1 Representations of Charge Carriers in Semiconductors

To model devices, we require a language by which to discuss charge carriers and their properties in semiconductors which is relevant to the operation and design of devices. There are two useful phenomenological descriptions of charge carriers in semiconductors: the bond model and the band model. For modeling devices, we typically use the band model, although the bond model is useful as a conceptual tool.

We will focus exclusively on the carrier properties at equilibrium. Equilibrium describes the state of rest of the unperturbed system. At equilibrium there are no external potential differences, magnetic fields, pressure or temperature gradients acting on the semiconductor. Additionally, all quantities of interest do not vary with time.

A caveat is that many of the equations presented herein will be provided without justification. A thorough treatment of quantum mechanics and statistical mechanics would be required, which is beyond the scope of the course. Here we focus on the main results, how to interpret and apply them.

1.1 Bond Representation

1.1.1 Silicon Atom

Silicon has an atomic number of 14, therefore it has 14 electrons associated with the atom (Figure 1). The electron configuration is $1s^22s^22p^63s^23p^2$. Based on the electron configuration, the 14 electrons occupy 3 distinct energy levels ($n = 1, 2, 3$). Each of these electrons do not contribute equally in bonding. Some electrons are so strongly bound to the atomic core that they don’t interact much with anything else ($n = 1, 2$). We refer to these as core electrons. With the binding energy being a measure of the interaction strength between an electron and the nucleus, we say that the binding energy is large. Silicon has a total of 10 core electrons. The remaining 4 electrons are loosely bound to the atomic core. We refer to these electrons as valence electrons. Valence electrons are important as they dictate chemical reactions and bonding.

1.1.2 Silicon in the Solid State

Now that we have a model of the Silicon atom, we can talk about the solid state. We know that silicon bonds together in a covalent network of bonds. We also know that the valence electrons are all...
that matter with respect to bonding. Therefore, we can visualize what is expected, conceptually, by bringing silicon atoms closer together until bonding occurs by looking at Figure 2. When covalently bonded, silicon completes its octet, having 8 neighboring electrons, 4 of which have been contributed by each of the neighboring silicon atoms. This is what is meant by a covalent bond, that is, electrons are shared equally among its neighbors.

### 1.1.3 Carrier Motion in the Bond Model

When we first attempt to model charge carriers in a semiconductor, we begin by ignoring the many details regarding bonding and the fact that there are positively charged atomic cores that interact with these electrons. These details are certainly important when seeking to obtain accurate quantitative agreement to experiment, but are unnecessary for a basic qualitative description. It turns out that most of the aspects of simple device behavior can be described by treating charge carriers in semiconductors as non-interacting gases of particles. This is the so-called Boltzmann
limit that we will discuss later in the class.

Focusing on the outermost valence electrons, in our simplistic view, charge transport occurs by a repetitive sequence of breaking and forming silicon bonds (Figure 3). This process requires energy. In a pure semiconductor at a temperature of absolute zero kelvin, free electrons and free holes do not exist because all bonds are occupied by electrons. In this case, the energy required to free an electron from a bond, thus creating an electron/hole pair is the bandgap energy, which we will discuss later and at greater length in future lectures. The energy needed to create electron/hole pairs typically comes from either an increase in lattice temperature (i.e. phonon absorption) or through absorption of light.

1.2 Band Representation

Although the bond representation is useful in visualizing charge carriers spatially in relation to other silicon atoms and each other, in crystalline solids we rarely care about spatially dependent behavior, at least within the bulk of a semiconductor, since it is assumed that the semiconductor is an infinite periodic crystal. Instead, we are usually interested in the energy of carriers and information which can be derived from their energy – density of states, carrier concentration, scattering rates, absorption coefficient.

Fundamentally, when talking about microscopic particles such as electrons, it is necessary to use quantum mechanics, which dictates that we cannot draw simple classical diagrams that explicitly localize a carriers position and momentum. More accurately, we can discuss carrier energies. The energy levels accessible to electrons differ as we move from an isolated silicon atom to a covalently bonded silicon crystal. Roughly speaking, as silicon atoms are brought closer and closer together, the isolated atomic energy levels split into bands (Figure 4). At some position, the energy is a minimum, this is referred to as the lattice constant of the material and defines the distance between neighboring silicon atoms.

What does this all mean? The main takeaway is that, in the solid state, the energy levels available for electrons are modified from that of the isolated case. Unlike the electrons in the isolated
atoms, electrons occupying bands can no longer be associated with any one particular silicon atom. To put it differently, every electronic state we speak of in a crystal is associated with the entire crystal as a whole and not any individual silicon atom. Thus, at any position in space, the electronic energies are the same, they are spatially-invariant!. We represent this visually using energy band diagrams or just band diagrams (Figure 5). In a band diagram, the conduction band, $E_C$ is the lowest unoccupied energy level above the valence band. The valence band, $E_V$ is the highest occupied energy level. The bandgap energy is the energy difference between the conduction and valence bands.

$$E_G = E_C - E_V$$  \hspace{1cm} \text{(Bandgap Energy)}

To visualize carriers in bands, we ignore all of the electrons in the occupied states. These form the so-called ground state of the system and are not relevant for electronic considerations with regard to carrier motion. Why? How can no current flow due to the occupied ground state electrons? The answer is simple, just as water cannot slosh around in a completely filled container, no electronic current can flow in a completely filled valence band. Thus, from here on, electrons will be used to describe de-localized charge carriers in the conduction band.

