

XI. ELECTRONIC PROPERTIES (DRAFT)

11.1 THE ALLOWED ENERGIES OF ELECTRONS

Over the next few weeks we are going to explore the electrical properties of materials. Our starting point for this investigation is simply to ask the question, “Why do some materials conduct electricity and others don’t?” It should come as no surprise that the answer to this question can be found in structure, in this case the structure of the electrons density, which in turn is related to the electron energies and how these may change when a material is subjected to an electrical potential difference, i.e., hooked up to a battery.

Up until the early part of the twentieth century it was thought that electrons obeyed the laws of classical mechanics, and, just like everything we could observe at that time, an electron could be made to move in a way that it would take on any energy we wished. For example, if we want a ball with the mass of 0.25 kg to have a kinetic energy of 0.5 J, all we need do is accelerate it to exactly 2 m/sec. If we want its kinetic energy to be 0.501 J, then we need to accelerate it to 2.001999 m/sec. If we want it to have a kinetic energy of X , it must have a velocity of exactly $(8X)^{1/2}$. According to the principles of classical mechanics, there is nothing that prevents us from doing this.

However, it turns out that these principles are not quite right, under some circumstances the ball cannot be made to take on any energy we desire, it can only possess specific energies, which we often denote with a subscript, E_n . We would then describe our ball by its energy state, sometimes written as ψ_n . If I told you a ball was in state ψ_{10} , you would know that it was in its 10th lowest allowed energy and moving with velocity, momentum, etc., necessary for the ball to have this energy. If I wanted to increase its energy, I would do so by exciting it to another energy state, say ψ_{11} . And because energy is conserved, I would need to add a quantity of energy $\Delta E = E_{11} - E_{10}$ to “move” the ball from one state to another. To move the ball from any initial state to any final state will always require $\Delta E = E_f - E_i$; ΔE is called a quantum of energy and it is impossible to add or remove energy from the ball if it does not satisfy this “quantum” condition.

In the world we observe, e.g., baseballs in ball parks, people walking on sidewalks, cars on streets, energy quanta are too small to observe. (Energy quanta are not required to be small, there can be very large quanta. The important point is that the word quanta does not imply small, rather it refers to a specific quantity of energy.) However, in the world of electrons moving in crystals, the quantum world becomes obvious.

One of the ways energy is added to a crystal is by exciting the electrons in the crystal from one of its allowed energy states to another. For example, we can do this by shining light on a crystal. The photon of light may be absorbed by an electron in the crystal causing it to move from one energy state to another, but only if the energy of the photon exactly matches the energy difference between the two states. If it doesn't, the photon will pass right through the crystal. This is why some crystals, like diamond, are transparent to visible light, and others, like copper, are not.

There are two classes of solids, metals and nonmetals. Metals conduct electricity, nonmetals do not. What makes a solid a conductor is that the energy necessary to excite electrons is immeasurably small, essentially zero. On the other hand, in nonmetals this excitation energy is substantial. Depending on its magnitude, nonmetals are further divided into classes as insulators or semiconductors—more on that later.

For both metals and nonmetals, the allowed energies for electrons come in what we call bands, which are often pictured as in Figure 11-1. The allowed energies for electrons in some regions are so close together that they form a continuum called a band. Between these bands are forbidden areas, also called energy gaps, where an electron cannot possess the corresponding energy. As a simple analogy, let's imagine a world where cars are governed by the laws of quantum mechanics. In this world speed limits on residential streets do not exceed 35 mph. On freeways speed limits range from 55 to 75mph. Speeds between 35 and 55 are forbidden. In our quantum world, allowed car speeds would form two bands, one with speeds between 0 and 35 mph and another with speeds between 55 and 75 mph. Speeds between 35 and 55 are impossible and we would never find a car moving with these speeds. In this world, there are no acceleration ramps. The whole idea of having a speed of 45 mph is unknown to the occupants of this world.

