CHAPTER 4:
Solar Cells, Single Crystal Semiconductors, and High Efficiency

There are several different types of solar cells made from materials ranging from single crystals to amorphous silicon. The goal here is to describe the different types of solar cells and their advantages and limitations. A fundamental description of the nature of semiconductors is presenting beginning with electrons in atoms as waves. The discussion of electrons as waves then leads to a description of semiconductors as single crystals. The theory of single crystal semiconductors is then used to describe how diodes and solar cells work. The effects of various defects in semiconductor materials on solar cell performance follows. Finally, a table of the performances to date of the various types of solar cells is presented. The reader will see that the performances enumerated are consistent with the simple concepts presented. More detailed descriptions of the various types of solar cells will follow in subsequent chapters. This chapter explains why high efficiency cells require good single crystal materials.

Electrons in atoms as waves and the periodic table of the elements

In the last chapter, it was noted that the sun's rays are really electromagnetic waves with varying wavelengths. Electromagnetic radiation includes radio waves, microwaves, infrared, visible, and ultraviolet waves. When one thinks about longer wavelength radiation like radio waves, one always thinks about waves. However, for the shorter wavelengths associated with infrared and visible light, physicists start to talk about photons. A photon is like a particle or wavelet having a specific wavelength and energy. A photon is a quantum of energy or discrete packet of energy. Now, is radiation a wave or particle? The answer is both! This is the wave–particle duality, a subject called quantum mechanics [1], a subject normally taught in graduate school physics classes along with a lot of mathematics. Please don't be afraid. The key ideas can actually be described in simple non-mathematical terms and these ideas are important to the understanding of solar cells.

While one normally thinks of electromagnetic radiation as waves, one generally thinks of electrons as particles circling an atomic nucleus just as planets circle the sun. However, an atom is really extremely small, so small that in crossing a human hair, one will pass by 200,000 atoms. Intuition based on everyday experience fails us at this small size. It turns out that electrons around atomic nuclei are described by wave functions. Here is the wave-particle duality again.

However, one can describe the rules that govern electrons in atoms and solids in fairly simple terms. In figure 4.1, we start with the simple hydrogen atom with a single negatively charged electron and a single positively charged proton.[2] The oppositely charged proton and electron attract each other and as they get closer and closer to each other, it is harder and harder to pull them apart. The electron is said to be in an energy-well or potential well as shown on the left of figure 4.1. The question is then: Can the electron collapse down and sit on the proton? The answer is no. How do we know this? We study the electromagnetic spectra emitted by atoms and we find discrete wavelengths and energies as shown on the right in figure 4.1. Not all energies are possible. How is this explained? Scientists hypothesize that the electron position is described by a wave function that then gives its probable position. Since one knows that the electron cannot be outside the potential well, one knows the wave functions have to be zero outside the well. Now, since we are talking about waves, we observe that the waves will have to have one, two, and three (etc.) nodes as is shown in the wells at the left in figure 4.1. For historical reasons, the state with one peak node is labeled S, and the states with two nodes are labeled Px, Py, and Pz. (X, Y, and Z are the three direction in 3 dimensional space.) The next rule is that electrons can have positive and negative spin and only one electron can occupy each state. So there will be two S states with opposite spins and two Px, two Py and two Pz states for a total of 8 state configurations possible. This wave hypothesis has proven to be very successful as it explains atomic spectra and the periodic table of the elements [2] and all of chemistry.

