Solid State Physics

SEMICONDUCTORS - I

Lecture 22

A.H. Harker
Physics and Astronomy
UCL

9 Physics of Semiconductors

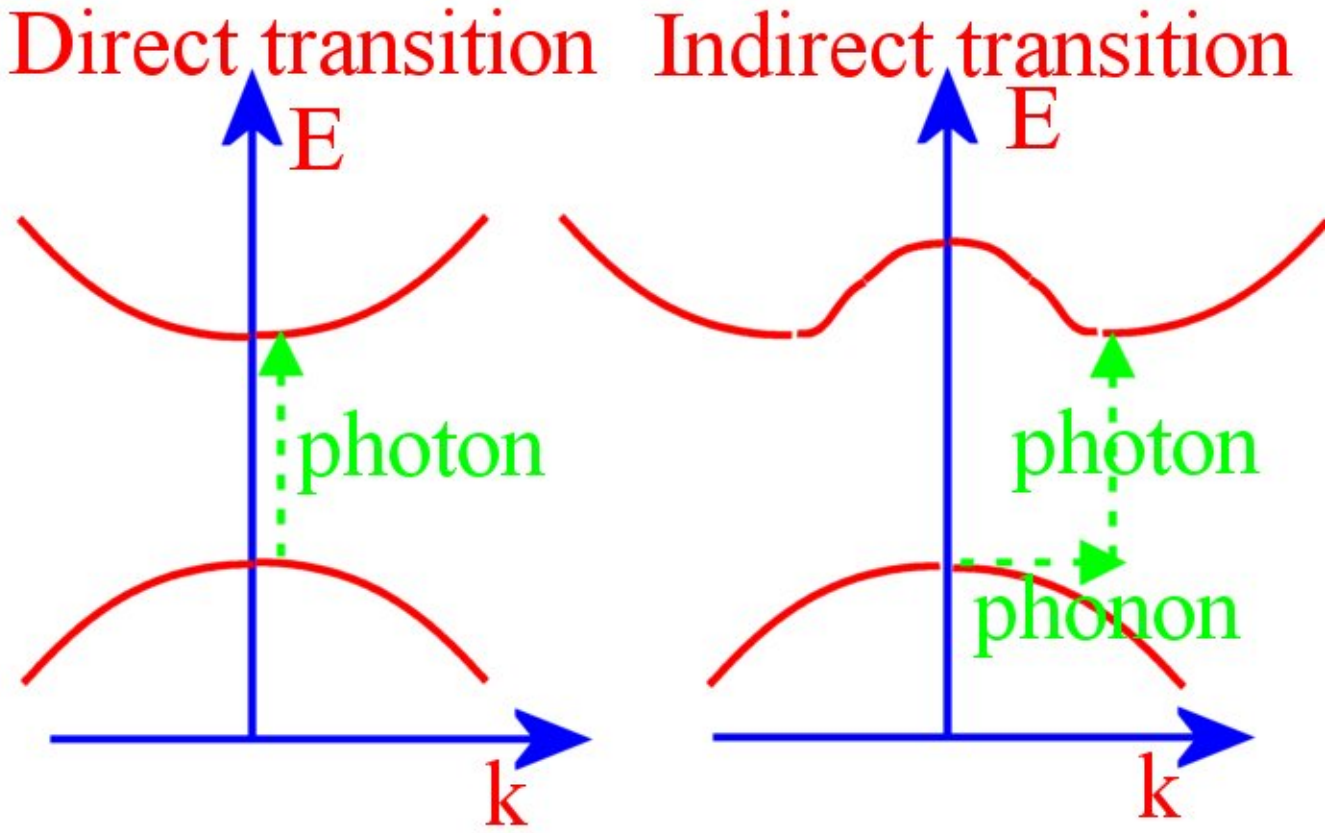
9.1 Creating free carriers

At absolute zero, a pure semiconductor has a full valence band and an empty conduction band – there are no *free carriers*. Create free carriers by:

- **absorbing photons**
- **thermal excitation**
- **doping with impurities**

9.2 Photon absorption

Photons with energy greater than the band gap E_g can excite an electron, creating a hole in the valence band and an electron in the conduction band.