Bands hold a fixed number of electron and fill from the lowest to highest electron energies. If a solid has only enough electrons to partially fill a band, it is a metal. If a solid has the right number of electrons to just fill a band, it is a nonmetal.

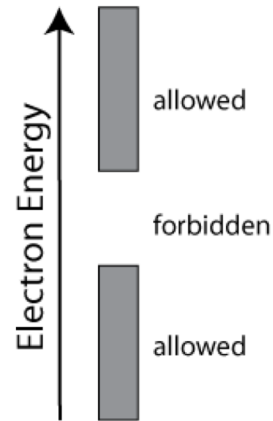


Fig 11-1 *Electrons in solids may only have energies that fall within energy bands.*

11-2 ELECTRICAL CONDUCTION

Imagine a wire made of some unknown material. We may determine if this material is a conductor by establishing a potential difference between its two ends. Though the analogy is not perfect, think of this process in terms of a reservoir just filled to its overflow. The stream at the reservoir inlet is blocked by gates that can be opened or closed. When the gates are closed, water does not flow from the inlet to the outlet. Now we open the gates and water, which is at a higher potential at the stream at the inlet, flows into the reservoir raising its level ever so slightly, which allows water to flow out at the outlet and lower its potential. The resulting water current may be used to do work. And as we have discussed in great detail, the maximum work that can be derived from this flow is simply given as a change in the potential energy difference between the water top of the inlet and at the bottom of the outlet. In this case, the reservoir acted as nothing more than a conduit—a conductor—to move water from the top of the inlet to the bottom of the outlet.

On the other hand, assume that the reservoir was covered, making it impossible to increase its level by even a tiny amount. In this case, water could not flow from the inlet to the outlet and there could be no current.

For an electrical conductor, there are energy states available that allow electrons to move across the its “surface” and then exit at the other end and move to a lower potential. In other words, a conductor must have a partially filled band of allowed electron energy levels. A nonconductor does not have energy levels available to the incoming higher potential electrons, and hence there can be no flow of electrons through the wire. A nonconductor has a totally filled energy band and there is an energy gap separating occupied and unoccupied bands.

11-3 ELECTRON VOLTS: A NATURAL UNITS FOR ELECTRON ENERGY

Just as water falling through a potential difference—a change in height—produces an equivalent amount of heat and work, so too the energy of electron falling through a potential difference. For an electron, however, it is not its height that is changing but rather its voltage. We express energy of electrons in units we call electron volts and denote as eV. One eV is defined as the change in potential energy as one electron falls through a one volt potential difference. Thus, an electron moving through a circuit powered by a 1.5 volt battery would change its potential energy by 1.5 eV. One eV is equivalent to 1.60218×10^{-19} Joules.

(Question: 1 watt is equal to 1 Joule per second so what is the theoretical minimum number of electrons required to light a 50 watt light bulb for 1 second using a typical 110 volt household current.)

Materials are further classified by the magnitude of their energy gap. A metal is obviously one where the energy difference between the occupied and unoccupied energy levels is 0 eV. Non-conducting materials are called semiconductors if their energy gap, E_g is between 0 and ~6 eV and are called insulators when $E_g > 6.0$ eV.

11-4 RECTIFICATION

Our electronic world is not only reliant on being able to harness the energy from moving electrons but also being able to direct these electrons. Central to this effort is the property of rectification. A rectifier acts as an electron gate, it allows electrons to move in one direction but not in the other.

Figure 11-2 provides a graphical representation of rectification where the current versus voltage is plotted. For a typical conductor, the current and voltage are linearly related. The greater the potential difference across the conductor the faster the electrons move, and if the potential difference is reversed the electrons reverse their direction of movement. A rectifier is a device that acts as an insulator when a potential is applied in one direction and an excellent conductor when the potential is applied in the other direction. Essentially a rectifier is a gate that allows electrons to move in only one direction and makes possible every electronic device you own.

