

## Topic 3: Energy Band Diagrams, Intrinsic, and Extrinsic Semiconductors

### Semiconductor Types:

Now that we have a concrete definition of what a semiconductor is, let's take a look at some. We start with two families of semiconductors, broken into **elemental semiconductors** and **compound semiconductors**.

**Elemental semiconductors are single elements that exhibit semiconductor properties.** Examples of such elements are silicon (Si) and germanium (Ge). It often surprises people that the first transistor was made from germanium instead of silicon. Likewise, **compound semiconductors are compounds that exhibit semiconductor properties.** If there is more than 1 element, it falls under the compound classification. I know that these definitions may seem overly simplistic, but they are necessary. Examples of such semiconductors are:

- Gallium Arsenide (GaAs)
- Indium Phosphide (InP)
- Gallium Antimony (GaSb)
- Aluminum Arsenide (AlAs)
- Aluminum Gallium Arsenide (AlGaAs)

It is worth noting that phosphorous (P), antimony (Sb), and arsenic (As) are commonly donor elements; with each being a group 5 element. We can even combine these compounds to enhance certain properties. For example, AlGaAs is a compound semiconductor with very high carrier mobility compared to silicon; do not worry, we will discuss mobility later in the course. Our study will be almost entirely with Silicon with either Boron or Phosphorous as a dopant.

Of these element and compound semiconductors, they fall into two more families: **intrinsic** and **extrinsic** semiconductors.

- An **intrinsic semiconductor** is a semiconductor that has not been doped or doped in such a way that no net charge carriers have been introduced into the material.
- An **extrinsic semiconductor** is a semiconductor that has been doped, changing the net concentration of charge carriers.

These definitions are quite qualitative, but we will elaborate on them more throughout this course. But first, let's do a thought experiment. If I dope a piece of silicon with exactly 10 holes and 10 electrons, have I changed the number of net charge carriers? These 10 holes and electrons will behave identically to the electron-hole pairs (EHP) formed by a broken covalent bond. Therefore, we can have an intrinsic semiconductor either by doing nothing to it, doping-wise or by doping with equal quantities of both acceptor and donor ions.

## Energy Band Diagrams (EBD):

The Energy Band Diagram is a powerful tool expressing the energy states which electrons can occupy in the lattice. Provided in Fig. 1 is the standard example of the diagram, but we need to define some terms first.

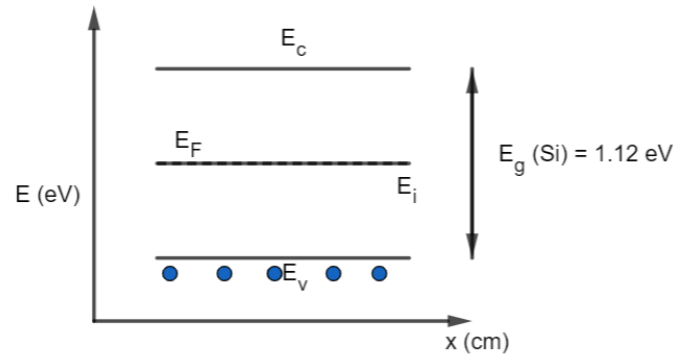


Figure 1: Energy Band Diagram for Silicon at 300 K.

The vertical axis represents the energy level of a given state that an electron can occupy. If an electron were floating around in a vacuum it would be at an extremely high energy state, whereas an electron in the first shell of an atom exhibit a very low energy state. Energy can be synonymous with the ability to move. If an electron is in a vacuum, there is nothing to stop it if it were moving, hence it has higher energy than a fixed electron in the lattice. The horizontal represents the length of the piece of semiconductor under study. Note that we are on the electron level, so we need to put ourselves in the mindset of quantum mechanics. These electrons within the lattice must occupy discrete levels of energy, hence there must be some vertical separation between energy states; visualized as horizontal lines.