Note that energy and crystal momentum must be conserved, and a phonon may be emitted or absorbed. In terms of initial electron energy and momentum E and $\hbar k$, final electron state (E', k'), photon energy and momentum $\hbar\Omega$ and $\hbar Q$, and phonon energy and momentum $\hbar\omega$ and $\hbar q$:

$$E' = E + \hbar\Omega \pm \hbar\omega,$$

and

$$k' = k + Q \pm q.$$

Note that if the photon energy is about 1 eV its wavelength is about $1.2\ \mu\mathrm{m}$, so its wavevector is $5.1 \times 10^6\ \mathrm{m}^{-1}$. The side of the Brillouin zone is $2\pi/a$, which is typically of order $10^{10}\ \mathrm{m}^{-1}$. On the scale of the reciprocal lattice, then, the photon wavevector is essentially zero – a photon transition is *vertical*.

9.3 Thermal excitation

We can find the number of electrons in the conduction band by taking the density of states in the conduction band, $g_{\mathrm{c}}(E)$, multiplying it by the probability that the state is occupied (the Fermi function), and integrating. If the energy of the bottom of the conduction band is E_{c} the number of electrons is

$$N_{\mathrm{e}}(T) = \int_{E_{\mathrm{c}}}^{\infty} \frac{g_{\mathrm{c}}(E)\mathrm{d}E}{\exp((E-\mu)/(k_{\mathrm{B}}T)) + 1}. \tag{1}$$

Note that

- N_{e} **will depend on the temperature**
- **we need to know the chemical potential, μ.**

The number of holes depends on the probability that an electron state is unoccupied, but

$$1 - \frac{1}{\exp((E-\mu)/(k_{\mathrm{B}}T)) + 1} = \frac{\exp((E-\mu)/(k_{\mathrm{B}}T))}{\exp((E-\mu)/(k_{\mathrm{B}}T)) + 1} = \frac{1}{\exp((\mu-E)/(k_{\mathrm{B}}T)) + 1},$$

so the number of holes is

$$N_{\mathrm{h}}(T) = \int_{-\infty}^{E_{\mathrm{v}}} \frac{g_{\mathrm{v}}(E)\mathrm{d}E}{\exp((\mu-E)/(k_{\mathrm{B}}T)) + 1}, \tag{2}$$

where E_{v} is the energy of the top of the valence band and $g_{\mathrm{v}}(E)$ is the density of states in the valence band.

Equations 1 and 2 can be simplified if the numbers of electrons and holes are small. If

$$\frac{1}{\exp((E-\mu)/(k_{\mathrm{B}}T))+1} << 1,$$

it follows that the exponential is large, so that

$$\frac{1}{\exp((E-\mu)/(k_{\mathrm{B}}T))+1} \approx e^{(\mu-E)/(k_{\mathrm{B}}T)},$$

which is true if

$$E-\mu >> k_{\mathrm{B}}T.$$

In the conduction band, $E \geq E_{\mathrm{c}}$, so the condition is

$$E_{\mathrm{c}}-\mu >> k_{\mathrm{B}}T. \tag{3}$$

Similarly, provided

$$\mu - E_{\mathrm{v}} >> k_{\mathrm{B}}T. \tag{4}$$

we can write in the valence band

$$\frac{1}{\exp((\mu-E)/(k_{\mathrm{B}}T))+1} \approx e^{(E-\mu)/(k_{\mathrm{B}}T)}.$$

This low carrier density is the *nondegenerate* case. The other extreme, in which the probability of occupation of a level is close to 1, is the *degenerate* case, typified by the occupied states in a metal.

9.3.1 Law of mass action

In the nondegenerate limit,

$$\begin{aligned} N_{\mathrm{e}}(T) &\approx \int_{E_{\mathrm{c}}}^{\infty} g_{\mathrm{c}}(E) e^{(\mu - E)/(k_{\mathrm{B}}T)} \, \mathrm{d}E \\ &= e^{(\mu - E_{\mathrm{c}})/(k_{\mathrm{B}}T)} \int_{E_{\mathrm{c}}}^{\infty} g_{\mathrm{c}}(E) e^{-(E - E_{\mathrm{c}})/(k_{\mathrm{B}}T)} \, \mathrm{d}E \\ &= e^{(\mu - E_{\mathrm{c}})/(k_{\mathrm{B}}T)} N_{\mathrm{c}}(T). \end{aligned} \tag{5}$$