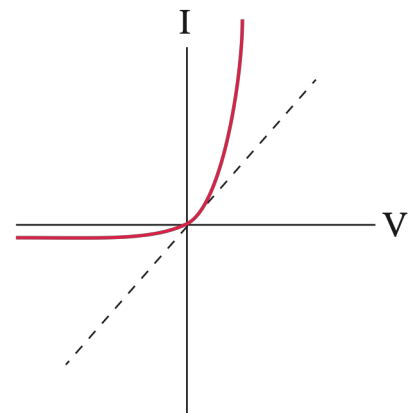


Fig 11-2 The IV (current-voltage) curves of a rectifier (red) and conductor (dashed black). Current flows in a rectifier in only one direction, effectively operating as a gate to electron motion.

Rectifiers are built from semiconductors that have been chemically modified and then processed to produce a junction with rectifying properties. We will begin our discussion of rectification by considering pure semiconductors, those that are free of all defects. These chemically and structurally perfect materials are called intrinsic semiconductors. When chemically modified an intrinsic semiconductor becomes an extrinsic semiconductor.

11-5 INTRINSIC SEMICONDUCTORS (*WHAT FOLLOWS IS NOT ORIGINAL WORK OF MEE*)

Pure carbon diamond, silicon and germanium are simple examples of intrinsic semiconductors. They are all in Group IV of the Periodic Table, and form a tetrahedral crystalline structure called diamond cubic, which is an FCC lattice with a two-atom motif. Each atom of diamond, silicon and germanium has four electrons in its outermost electron shell and is connected to its four nearest neighbors by a bond path (Figure 11-3). The energy gaps at 300K for diamond, silicon and germanium are 5.5 eV, 1.1eV and 0.7eV respectively.

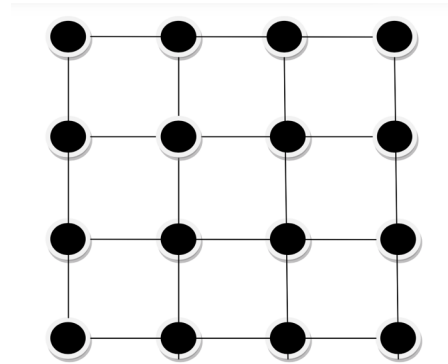


Fig. 11-3 *Two-dimensional illustration of a crystal of pure Si. If any individual atom of silicon is considered, it can be seen that each of its four valence electrons is used in maintaining covalent*

Figure 11-4 provides a graphical representation comparing the bands of silicon and germanium. For reasons that will become obvious the unoccupied band is called the conduction band and the occupied band is called the valence band. Though the E_g is sizable that does not mean that electrons cannot be excited across the gap into the conduction band. In fact, second law of thermodynamics demands that some electrons be found in the conduction band. We can easily calculate the probability that an electron will make this jump using Boltzmann's equation. (See if you can do this.)

Electrons in the conduction band are free to change their energy ever so slightly just as can electrons in partially filled bands. Hence these excited electrons will now support a current which is why these electrons are called conduction electrons or electron charge carriers. It is important to keep in mind however, that the number of electrons in the conduction band is exceedingly small hence the magnitude of the current derived from an applied voltage is tiny.

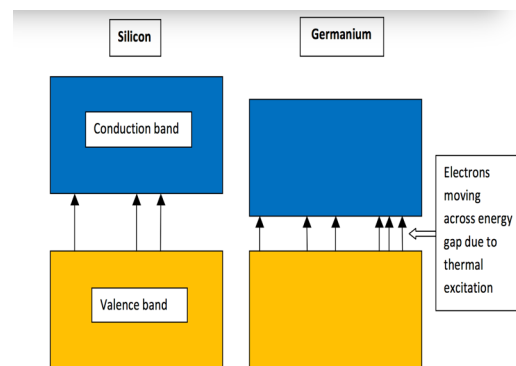


Fig. 11-4 *It is possible for significant numbers of electrons to cross the energy gap in semiconductors.*