Now for some terminology:

- **Band:** A set of energy states which a charge carrier may occupy.
- **Valence level:** The energy level at the boundary of the valence band.
- **Conduction Level:** The energy level at the boundary of the conduction band.
- **Valence Band:** The set of energy levels where electrons are unable to conduct a current. This band includes the valence level,  $E_v$ , and all states below it.
- **Conduction Band:** The lowest energy level that an electron may begin to conduct. This represents a covalent bond being broken and the electron is now free to move within the lattice. This band includes the conduction level,  $E_c$ , and any levels above it.
- **Bandgap Energy,  $E_g$ :** The energy difference between the conduction and valence band. This energy represents the amount of energy an electron needs to gain to break free of the host atom and become a free electron. Bandgap energy is commonly used to categorize a material as an insulator, semiconductor, or conductor.
- **Intrinsic Level,  $E_i$ :** The midpoint between the conduction and valence bands. This point where the probability of an electron occupying this state is 50% in an **intrinsic** semiconductor.

- **Fermi Level,  $E_F$ :** The point where the probability of an electron occupies this state is 50% in an **extrinsic** semiconductor.
- **Forbidden Zone:** The region in between the conduction and valence band where there are no energy states for an electron to occupy. A carrier is either in the conduction or valence band.

For a given material, the bandgap energy, valence, conduction, and intrinsic energy levels are fixed. The freedom we have is over the Fermi level. I will discuss the mathematics in a separate section, but the Fermi level is a function of doping quantities. If we have an N-type semiconductor the Fermi level will be closer to the conduction band. Inversely, a P-type semiconductor will have its Fermi level closer to the valence band. This shift in level occurs because doping introduces either holes or electrons. If we have more electrons within the lattice, the probability of finding an electron toward the conduction band must be higher. This is also true for P-type semiconductors, where the probability of finding a hole is increased implying the Fermi level is closer toward the valence band.

Energy Band Diagram Simulation:  
<https://www.geogebra.org/m/ztcnp2bm>

Above is a link to an interactive simulation I have made to provide a more intuitive feeling behind the Energy Band Diagram. In this simulation, you will see how the electrons travel between energy states and will be able to change the doping level to see how it influences both the intrinsic and Fermi levels, respectively.

As mentioned earlier, bandgap Energy is a convenient method of determining whether a material is an insulator, conductor, or semiconductor. The figure below visualizes the types of energy band diagrams for these three material families.

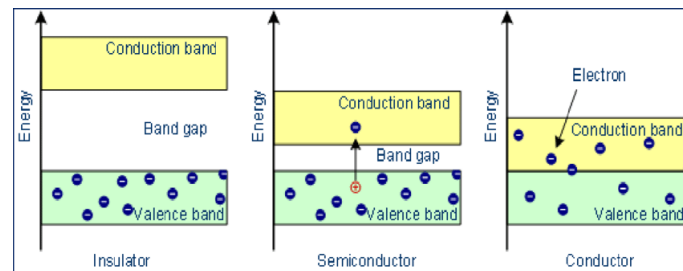


Figure 2: Energy band diagrams for insulators, semiconductors, and conductors.(Ali)

The difference in diagrams is minor between insulators and semiconductors. The primary difference is only the size of the bandgap. In silicon, the bandgap energy is approximately 1.12 eV, which is much lower than the 5.5 eV required for diamond. Every non-conductor material has a bandgap energy as a material property but even closely related elements may be different. For example, silicon dioxide,  $\text{SiO}_2$ , has a bandgap of approximately 9 eV. For our discussion, bandgap energies below 2 eV may be considered semiconductors.

It would seem that energy band diagrams encode some useful information for us, but what about conductors? The right-most diagram in Fig. 2 shows an overlap between the conduction and valence band. This overlap is what gives conductors, specifically metals, such high conductivity. Recall from chemistry that metals have a “sea of electrons”, this is that sea. Metals do not bond in the same way as non-metals or metalloids, so their electrons are free to travel

between bands and easily conduct a current.

## Fermi-Dirac Distribution:

I mentioned in the last section this idea of the probability of an electron being at some state. This probability is expressed with the Fermi-Dirac distribution, named after the physicists Enrico Fermi and Paul Dirac, and gives us a way of quantifying how many electrons are in a given energy state. We will not delve into the derivation of this distribution, only its resulting observations. The key observations of this distribution are that the distribution is heavily dependent on temperature and outputs a probability. We would assume that temperature is proportional to the probability of finding an electron. If the temperature is quite hot, then more bonds will be broken and hence more electrons will be in the conduction band; higher energy states. If the temperature is quite cold then there will not be sufficient energy to break bonds, leaving the electrons in lower energy states.

