Introduction to Part 4:   Semiconductors

1. **Conductors, Insulators, Semiconductors, and Semimetals**

The existence of an energy gap allows us to distinguish four types of materials.   But to do so, we need to recognize that the energy gap will separate the continuous energy band of the free electron into different bands separated by energy gaps at the zone boundaries.   We refer to the band that is filled at T=0K as the *valence* band, and the band above the valence band that is empty at T=0K as the *conduction* band.

Insulators: have a filled valence band separated by a LARGE energy gap from an empty conduction band.   Electrons in the valence band do NOT have an unfilled energy level close to their present energy amount, and so cannot accept small energy amounts, and so cannot carry a current.

Conductors: have a half-filled valence/conduction band, or have overlapping conduction and valence bands.   Thus the electrons CAN accept small energy amounts and move up to available energy levels, and so CAN carry a current.

Semiconductors: have a filled valence band and an empty conduction band separated by a SMALL energy gap.   Electrons in the valence band can be excited into the conduction band by thermal energy.   The higher the temperature, the more electrons will be able to get into the conduction band.   Thus, the conductivity should increase with temperature!

Semimetals: have a filled valence band that slightly overlaps a conduction band.

To give you some idea of the conduction electron concentrations in number per cm^3:

Cu (example of a metal, copper)	10^{23}
As (example of a semimetal, arsenic)	10^{20}
Graphite (semimetal)	10^{18}
Ge (semiconductor at room temperature)	10^{13} (this changes from 10^{10} at T=200K to 10^{13} at T=300K)

2. **Semiconductor materials**

Materials that are semiconductors are generally one of the following: a valence 4 material (Carbon, Silicon, Germanium), a compound of valence 4+4,   3+5,   or   2+6.   [Note: carbon in diamond form has a rather large energy gap (5.4 eV) and is more of an insulator than a semiconductor.]   Table 1 in Chapter 8 of Kittel 6th ed. lists some semiconductors along with their energy gaps.   Here are a couple for reference (at room temp of T=300K):   Si: 1.11 eV;   Ge: 0.66 eV;   GaAs: 1.43 eV;   CdSe: 1.74 eV.

3. **Optical absorption**

One of the main, most straightforward methods of determining the energy gap is by optical absorption: photons strike the material causing electrons to absorb the photon energy and jump up to the conduction band - but only if the photons have enough energy to lift the electrons past the band gap.   For photon energies below the energy gap (and hence for frequencies below a cut-off frequency, or wavelengths above a cut-off wavelength) the electrons cannot absorb the photon and so the material will be transparent to that light.   Hence we can get the energy gap by simply observing the cut-off frequency or wavelength for photo-conduction.

But in the absorption and emission process, both energy AND momentum must be conserved.   The photon momentum per energy is very small compared to that of the electron: for photons, E=pc   or   p=E/c; for electrons $E=p^2/2m$ or $p=[2mE]^{1/2}$.   **Example**:   for an energy of 1 eV = 1.6×10^{-19} J, the momentum of the photon would be 1.6×10^{-19} J / 3×10^8 m/s = 5.3×10^{-28} kg*m/s;   for the electron, the momentum would be $[2*9.1 \times 10^{-31}$ kg * 1.6×10^{-19} J$]^{1/2} = 5.4 \times 10^{-25}$ kg*m/s, or , for the same energy, the momentum of the electron is about 1,000 times greater than the photon.

If the bottom of the conduction band is directly over the top of the valence band in the E vs k plot for the material (remember that $p = h/\lambda = \hbar k$ so the E vs k plot is equivalent to an energy versus momentum plot), then the

electron in the valence band can absorb the photon energy and the very small amount of photon momentum and move up to the conduction band. This is called **direct** absorption. (In the above list, GaAs and CdSe are both direct.) However, in some semiconductor materials, the bottom of the conduction band is NOT directly over the top of the valence band (in the E vs k plots), so an electron at or very near the top of the valence band needs to lose or gain some momentum (more than that contained in the photon) before it can jump up from the top of the valence band to bottom of the conduction band. This can happen if a **phonon** is absorbed or created in the process since the energy of a phonon is low while its momentum is high:

$$\text{recall:} \quad v_{phonon} = f\lambda = \Omega/K, \quad v_{phonon} \ll c \quad \text{so} \quad \Omega_{phonon}/K_{phonon} \ll \omega_{photon}/k_{photon} \,;$$

$$\text{thus} \quad \Omega_{phonon} \text{ (and } E_{phonon}) \ \text{ can be } \ < \ \omega_{photon} \text{ (and } E_{photon}) \quad \text{while at the same time}$$

$$K_{phonon} \text{ (and } p_{phonon}) \ \text{ can be } \ > \ k_{photon} \text{ (and } p_{photon}). \text{ Thus } K_{phonon} \ \text{ can be } \approx \Delta k \text{ for electron while } \Omega \text{ is}$$

$$\text{small so} \quad \hbar\Omega = E_{phonon} \ \text{ is small compared to } \ \hbar\omega = E_{photon}.$$

This is called **indirect** absorption. (In the above list, Si and Ge are both indirect.) But this added condition will make the absorption less probable. Thus the absorption process near the energy gap is less probable than in the direct absorption process. However, if the incident photon is higher in energy, then the electron can jump directly from the valence to the conduction band and the phonon is no longer needed, and so the absorption probability will be much higher. See figures #4 & #5 in Chapter 8 of Kittel 6th ed. or https://warwick.ac.uk/fac/sci/physics/current/postgraduate/regs/mpagswarwick/ex5/phonons/indirect_absorption/ . Note that in both references, this is not a spatial plot, but rather a plot of energy versus wavevector (ε vs k) and hence energy versus momentum. The excel spreadsheet linked at the end of Part 3 shows the energy gap near the zone boundary and is an example of an indirect gap.

One way to think about this classically is that the photon has zero rest mass and only a tiny moving mass ($E=mc^2$), so it can have only a tiny momentum; the electron has rest mass and so can have more momentum than a photon of the same energy; and the phonon has essentially the mass of the atoms and so can have a large momentum compared to an electron of the same energy: classically, $KE = \frac{1}{2}mv^2 = p^2/2m$, or $p=[2mKE]^{\frac{1}{2}}$ -- for the same energy, the bigger mass will have the more momentum.

4. Energy gap and electron density

We can also determine the energy gap by looking at the electron density versus temperature, n(T). For semiconductors at absolute zero (T=0K) all the electrons should be in the lowest possible state which means that the valence band will be filled and the conduction band will be empty, and this means that the material should act as an insulator. However, at higher temperatures, more energy is available to the electrons in the valence band, and so there should be a higher probability for some of the electrons near the top of the valence band to use some of that energy to jump up to the bottom of the conduction band and hence increase n, the electron density in the conduction band. But the bigger the energy gap, the harder (and so less probable) it is for the electrons to jump up to the conduction band. Thus by measuring the electron density as a function of temperature, we should be able to get some idea of the energy gap. (We will be more quantitative about this later.)

The electron density, n, can be determined by measuring the conductivity, σ, [recall that $\sigma = ne^2\tau/m$]. The electron density can also be determined from the Hall coefficient: $R_H = -1/ne$, or $n = j_x B_z/(-eE_y)$.

Note: as we mentioned before, for some semiconductors, the Hall coefficient turns out to be positive (instead of negative). This indicates that there are positive charges carrying the current. But how can this be? That is our next topic.

Note: We will run into relations between electron energies, ε, and electron wavevectors, k, often in this part. Keep this in mind as we run through derivations.