Once an electron jumps up to the conduction band in the crystal lattice, it leaves behind a 'hole' in the valence bond. This hole can enable another neighboring valence band electron to move into it. As such, a hole behaves rather like a positive charge carrier, even though it is actually

a vacancy for an electron. A hole can travel through the crystal lattice of the semiconductor. A helpful analogy might be to consider a line of cars on a road. If a space appears at the front of the line, cars may move forward in turn. Each time a car moves forward, it leaves a space behind it, into which the next car may now move. An observer from above might consider that the cars are moving forwards or that the space is moving backwards.

Intrinsic semiconductors must always contain equal numbers of conduction electrons and holes. If an electron can move from its place then it must leave behind a hole (Figure 11-5).

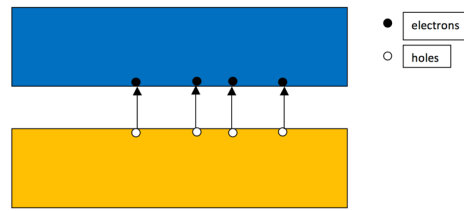


Fig. 11-5 *In intrinsic semiconductors like pure silicon or germanium, every electron that moves up to the conduction band must leave a hole in the valence band. Electrons and holes exist in equal numbers and both contribute to conduction. There are no majority charge carriers in intrinsic semiconductors.*

Electrons in the conduction band can fall into holes in the valence band. This process is called recombination. Electrons falling to the valence band have changed their energy. You know however, that this energy is not lost but must go somewhere, speculate as to where it may go.

11-6 EXTRINSIC SEMICONDUCTORS

This is all well and good, but we want to control the number of conduction electrons if we are to control electronic properties. We can do that by substituting a different element for one of the silicon atoms, usually by deliberately introducing very small proportions of a Group III such as boron or Group V element such as phosphorous. This is known as doping and results in what is called an extrinsic semiconductor.

Consider a semiconductor that is doped with a Group III element such as boron (Figure 11- 6). Each atom of boron has only three valence electrons in its outer shell. This is insufficient to form the four bonds with its Group IV neighbors and therefore produces a hole. Countless holes are now built into the semiconductor’s crystal lattice and they far outnumber the number of thermally excited electrons in the intrinsic semiconductor. The resulting extrinsic semiconductor is called p-type the majority charge carriers are positively charged holes. As a result of the doping process, a given applied voltage will produce a greater current than in the intrinsic semiconductor, its conductivity is greatly enhanced. For p-type semiconductors, conduction occurs in the valence band. In effect, the doping agent adds an extra energy level just above the valence band, sometimes called an acceptor band.

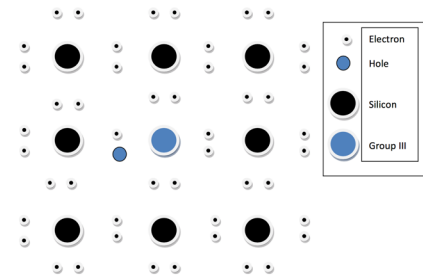


Fig. 11-6 *Introducing small quantities of Group III atoms into a silicon lattice (in practice only around one part in a million) leaves holes built into the valence band.*

A similar process is involved if a Group V element is used for doping. This gives an extra electron above what is required to bond to the four neighbors for each atom around the doping agent. These electrons are negatively charged and so an n-type semiconductor has been produced. In an n-type semiconductor, the majority charge carriers are electrons. The conductivity has been greatly enhanced as before, but this time conduction occurs in an extra energy level just below the conduction band, which is sometimes called the donor band. Therefore, in p-type and n-type semiconductors conduction can occur easily because there is effectively unfilled space within either the valence or the conduction band, respectively.