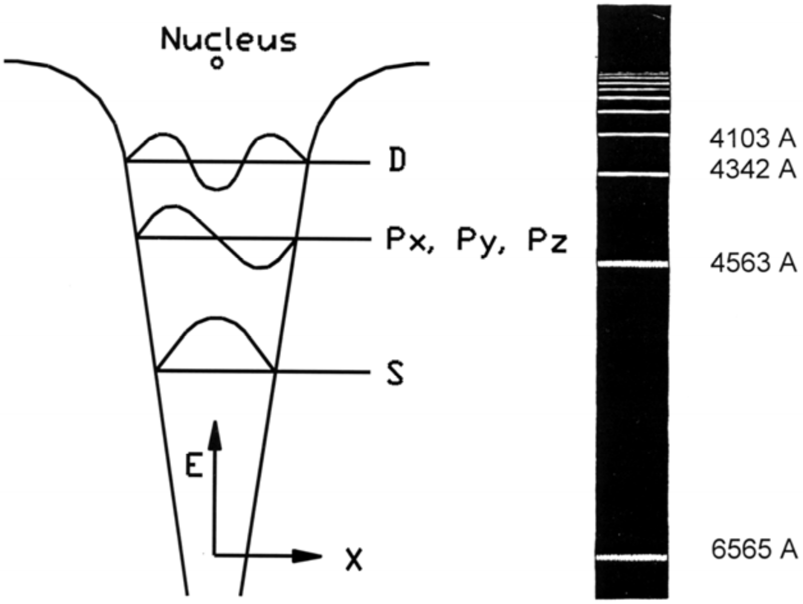


Figure 4.1: LEFT: Potential well for electron around nucleus in atom with energy level S, P, & D wave functions. RIGHT: A spectral line sequence for hydrogen.

The rule of eight including S and P orbitals explains the second and third rows of the periodic table. Table 4.1 is a summary of the important features of the periodic table including the common commercial semiconductor materials. The D level transition metals are not shown since they are not relevant here.

Table 4.1: Periodic Table of the Elements

I	II	III	IV	V	VI	VII	VIII
H Hydrogen							He Helium
Li Lithium	Be Berilium	B Boron	C Carbon	N Nitrogen	O Oxygen	F Fluorine	Ne Neon
Na Sodium	Mg Magnesium	Al Aluminum	Si Silicon	P Phosphorus	S Sulfur	Cl Chlorine	Ar Argon
		Ga Gallium	Ge Germanium	As Arsenic			
		In Indium		Sb Antimony			

Semiconductors as crystals

Why is it important to know about electrons as waves? The answer is that waves are intrinsically periodic as are the atom locations in single crystals. It is this periodicity that makes semiconductors special. Historically, the semiconductor revolution started 50 years ago with the discovery of the importance of high purity single crystals and the technology to obtain these high purity single crystals.

However, history is one thing but our goal here is to explain the reasons why single crystals are important to solar cells and to probe the question of how pure and how perfect do solar cell materials need to be. Most importantly, how are we going to make solar cells economical?

Before describing semiconductors, let us return to our periodic table and contrast the semiconductors with metals and insulators to see why semiconductors are special and why they are needed to make solar cells. To preview the answer, we note that in order to deliver electric power, a solar cell needs to generate both current and voltage. Generating current requires electron mobility and generating voltage requires a gap between electron energy states. Metals have electron mobility and insulators have gaps between energy states but only semiconductors have both.

The metals like sodium and magnesium are on the left in the periodic table. These atoms have only a few loosely bound electrons each and they can be tightly packed with up to twelve nearest neighbors. Because the atoms are closely packed, the potential energy well for a metal looks like a flat bottom well with the well bottom extending to the surfaces of the piece of metal. The metal surfaces form the energy barriers confining the electrons. Because this well is so large compared to one atom, all electron wave function wavelengths and energies are possible. Electrons are then free to move around in the metal but there are no energy gaps between energy states. Since the electrons hardly feel the metal atom core positions with the flat bottom potential well, crystallinity is not important to metallic properties.

The elements at the right of the periodic table like oxygen and chlorine have tightly bound electrons and are hungry to grab more. They readily form ionic compounds like salt (sodium chloride) and glass (silicon dioxide). The energy levels in these compounds are much like those of atoms in that the electrons only are excited between atomic energy states. There are gaps in energy but the electrons are not mobile. Crystallinity is not very important since electrons are localized on ions.

This brings us to the group IV elements like silicon. The structure of silicon in a silicon crystal is shown in figure 4.2. Silicon has 4 electrons and likes to form 4 tetrahedral bonds as shown. Looking at a row of silicon atoms along the diagonal in a silicon crystal, we see alternating bonded and non-bonded spaces between silicon atoms. The energy potential well profile for this row is shown in the middle of this figure along with two wave patterns, one drawn as a solid line and one drawn as a dashed line.[3] The peaks in the solid line wave pattern localize the electrons in the bonded regions with lower average energy potential. Meanwhile, the peaks in the dashed line wave pattern are localized in the non-bonded regions with higher average energy. However, both waves allow the electrons to be near any silicon pair in the crystal implying electron mobility throughout the crystal. Because of the periodic nature of the atomic positions in a single crystal, the wave functions allowed describing the electrons in a single crystal must have a corresponding wavelength. Thus the two types of states with bonding and anti-bonding electron locations between nearest silicon pairs or farthest silicon pairs are the only states allowed. There is an energy gap between these states because no other electron wave functions are allowed. The states representing the bonding states form what is called the valence band and the states representing the anti-bonding states form what is called the conduction band.