Quantitatively, the Fermi-Dirac Distribution is given by:

$$P\{E\} = \frac{1}{1 + e^{\frac{E-E_F}{kT}}} = \frac{1}{1 + \exp(\frac{E-E_F}{kT})} \quad (1)$$

Where, E is a given energy level, k is Boltzman's constant ( $k = 1.381 \cdot 10^{-23} \frac{J}{K} = 8.617 \cdot 10^{-5} \frac{eV}{K}$ ), and T is the temperature in Kelvin. If we use the Fermi Level as the input, the exponential term evaluates to  $e^0$ , giving us the probability of 1/2 as mentioned earlier.

We often visualize this distribution with the following plot. Note that the horizontal axis is normalized with respect to  $E - E_F$ , but still applies to energies above and below the Fermi level.

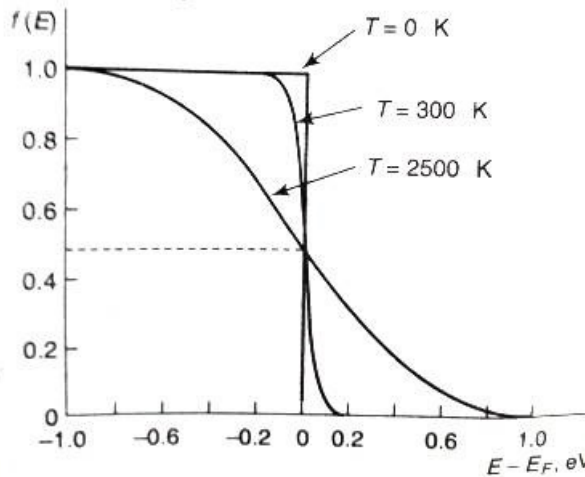


Figure 3: The Fermi-Dirac distribution over several temperatures. (ElProCus)

If we plug 0 K into Eq. (1) the exponential term tends toward infinity. Implying that the denominator of this fraction will grow towards infinity, driving the probability toward 1. Intuitively we know this must occur because there is approximately zero energy, or motion, in a particle at absolute zero. Hence the probability of finding an electron at any energy level below 0 eV is almost guaranteed. As temperature increases, the distribution “rounds out” and the probability of finding higher energy electrons is greater. Again, this increase in probability for energies above 0 eV is due to the thermal energy in the system.

## Boltzmann constant conversion:

Instead of memorizing these two values for Boltzmann's constant you can always convert from one unit to another. Converting from eV to Joules requires multiplying by the charge of the electron. Inversely, converting from Joules to eV requires dividing by the charge of the electron. I encourage you to do the unit analysis to confirm this fact for yourself.

## Energy State Density (Optional):

This section is not heavily emphasized in the course, however, I recommend reading through this to get a deeper understanding of later equations. One of the terms discussed in the next section is the density of energy states. This idea of energy states being spread over a range seems abstract, and it is. If we were to take a magnifying glass and look at the conduction and valence bands we would see many, many energy levels. The idea of calling this set a band is to make it seem like a continuous structure. However, quantum mechanics tells us that these levels are discrete, separated by some finite energy.

I mention this because there is a stark difference between looking at a silicon atom and the silicon lattice. Let's do a thought experiment. Imagine I have a single silicon atom. We know that it has an orbital notation of  $1s^2 2s^2 2p^6 3s^2 3p^2$ . Each of these terms corresponds to an energy level of the atom. Any two atoms will have the same structure of energy levels. Now imagine if we took a second silicon atom and forced it very close to the first atom such that neither of them could move. What would happen to their energy levels? We know that a double bond is formed but there is much more happening beneath the valence shell.

As more and more atoms are forced together, as in the forming of a solid crystal, the orbitals are compressed together. We still have discrete energy levels, but the 3s orbital of one atom cannot physically be in the same space as another atom's 3s orbital; they will repel each other. Therefore as the number of atoms increase the energy levels are compressed into what we call a band. You might recognize this figure from the textbook, and it helps to illustrate this idea.