In a pure semiconductor, the creation of an electron necessarily creates another type of charge
carrier called a **hole**. Holes are the absence of an electron, yet can move around freely just like an electron. Strictly speaking, **holes** describe the absence of a localized electron (i.e. valence band electron). Since they are the absence of an electron, the region in which they occupy has a net positive charge (less negative charge is equivalent to more positive charge). The simple analogy of a hole is an air bubble in a container of liquid. The bubble can move around freely as though it were a particle, despite the fact that it is the absence of a particle (or liquid in this case). Eventually, the language of charge carrier motion will be equally interchangeable between that of electrons and holes. We will think of them together along very similar physical terms.

### 1.3 Doping

So far, we’ve restricted our discussion of charge carriers to pure semiconductors. Pure semiconductors are referred to as **intrinsic**, meaning there are no **impurities**. Impurities can be intentionally added or unintentionally incorporated into the semiconductor during processing (Remember our discussion on purification?). Typically, a starting purity of $1 \times 10^{15}$ cm$^{-3}$ is achieved for silicon wafers. Compare this to the atomic density of silicon, $5 \times 10^{22}$ cm$^{-3}$. This is greater than ppm (parts per million) purity and is necessary for electronic grade silicon. When impurities are added intentionally, we refer to this as **doping**. Doping thus refers to the addition of impurities to either raise or lower the concentration of electrons or holes in a semiconductor. A **dopant** is an atom that has a different number of valence electrons from the host atom (e.g. silicon). When a dopant atom replaces a host, there will be either a net increase or decrease in electron concentration.

- Dopants that have a higher number of valence electrons than the host atom are called **donors** (e.g. As, P, Sb).
- Dopants that have a lesser number of valence electrons than the host atom are called **acceptors** (e.g. B, Al, Ga, In).

We can visualize doping via the bond model and band model as shown in Figure 7. We can also express the doping process in the language of solid state chemistry.
2 Carrier Modeling

Bands aren’t just simply represented in energy vs space band diagrams. This thinking originates from a deeper concept of the overall band structure, derived from Quantum Mechanics. For band diagrams, we typically just draw the lowest unoccupied level as the conduction band $E_C$ and the highest occupied level as the valence band, $E_V$. Band structures are much more complex, but to use them requires a basic understanding of quantum mechanics.

2.1 A Note on Quantum Mechanics

Carriers are accurately modeled using quantum mechanics. Schrodinger’s equation describes the steady-state and temporal evolution of microscopic particles (e.g. electrons and holes). For this class, we will present the main result, but list a few useful equations here.

For stationary states (time independent), we use the time-independent form of the Schrodinger equation.

$$\hat{H}\Psi = E\Psi \quad \text{(Time Independent Schrodinger Equation)}$$

This includes an operator, $\hat{H}$, known as the Hamiltonian, which includes a kinetic energy, $-\frac{\hbar^2}{2m}\nabla^2$ and potential energy $V(\vec{r})$ component.

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) \quad \text{(Hamiltonian Operator)}$$

This is a linear system of equations that reduces to an eigenvalue, eigenvector problem. The Hamiltonian is a matrix operator and the energies are energy eigenvalues. These energies are the same energies we are interested when discussing visual representations of carriers in the form of band diagrams. They are the allowed energies that an electron can occupy in a crystal.
2.2 Nearly Free Electron Model

It can be shown that for a free electron in a vacuum, a new quantity emerges, known as the wave vector, \( k \) which is related to the momentum of an electron. This can be proven by solving Schrodinger’s Equation for a free-electron in vacuum (\( V(\vec{r}) = 0 \)). Without going through the details, the result is a wavefunction of the following form, which is known as a plane wave.

\[
\Psi(\vec{r}) = Ae^{-i\vec{r} \cdot \vec{k}} \quad \text{(plane wave)}
\]

The dispersion relation is an expression relating the electron wave vector to its energy eigenvalues. In the case of an electron in a vacuum, the dispersion relation is parabolic.

\[
E = \frac{\hbar^2 k^2}{2m_e} \quad \text{(dispersion relation)}
\]

The wave vector, \( k \), appearing in the dispersion relation is a direct result of the translational symmetry in the crystal.

\[
k = \frac{\sqrt{2m_eE}}{\hbar} \quad \text{(wave vector)}
\]

This is fundamentally related to the fact that the Hamiltonian is spatially-invariant (i.e. it does not depend on spatial position).