Figure 4.2 also shows the energy potential and wave functions for a group III-V semiconductor. In this case, a group three (III) element like gallium can form tetrahedral bonds with a group five (V) element like arsenic where the result is the sharing of 4 electrons per atom as in silicon. The III-V's are a rich class of semiconductors.

It turns out that because of the crystal periodicity, there is both an energy gap and electron mobility in semiconductors. Figure 4.3 allows us to visualize this more easily.

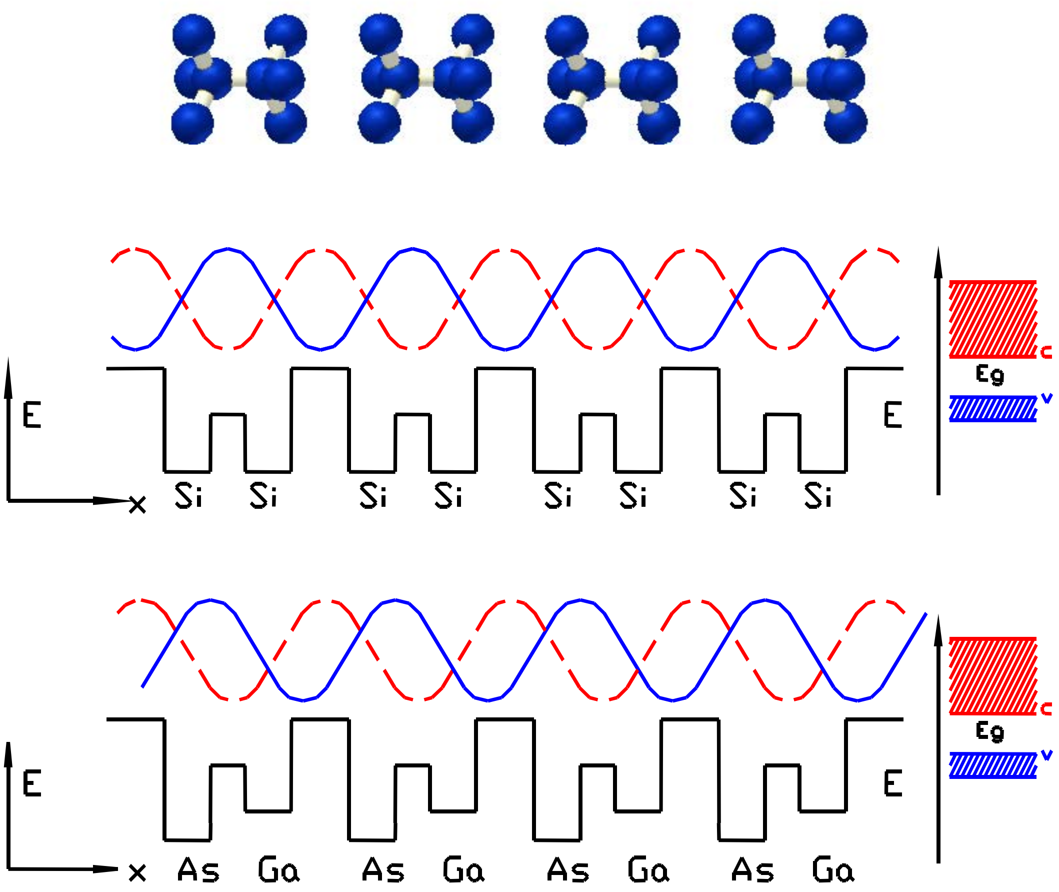


Figure 4.2: TOP: Tetrahedrally bonded Silicon atoms in groups along cube diagonal in silicon crystal showing alternate bonded and non-bonded pairs.
MIDDLE: Energy potential for top atom sequence with valence band bonding wave function as solid line and conduction band anti-bonding wave function as dashed line.
BOTTOM: The potential and wave functions for GaAs crystal.