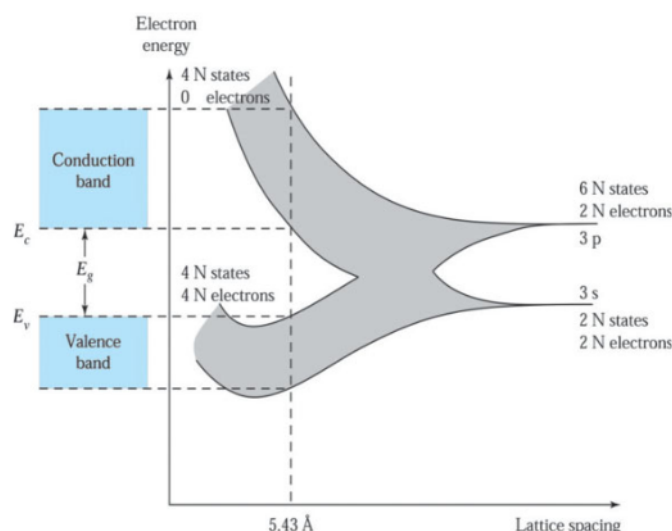


Figure 4: Splitting of orbitals into conduction and valence bands.

On the far-right side of the figure, we have the two lines corresponding to the 3s and 3p orbitals. The cramming of atoms together into the lattice is represented by moving left across

the horizontal axis. As more atoms are in the same region of space, the orbitals are compressed into the conduction and valence bands. You can imagine within the dark grey band many energy levels very close to one another. The value of 5.43 Angstrom ( $\text{\AA}$ ) is noted because it is the dimension of the unit cell for silicon. Meaning individual silicon atoms are separated on the order of about 2-3 Angstrom. In terms of recognized units,  $1\text{\AA} = 1 \cdot 10^{-8}\text{cm}$ , or  $1\text{\AA} = 0.1\text{nm}$ . The actual number for the density of states is found from the Fermi-Dirac distribution, but that is beyond our scope.

## Definitions:

Before we can start a more quantitative discussion, we need to define several terms used throughout the remainder of the course. I will use the notation of (Si) to indicate a parameter for silicon at 300 K. These various material parameters will change with the semiconductor material.

- Effective Mass: The equivalent mass of a particle constrained within a solid.
- $m_o$ : The mass of an electron in a vacuum.  $m_o = 9.11 \cdot 10^{-31}\text{kg}$
- $m_n$ : The effective mass of a hole.  $m_n(\text{Si}) = 0.19m_o$
- $m_p$ : The effective mass of the electron.  $m_p(\text{Si}) = 0.49m_o$
- $N_c$ : The density of states within the conduction band.  $N_c(\text{Si}) = 12\left(\frac{2\pi m_n kT}{h^2}\right)^{\frac{3}{2}}$
- $N_v$ : The density of states within the valence band.  $N_v(\text{Si}) = 12\left(\frac{2\pi m_p kT}{h^2}\right)^{\frac{3}{2}}$
- $n$ : Free electron concentration;  $\frac{\#ofelectrons}{\text{cm}^{-3}}$ .  $n = N_c \cdot e^{-\frac{E_c - E_F}{kT}}$
- $p$ : Hole concentration;  $\frac{\#ofholes}{\text{cm}^{-3}}$ .  $p = N_v \cdot e^{-\frac{E_F - E_v}{kT}}$

Where  $h$  is Planck's constant,  $h = 6.628 \cdot 10^{-34} \frac{\text{J}}{\text{Hz}}$ . Please be aware of the negative attached to each exponential term. If we analyze these two equations for  $n$  and  $p$ , we see that it depends heavily on the Fermi level and either the valence or conduction energy levels. If the Fermi level is midway between the conduction and valence band, then the exponential terms are equal, implying the density of energy states heavily influences the number of carriers. Ideally, the fraction in the exponential will be negative, since the Fermi level is typically bounded between the conduction and valence bands.

Another example of these equations is if the Fermi level is not in the center of both bands. For example, if the Fermi level is closer to the conduction band, the difference  $E_c - E_F$  will be smaller than when  $E_F$  is at the midpoint. If we reorder the equation for  $n$ , we see that  $n$  will become larger because the denominator is decreasing:

$$n = \frac{N_c}{e^{\frac{E_c - E_F}{kT}}}$$

If the Fermi level is closer to the conduction band, it is by definition that the probability of an electron in the conduction band is larger. The same train of thought applies for the hole concentration. A Fermi level closer to the conduction band increases the value of  $E_F - E_v$ , driving the denominator larger, hence decreasing the hole concentration.