For our simple example of a free electron in a vacuum, the wave vector \( k \), directly corresponds to the carrier momentum. For electrons in a crystal, the wave vector corresponds to the crystal momentum. Thus, the crystal momentum is the conserved quantity.

The main takeaway from this is that, when discussing the electronic energies, we need not discuss spatial dependencies, but we should absolutely discuss wave vector or momentum dependencies. The full wave vector vs energy dependence is referred to as a band structure as we discuss in the following section.

2.3 Band Structures

A complete discussion of band structures is well beyond the scope of this course. Instead, for our purposes, we discuss the main results as they are applicable to understanding device behavior. As shown in Figure 8, the band structures can vary substantially for different materials. GaAs, for example, is a direct bandgap semiconductor. Si, on the other hand, is an indirect bandgap semiconductor.

- **direct semiconductor**: No additional momentum is required for band-to-band transitions.
- **indirect semiconductor**: Additional momentum is required for band-to-band transitions. The additional momentum usually comes from a single or multiple phonons.

Without explicit knowledge of this, through a complete calculation of the band structure, we would be trying to optimize silicon LEDs not knowing it would forever be an uphill battle!

2.4 Effective Mass

From the Nearly Free Electron Model, we approximate the electron energies using a modified mass. This mass is referred to as an effective mass, since it is a construct we impose on actual electrons.
Figure 8: Comparison of a direct (GaAs) and indirect (Si) semiconductor in terms of band structure. As shown, the red arrow indicates the absorption process. For a direct semiconductor, light is absorbed by an electron in the valence band. For an indirect semiconductor, light is absorbed through the absorption of a photon and a phonon.

to be self-consistent with the assumption that carriers are free. To add more complication, it turns out that there are multiple types of effective masses, although for this class we only focus on two types:

- **Density of States Effective Mass**: $m^*_{DOS}$
- **Conductivity Effective Mass**: $m^*_{CON}$

### 2.4.1 Density of States Effective Mass of Silicon

The *density of states effective mass* is essentially a defining relation between a simple spherical Fermi Surface (which is the same in any $k$ direction) and the actual Fermi Surface (which depends on the $k$ direction).

The density of states effective mass of Silicon is given by (See Neamen 4th Edition, Appendix F for a derivation):

$$m^*_{DOS,e} = 6^{2/3} \left( (m^*_t)^2 m^*_l \right)^{1/3}$$

When we discuss density of states in the next lecture, we will see where this comes from clearly. For now, take my word for it!

### 2.4.2 Conductivity Effective Mass of Silicon

The *conductivity effective mass* is typically used for transport-related calculations. Like the density of states effective mass, it will essentially be a defining relation, but with a new twist. We
have to do a bit of **averaging** in momentum space in order to arrive at a meaningful result. Why?

- **The short answer:** normal scattering processes randomize the carrier momentum such that *on average* a carrier will *see* all possible momentum states consistent with its energy.

- **The long answer:** When a carrier moves in a semiconductor, if it is in thermal equilibrium with the semiconductor lattice (i.e. phonons), then it will be constantly colliding with the phonons and exchanging energy with them in order to maintain equilibrium. This process is to ensure that the electron is in **thermal equilibrium** with the lattice and therefore has the same temperature $T_{\text{electron}} = T_{\text{lattice}}$. Each collision sends the electron whizzing in a particular direction that is mostly random. This leads to a random velocity component known as the **thermal velocity**. When we apply an electric field, the **drift velocity** of a carrier on average is in the direction of the applied field, *but it is not exclusively in that direction at all times*, otherwise it would not be in thermal equilibrium with the lattice! Thus, the drift velocity is superimposed onto the thermal velocity to make up the total carrier velocity. Now, we know that a moving carrier has kinetic energy associated with translation. The question arises as to how to associate that energy with the different axes of translation (i.e. x, y, z). We could associate the energy exclusively with the axis that is in the direction of the applied field, but that seems to contradict the previous equilibrium argument. So what do we do? In practice, we distribute the energy equally among all of its translational axes. To do so formally is to take a **thermal average** over all possible translations. In essence, we neglect the contribution to the translational momentum due to the drift velocity and only use the thermal velocity. Strictly speaking, this is an approximation that is only valid at low electric fields and/or low electron mobility systems. For example, assuming an electron mobility of 1400 cm$^2$ V$^{-1}$ s$^{-1}$ and an electric field of 1 kV cm$^{-1}$, the drift velocity is approximately $1 \times 10^6$ cm s$^{-1}$ which is about an order of magnitude smaller than the thermal velocity at room temperature ($1 \times 10^7$ cm s$^{-1}$). This condition is typically referred to as **low-field transport**, and is the starting point for understanding basic transport physics in semiconductors, since equilibrium conditions apply.

Given these considerations, it can be shown that the conductivity effective mass for electrons in silicon, is given by (See Neamen 4th Edition for derivation):

$$m_{\text{cond},e}^* = \frac{3}{\frac{2}{m_t} + \frac{1}{m_l^*}}$$