Similarly,

$$\begin{aligned} N_{\mathrm{h}}(T) &\approx \int_{-\infty}^{E_{\mathrm{v}}} g_{\mathrm{v}}(E) e^{(E - \mu)/(k_{\mathrm{B}}T)} \, \mathrm{d}E \\ &= e^{(E_{\mathrm{c}} - \mu)/(k_{\mathrm{B}}T)} \int_{-\infty}^{E_{\mathrm{v}}} g_{\mathrm{v}}(E) e^{-(E_{\mathrm{v}} - E)/(k_{\mathrm{B}}T)} \, \mathrm{d}E \\ &= e^{(E_{\mathrm{v}} - \mu)/(k_{\mathrm{B}}T)} N_{\mathrm{v}}(T). \end{aligned}$$

$N_{\rm c}(T)$ and $N_{\rm v}(T)$ are only slowly-varying functions of T. We still cannot determine the individual carrier concentrations without knowing μ, but if we take the product

$$\begin{aligned} N_{\rm e}(T)N_{\rm h}(T) &= e^{(\mu-E_{\rm c})/(k_{\rm B}T)}N_{\rm c}(T)e^{(E_{\rm v}-\mu)/(k_{\rm B}T)}N_{\rm v}(T) \\ &= e^{(E_{\rm v}-E_{\rm c})/(k_{\rm B}T)}N_{\rm c}(T)N_{\rm v}(T) \\ &= e^{-E_{\rm g}/(k_{\rm B}T)}N_{\rm c}(T)N_{\rm v}(T). \end{aligned}$$

the result is independent of μ. This is the *law of mass action*: if we know the number of one of the carriers, we can find that of the other.

9.4 Parabolic bands

We saw that, near the top and bottom of bands, a parabolic approximation was appropriate, and we can combine this with the effective mass to write, for conduction electrons,

$$E(\mathbf{k}) = E_{\mathrm{c}} + \frac{\hbar^2 |\mathbf{k} - \mathbf{k}_0|^2}{2m_{\mathrm{e}}^*},$$

and in the valence band

$$E(\mathbf{k}) = E_{\mathrm{v}} - \frac{\hbar^2 |\mathbf{k} - \mathbf{k}_0|^2}{2m_{\mathrm{h}}^*}.$$

Using, as usual,

$$g(k)\mathrm{d}k = 2\left(\frac{L}{2\pi}\right)^3 4\pi k^2 \mathrm{d}k$$

and

$$\frac{\mathrm{d}E}{\mathrm{d}k} = \frac{\hbar^2 k}{m^*}$$

and noting that the same result is valid whether we expand about $\mathbf{k} = 0$ or $\mathbf{k} = \mathbf{k}_0$, for the conduction band

$$\begin{aligned} g_\mathrm{c}(E) &= \frac{L^3}{\pi^2}\frac{m_\mathrm{e}^* k}{\hbar^2} \\ &= \frac{V}{\pi^2}\frac{m_\mathrm{e}^*}{\hbar^2}\sqrt{\frac{2m_\mathrm{e}^*(E-E_\mathrm{c})}{\hbar^2}} \\ &= \frac{V 2^{1/2}(m_\mathrm{e}^*)^{3/2}}{\hbar^3\pi^2}\sqrt{E-E_\mathrm{c}}. \end{aligned}$$

Similarly, for the valence band,

$$g_\mathrm{v}(E) = \frac{V 2^{1/2}(m_\mathrm{h}^*)^{3/2}}{\hbar^3\pi^2}\sqrt{E_\mathrm{v}-E}.$$

Now we can evaluate the integrals

$$N_{\rm c}(T) = \int_{E_{\rm c}}^{\infty} g_{\rm c}(E) e^{-(E-E_{\rm c})/(k_{\rm B}T)}\,{\rm d}E$$
$$= \frac{V 2^{1/2}(m_{\rm e}^*)^{3/2}}{\hbar^3\pi^2}\int_{E_{\rm c}}^{\infty}\sqrt{E-E_{\rm c}}e^{-(E-E_{\rm c})/(k_{\rm B}T)}\,{\rm d}E.$$