11-7 P-N JUNCTIONS

Rectifiers are made by doping one end of a single semiconducting crystal p-type and the other end n-type. The interface between the p-type and n-type sections is known as a p–n junction. In this boundary region, electrons from the n-type material may diffuse across the boundary and combine with holes from the p-type material, and vice versa. This results in a lack of majority charge carriers in the immediate vicinity of the junction and as such the region is known as the depletion zone. The p–n junction greatly affects the conductivity of the semiconductor as a whole. When electrons from the n-type material diffuse into the p-type material they leave behind positive ions locked in the crystal by chemical bonds. Likewise, these electrons combine with the p-type

dopant to create negative ions. As an illustration, in a p-n junction made from doping Si with P on one side and B on the other, electrons from P on the n-side of the semiconductor will move to the p-side and combine with B as shown in Figure 11-7. Remember while the electrons and holes are mobile, these ions cannot move and hence as more electrons from the p-side of the junction move across the boundary they will leave behind more cations (positive ions) and produce more anions (negative ions) all separated by some small distance amounting to a few tens of angstroms. Of course, the cations attract the electrons back across the boundary and the anions attract the holes in an attempt to undo the charge transfer. In actuality the boundary will come to an equilibrium where the attraction between the electrons and the holes is just cancelled by attraction for the charge carriers and the immobile ions. At this point net diffusion of electrons and holes comes to a stop and produces a permanent ion concentration in the depletion zone.

Now we may apply a voltage to the junction that will cause electrons to move from its *n*- to *p*-side, which is equivalent to holes moving from the *p* to *n*-side of the junction. Such a voltage is called a forward bias. The

alternative or reverse biased junction injects higher potential electrons to the *p* side of the junction. However, the ions in the depletion region will oppose this motion through coulomb interactions. Hence while electrons flow easily when a p-n junction is forward biased it will be opposed when reversed biased. In fact in the reverse bias situation the depletion zone becomes a greater and greater barrier to conduction. One can imagine the depletion zone illustrated in Figures 7 becoming a higher and higher barrier to conduction as electrons are driven further and further back from the depletion zone. The junction can only allow a tiny leakage current to flow because of the intrinsic

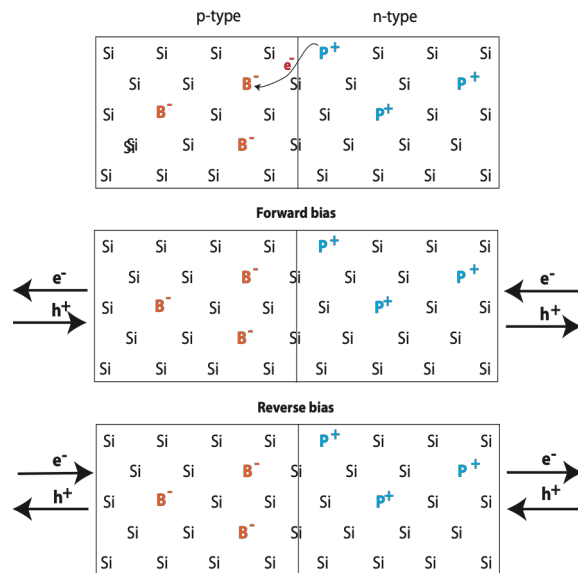


Fig 11-7. (top) At a p-n junction some electrons cross the barrier and produce ions, positive on the n-side and negative on the p-side. (middle) a junction is said to be forward biased when a potential is applied that injects electrons of higher potential on the n-side of the junction. This is equivalent to injection holes into the p-side of the junction. Note that the ions in the depletion zone do not provide a barrier to current moving in this direction. (bottom) In a reverse bias a potential is applied that will extract electrons from the n-side. Note that this process will be opposed by the electrostatic forces between the ions and the moving electrons

semiconductor's electrons and holes. This is exactly the behavior we expect of a rectifier as shown in Figure 11-2.