We can make a similar argument with temperature. For a fixed Fermi, conduction, and valence level increasing the temperature decreases the argument of the exponential. A smaller argument causes both  $n$  and  $p$  to increase. I encourage you to walk through these steps if the Fermi level is closer to the valence band.

## Intrinsic Semiconductors:

With all of these definitions, we may ask ourselves, “what next?” We needed to establish these definitions to further our intuition of the mechanics behind semiconductors. Now we can make our first observation, and subsequent contradiction, and analyze it quantitatively.

If we have a piece of silicon with **zero** doping, what is the concentration of holes and electrons? Since the silicon is not doped, we know that the Fermi level is midway between the conduction and valence band. We could find the density of states for both bands, and calculate the answer but this is not necessary. We know that without doping, the only electrons and holes in the lattice are from broken covalent bonds. Each time a bond breaks, an electron, and hole are released into the lattice; commonly called an electron-hole pair. Therefore,

$$n = p \quad (2)$$

This equation will be our starting point for nearly every problem involving intrinsic semiconductors. Some examples could be determining the density of energy states without using lengthy expressions based on physical constants. After we know the densities, we could determine the bandgap energy. I will not go too detailed with these equations right now, but this is an incredibly important result which we will use often.

However, a question we should ask if we can show this equality quantitatively. We have expressions for  $n$  and  $p$ , in terms of the density of states, so let's explore this. If  $n$  and  $p$  are equal, then we have,

$$\begin{aligned} n &= p \\ N_c \cdot e^{\frac{E_c - E_F}{-kT}} &= N_v \cdot e^{\frac{E_F - E_v}{-kT}} \\ \Rightarrow \frac{N_v}{N_c} &= e^{\frac{E_c - E_F - E_F + E_v}{-kT}} \\ &= e^{\frac{E_c + E_v - 2E_F}{-kT}} \end{aligned}$$

Assuming the Fermi Level is midway between the conduction and valence bands,  $E_F = \frac{E_g}{2} = \frac{E_c + E_v}{2}$ .

$$\begin{aligned} \frac{N_v}{N_c} &= e^0 = 1 \\ \therefore N_v &= N_c \end{aligned}$$

At this point we reach an interesting observation. We believe that the Fermi level equals the intrinsic level when the semiconductor is not doped. Being in the middle of the bandgap, implying that the difference,  $E_c - E_F$ , and  $E_F - E_v$  must be equal. The  $kT$  term in the exponential must

also be equal because it is the same material, and is assumed to be at the same temperature throughout it. This leaves us with the claim that the  $N_c = N_v$ , which cannot be true from our definition involving physical parameters earlier. Even in terms of the bandgap energy, we arrive at a conflict.

There is a direct cause and effect of electron-hole pair in an intrinsic semiconductor. Implying we know that  $n$  and  $p$  must be equal. Hence there must be more going on in terms of the bands are composed, how we model electrons and holes within them, or the Fermi level might slightly off of the midpoint. This question is not in the scope of this course, but it gives an idea on the types of problems we will discuss. The value you get from a formula does not matter, what does matter is if you can reason and explain the device physics. Regardless, I encourage you to think about and debate possible explanations for this conflict.

## Conclusion:

I am ending this set of lecture notes here, in hopes to prevent this file from becoming too large. The next set of notes will start delving into the mathematics and observations we can derive from these definitions and equations. It is essential to know what each of these terms are, not just as a definition, but as a physical concept. Understanding what these terms represent will ease our next discussions, as well as provide a deeper understanding of why this is the way nature behaves.



## References

[Ali] Ali, J. K. Reasearch Gate. [https://www.researchgate.net/figure/Figure-2-12-The-energy-gap-and-distances-among-the-conductor-semiconductor-and\\_fig9\\_339089695](https://www.researchgate.net/figure/Figure-2-12-The-energy-gap-and-distances-among-the-conductor-semiconductor-and_fig9_339089695). [Online; accessed 28-August-2021].

[ElProCus] ElProCus. <https://www.elprocus.com/fermi-dirac-distribution-energy-band-diagram-an>  
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