Substitute $x = (E-E_{\rm c})/(k_{\rm B}T)$**, to obtain**

$$N_{\rm c}(T) = \frac{V 2^{1/2}(m_{\rm e}^* k_{\rm B}T)^{3/2}}{\hbar^3\pi^2}\int_0^{\infty}\sqrt{x}e^{-x}\,{\rm d}x$$
$$= \frac{1}{4}V\left(\frac{2m_{\rm e}^* k_{\rm B}T}{\pi\hbar^2}\right)^{3/2}, \qquad (6)$$

using the standard integral

$$\int_0^{\infty}\sqrt{x}e^{-x}\,{\rm d}x = \frac{\sqrt{\pi}}{2}.$$

If we set $V = 1$, we can work with concentrations of carriers $n_{\mathrm{e,h}}$ and corresponding values $n_{\mathrm{c,v}}$. If we put in numbers, we find

$$n_{\mathrm{c}}(T) = 5 \times 10^{21} \left(\frac{m_e^*}{m_e} \right)^{3/2} \quad T^{3/2}.$$

The expression for the valence band is quite similar:

$$n_{\mathrm{v}}(T) = \frac{1}{4} \left(\frac{2 m_{\mathrm{h}}^* k_{\mathrm{B}} T}{\pi \hbar^2} \right)^{3/2} .$$

9.5 Intrinsic behaviour

If all (or almost all) the electrons in the conduction band have been excited from the valence band, we have

$$n_{\mathrm{e}}(T) = n_{\mathrm{h}}(T) = n_{\mathrm{i}}(T),$$

with

$$\begin{aligned} n_{\mathrm{i}}(T) &= e^{-E_{\mathrm{g}}/(2k_{\mathrm{B}}T)}\sqrt{n_{\mathrm{c}}(T)n_{\mathrm{v}}(T)} \\ &= e^{-E_{\mathrm{g}}/(2k_{\mathrm{B}}T)}\frac{1}{4}\left(\frac{2k_{\mathrm{B}}T}{\pi\hbar^2}\right)^{3/2}\left(m_{\mathrm{e}}^* m_{\mathrm{h}}^*\right)^{3/4} \\ &= 5\times 10^{21}\left(\frac{m_e^* m_h^*}{m_e^2}\right)^{3/4} T^{3/2}\ e^{-E_{\mathrm{g}}/(2k_{\mathrm{B}}T)}. \end{aligned} \tag{7}$$

Now we can find the Fermi energy: if we equate the value for $n_{\mathrm{e}}(T)$ from equations 5 and 6 with that from 7 we find

$$e^{-E_{\mathrm{g}}/(2k_{\mathrm{B}}T)}\frac{1}{4}\left(\frac{2k_{\mathrm{B}}T}{\pi\hbar^2}\right)^{3/2}\left(m_{\mathrm{e}}^{*}m_{\mathrm{h}}^{*}\right)^{3/4}=\frac{1}{4}\left(\frac{2m_{\mathrm{e}}^{*}k_{\mathrm{B}}T}{\pi\hbar^2}\right)^{3/2}e^{(\mu-E_{\mathrm{c}})/(k_{\mathrm{B}}T)},$$

then

$$\mu=E_c-\frac{1}{2}E_{\mathrm{g}}+\frac{3}{4}k_{\mathrm{B}}T\ln\left(\frac{m_{\mathrm{h}}^{*}}{m_{\mathrm{e}}^{*}}\right).$$

Knowing the relationship between $n_{\mathrm{c,v}}$ and $m_{\mathrm{e,h}}^{*}$, we also have

$$\mu=E_c-\frac{1}{2}E_{\mathrm{g}}+\frac{1}{2}k_{\mathrm{B}}T\ln\left(\frac{n_{\mathrm{v}}}{n_{\mathrm{c}}}\right).$$

So

- **at $T = 0$, μ lies half-way between the valence and conduction bands**
- **as T increases, μ will move towards the band with the smaller effective mass (smaller density of states at the band edge)**
- **as the effective masses are generally of similar magnitude, μ does not move far from mid-gap**
- **note that**
  - **E_{G} is typically about 1 eV, which is large compared with $k_{\mathrm{B}}T$ which is 1/40 eV at room temperature**
  - **$\ln\left(\frac{m_{\mathrm{h}}^*}{m_{\mathrm{e}}^*}\right)$ is of order 1**
  - **so $E_{\mathrm{c}} - \mu$ is large compared with $k_{\mathrm{B}}T$**
  - **so we *are* in the nondegenerate regime**
- **note that the number of carriers varies as $e^{-E_{\mathrm{g}}/(2k_{\mathrm{B}}T)}$, *not* as**

$$e^{-E_{\mathrm{g}}/(k_{\mathrm{B}}T)}$$

– think of carriers being excited from the chemical potential, not from valence to conduction band.