11-8 LIGHT-EMITTING DIODES

When a diode is forward biased, electrons from the n-type semiconductor may move across the junction and combine with holes in the p-type material. The electrons in the n-type semiconductor move within the higher energy conduction band, and as they cross the junction they move briefly into the empty conduction band of the p-type material. Since the lower energy p-type valence band is only partially filled, however, the electrons rapidly fall into an energy level within that valence band. In effect, electrons fall into holes, and as this happens energy is released in the form of heat or as light. By selecting the right kind of semiconductor much of this energy can be released as light. This is the mechanism responsible for light emitting diodes, LEDs (Figure 11-9).

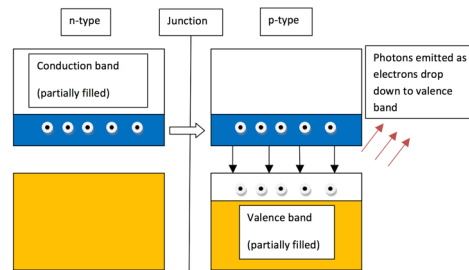


Fig. 11-10 In an LED electrons cross the junction from n to p in the conduction band. Once on the p side of the junction, they fall back across the energy gap to the valence band. This releases photons of light with an energy (frequency) equivalent to the energy lost as the electron falls from the conduction to the valence band in other words energy equivalent to E_g

The frequency of the light emitted from LEDs is controlled by the size of the energy gap between the conduction and valence bands. A bigger gap will result in a larger energy change and, in accordance a higher energy photon. A small energy gap will result in red light and a much larger energy gap is required for green or blue light.

Since electrons usually drop from the bottom of the conduction band into the top of the valence band, light from LEDs tends to be nearly (although not completely) monochromatic, with a narrow emission spectrum. By using combinations of red, green and blue it is possible to produce any color of light and this has led to the advent of LED televisions.

11-9 PHOTOVOLTAIC CELLS

A photovoltaic cell consists of a very thin layer of p-type semiconductor that is in contact with a layer of n-type material. The conduction electrons are freed through the action of photons of light. The photons provide sufficient energy to the electrons to enable them to jump up across

the energy gap to the conduction band, leaving behind a hole. The band gap energy for silicon is of the order of 1.1 eV, and so only photons with at least 1.1 eV of energy can cause the release of conduction electrons. The wafer of semiconductor is very thin and so there is a good chance that this process will happen at or

very close to the p–n junction. The electric field produced by the depletion layer at this junction forces the electron and hole apart, creating a potential difference, and so a current can flow if the cell is connected to a circuit. The p-type layer must be very thin, perhaps 1 μm thick, to prevent conduction electrons from recombining with holes.

A solar cell must also have a layer of antireflective coating (not shown in Figure 9) to improve efficiency because a silicon crystal is so shiny that without this layer many of the photons would be reflected before they could cause the release of an electron. Even so, typical efficiencies of solar cells stand close to 15% and the greatest efficiencies rarely exceed 25%. Finally, the cell must be coated in glass to reduce damage from the elements.

A compromise must be reached in the choice of materials used to optimize the performance of the solar cell. By reducing the band gap energy in the semiconducting material, photons with longer wavelengths and lower frequencies may be harnessed to free electrons and holes. Although this may seem desirable and will release more charges, it has the effect of reducing the strength of the electric field across the junction. It turns out that a band gap energy of about 1.4 eV is close to ideal, maximizing the current and voltage and therefore the power of the cell.

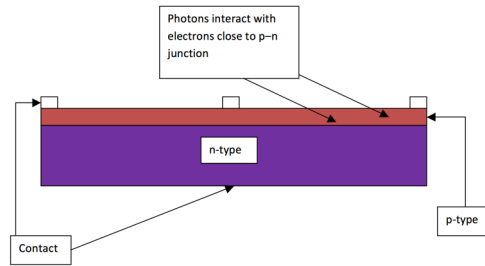


Fig. 11-11 *Simplified photovoltaic cell in cross-section*