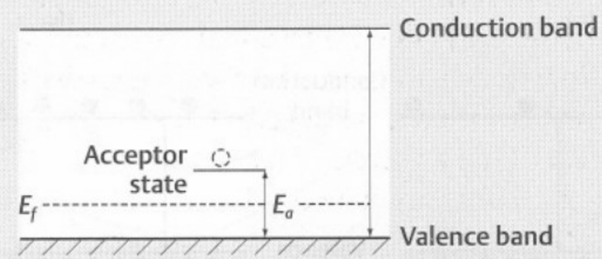


Figure 5.17 The energy band diagram for a p-type semiconductor. The acceptor state is at an energy E_a above the valence band edge, where $E_a \ll E_g$. At $T = 0$ K the Fermi energy is midway between the valence band edge and the acceptor state.

Important Terms

- Before we go any further it is time to bring in some important terms. Understand these as they will be needed later!
- N_d: concentration of donor atoms in an n-type semiconductor providing free electrons;
- N_a: concentration of acceptor atoms in a p-type semiconductor providing free holes;
- n_i, n_p, n_n: concentration of electrons in intrinsic, p- and n-type materials;
- p_i, p_p, p_n: concentration of holes in intrinsic, p- and n-type materials.

Carrier Concentration

- Based on a simple formula you can calculate the number of carriers in a material:

$$n_0 p_0 = n_\mathrm{i}^2$$

- This holds for all concentrations and temperatures and relates the number of free hole and electron carriers at equilibrium in a doped material to an intrinsic material;
- The carrier concentration is important as it limits the amount of current that can be carried.

Important Formulae for Carrier Concentration

- $p_0 = N_\mathrm{V} e^{\frac{-(E_\mathrm{F}-E_\mathrm{V})}{k_\mathrm{B}T}} = n_\mathrm{i} e^{\frac{(E_\mathrm{i}-E_\mathrm{F})}{k_\mathrm{B}T}}$;
- $n_0 = N_\mathrm{C} e^{\frac{-(E_\mathrm{C}-E_\mathrm{F})}{k_\mathrm{B}T}} = n_\mathrm{i} e^{\frac{(E_\mathrm{F}-E_\mathrm{i})}{k_\mathrm{B}T}}$;
- $f(E) = \frac{1}{1+e^{(E-E_\mathrm{F})/k_\mathrm{B}T}}$;
- $n_0 p_0 = n_\mathrm{i}^2$.
- Shallow donor and acceptor impurities are completely ionised at room temperature:
- $p_0 = N_\mathrm{a} + n_\mathrm{i} \approx N_\mathrm{a}$;
- $n_0 = N_\mathrm{d} + n_\mathrm{i} \approx N_\mathrm{d}$.

Example: Carrier Concentration Calculation

- The bandgap of silicon is 1.14 eV. What is the probability of finding a free electron 0.6 eV above the Fermi level?
- The silicon sample is now doped with 10^{17} arsenic (a donor) atoms/cm^3. Given the same energy level, how does the probability of finding an electron at that energy level change? $k_B = 8.62 \times 10^{-5}$ eV/K. Assume room temperature (T = 300 K) and $n_i = 1.5 \times 10^{10}$ cm^{-3}.
- What is the equilibrium hole concentration, p_0, at 300 K and where is the Fermi level with respect to the intrinsic level?

Example: Carrier Concentration Calculation

- $f(E) = \frac{1}{1+e^{(E-E_\mathrm{F})/k_\mathrm{B}T}}$ and $E - E_\mathrm{F}$ = 0.6 eV. Insert the values of k_B and T, we have $f(E) = 8.4 \times 10^{-11}$;
- $n_0 = n_\mathrm{i} e^{\frac{(E_\mathrm{F}-E_\mathrm{i})}{k_\mathrm{B}T}} \approx 10^{17}\ \mathrm{cm}^{-3}$ and $n_\mathrm{i} = 1.5 \times 10^{10}\ \mathrm{cm}^{-3}$. This allows us to solve for $E_\mathrm{F} - E_\mathrm{i}$. We have $E_\mathrm{F} - E_\mathrm{i}$ = 0.4063 eV;
- For intrinsic silicon, $E - E_\mathrm{i}$ = 0.6 eV and for doped silicon, $E_\mathrm{F} - E_\mathrm{i}$ = 0.4063 eV. We have $E - E_\mathrm{F}$ = 0.6 eV – 0.4063 eV = 0.1937 eV;
- We can now apply the Fermi-Dirac function again with $E - E_\mathrm{F}$ = 0.1937 eV, and obtain $f(E) = 5.6 \times 10^{-4}$;
- $p_0 = \frac{n_\mathrm{i}^2}{n_0} = \frac{(1.5\times 10^{10})^2}{10^{17}} = 2.3 \times 10^3\ \mathrm{cm}^{-3}$.

Impurity Compensation

- It is very important to obtain extremely pure samples of semiconductors, because only in this way can we use doping to effectively tune the conductivity of the material;
- If the concentration of accidental impurities is comparable with the dopant concentration, then the effects of doping a material could well be obscured;
- For example, if all of the accidental impurities happen to be acceptors, then the material which is intentionally doped with donors may turn out to have p-type characteristics.
- If $N_\mathrm{d} \gg n_\mathrm{i}$ and $N_\mathrm{a} \gg n_\mathrm{i}$, for an n-type material, $n_0 = N_\mathrm{d} - N_\mathrm{a}$. For a p-type material, $p_0 = N_\mathrm{a} - N_\mathrm{d}$.

Example: Impurity Compensation

- A silicon sample is doped with 10^{18} arsenic atoms/cm^3. Arsenic is a donor dopant. If this silicon sample were to be converted to *p*-type, what level of doping with boron would be required to move the Fermi-Energy level 0.2 eV BELOW the intrinsic energy level? $n_i = 1.5 \times 10^{10}$ cm^{-3}.

Example: Impurity Compensation

- A silicon sample is doped with 10^{18} arsenic atoms/cm^3. Arsenic is a donor dopant. If this silicon sample were to be converted to *p*-type, what level of doping with boron would be required to move the Fermi-Energy level 0.2 eV BELOW the intrinsic energy level? $n_i = 1.5 \times 10^{10}$ cm^{-3}.
- Solution: $p_0 = n_{\mathrm{i}} e^{\frac{(E_{\mathrm{i}} - E_{\mathrm{F}})}{k_{\mathrm{B}} T}} = \left(1.5 \times 10^{10}\ \mathrm{cm}^{-3}\right) e^{\frac{0.2}{8.62 \times 10^{-5} \times 300}}$, we have $p_0 = 3.43 \times 10^{13}\ \mathrm{cm}^{-3}$.
- $p_0 = N_{\mathrm{a}} - N_{\mathrm{d}}$, hence, $N_{\mathrm{d}} = N_{\mathrm{a}} + p_0 \approx 10^{18}\ \mathrm{cm}^{-3}$.

Current Flows

- Current is carried by both the electrons and holes in a semiconductor. Remember that we can create excess of both via doping;
- There are TWO main mechanisms for current flow:
  - Drift current – where charges move under the influence of an applied field (a field is an area where a charged body experiences a force);
  - Diffusion current – where charges move out of an area of high concentration to an area of low concentration.
- In a nutshell, the current density (J) should depend on:
  - How many carriers there are;
  - How heavy they are;
  - How long they can move before hitting anything else.
- The total amount of current flowing is the sum of the current from **both** the electrons and the holes.

Current Density, Conductivity & Mobility

- Current density: $J = \sigma E$;
- Conductivity: $\sigma = qn\mu_{\mathrm{n}}$ (in metals, $\sigma = n\mu e$) where n is the charge carrier concentration and q is its charge;
- Carrier mobility: $\mu_{\mathrm{n}} = \frac{q\bar{t}}{m_{\mathrm{n}}^*}$ (in metals, $\mu = \frac{e\tau}{m_e}$) and $\bar{t}$ denotes the mean time between collisions* and m_{n}^* is the effective mass of electrons;
- The equations for conductivity and carrier mobility are for electrons. There are two similar equations for holes;
- We have encountered all these equations when we discussed the Drude model of conduction.

In semiconductors, τ usually carries a different meaning (which you will see very soon). This is the reason that we use $\bar{t}$ instead of τ here.

The Einstein Relation

- The Einstein relation is a way to tie the two current mechanisms (namely, drift and diffusion) and charge carriers together in one understandable equation:

$$\frac{D_\mathrm{n}}{\mu_\mathrm{n}} = \frac{k_\mathrm{B}T}{q}$$

  D_n measured in m^2/s is the carrier diffusion coefficient, μ_n is the carrier mobility, k_B is Boltzmann constant (1.38×10^{-23} J·K^{-1}), q is the charge on the charge carrier, and T is temperature in kelvin. There is a similar equation for holes (replace D_n and μ_n with D_p and μ_p).

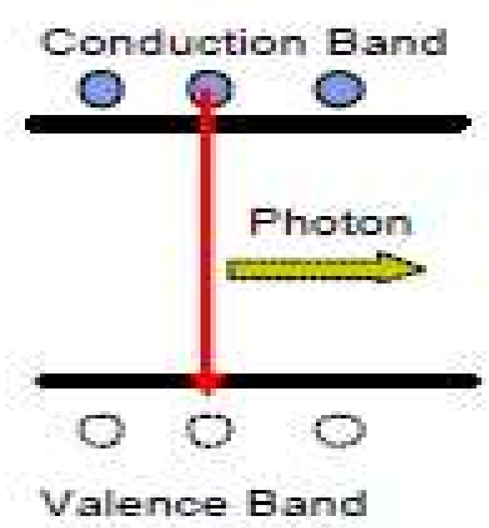
- Diffusion length (L_n or L_p): the distance, on average, a charge carrier moves between generation and recombination.

$$L_\mathrm{n} = \sqrt{D_\mathrm{n}\tau_\mathrm{n}} \text{ and } L_\mathrm{p} = \sqrt{D_\mathrm{p}\tau_\mathrm{p}}$$

  in which τ_n and τ_p are the carrier lifetimes.

Carrier Recombination

- We have lots of holes and lots of electrons. What do you think is going to happen?
- Lots of them will move as we want and current will flow.
- Some, however, will collide with each other. That is an electron falling into a hole, and then what happens? The charges will cancel each other but what happens to the energy that they have?
- Typically, the energy is released as either heat or light!



Carrier Recombination

- What effect will carrier recombination have on the total current flow?
- If the charges recombine, we will have fewer carriers. Current is dependent on the total number of carriers and how fast the carriers move. Therefore, the recombination will reduce the total current. Note that this is for a system where the velocity of the charge carriers is fixed as the rate of charge carrier movement is also a factor in the total amount of current flowing.
- We can define a carrier lifetime (τ) which is the average time it takes for a minority carrier to recombine.
- Does carrier recombination matter? Well, it depends. If the EHP's are generated by external means, e.g., heat or light, then we do need to take carrier recombination into account.