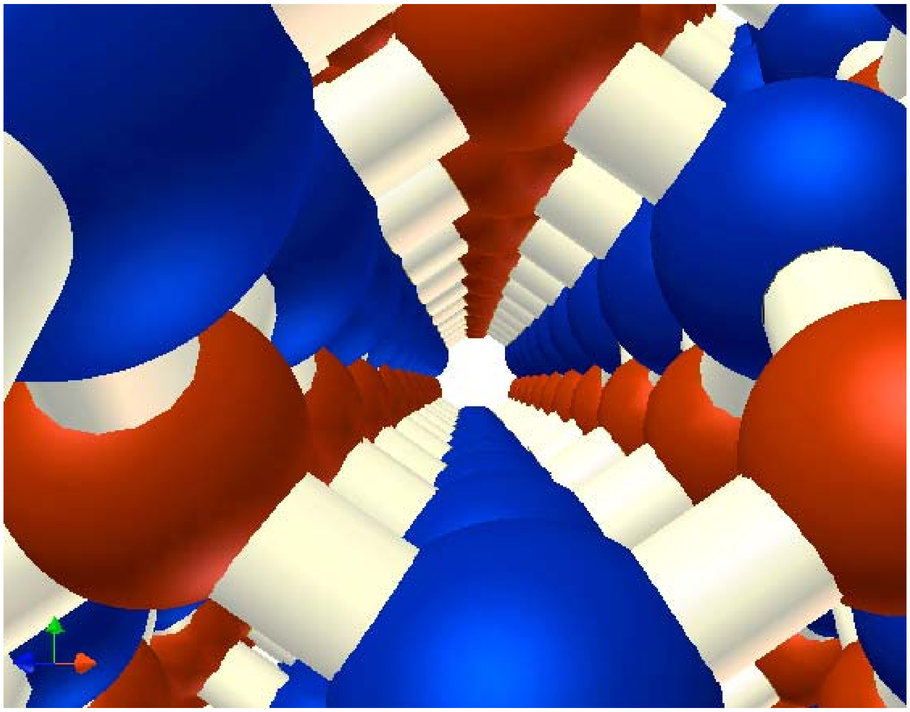


Figure 4.3: A view of a channel open for conduction electron movement in a GaAs single crystal. Small sphere = Gallium atom; Large sphere = Arsenic atom; White cylinders = valence bonds.

In this figure, one can see both connected bonded regions and open channels in between. One can imagine electrons traveling in the bonded regions or separately in more energetic states in the open channels. Propagating electrons in the bonded region have energies in a valence band and propagating electrons in the open channels have energies in a conduction band. The separation between these regions provides the energy gap. Looking at figure 4.3, one can also imagine a large foreign atom or a crystal boundary or defect interfering with flow in the channels or a total disruption of the channels smearing the two sets of energy states into each other.

Figure 4.3 suggests intuitively that electrons will have higher mobility in single crystals than in amorphous or small crystal size thin films. This is in fact true quantitatively. Electron mobility is easily and routinely measured. The electron mobility in single crystal silicon is typically 1500 $cm^2/Vsec$ and in single crystal gallium arsenide, it is 4500 $cm^2/Vsec$.[4] However, in amorphous silicon and copper indium diselenide (CIS), two common thin film solar cell materials, it is only 4 $cm^2/Vsec$. This is a difference by a factor of 1000 consistent with our intuitive expectations based on figure 4.3.

Junctions and Diodes

We have now established that carriers are mobile allowing current to flow in solar cells. How do we use an energy gap to create voltage. We need a P / N junction (P = Positive, N = Negative).

In the above description of electron movement in semiconductors, we need now to add that it is important to count electrons. If the semiconductor is very pure (a state we call intrinsic), then all of the bonding states will be occupied by electrons and there will be no electrons to move in the conduction band. Electrons can not move in the valence band either because there are no empty spaces to move to. Substituting a small number of phosphorus atoms for silicon atoms can rectify this problem (one in a million). Since phosphorus is from group V, it has one more electron than silicon. The resultant material is labeled N-type because the extra electrons are negatively charged.

Alternately, as a complement to our N-type material, we can substitute an aluminum atom for a silicon atom leaving the bonding or valence band one electron deficient because aluminum from group III has one less electron than a silicon atom. Now instead of thinking about a million electrons in the valence band, we talk about the missing electrons in the valence band. We call this a hole. It is like watching a bubble move in water. The hole has a positive charge and we call this material P-type.

Now what happens when N-type material and P-type material are brought together? The result is a P / N junction diode [4, 5] as shown in figure 4.4. The band edge diagrams at the bottom of this figure describe how a diode works. When the P region and N regions first come together, the electrons and holes from each side diffuse together eliminating each other leaving an electric field region in the junction. This happens until the valence band edge (v) in the P material almost lines up with the conduction band edge (c) in the N material as shown on the left in this figure. At this point, the free electrons and holes on both sides of the junction have the same energy as shown by the dashed horizontal line. This is the zero voltage band diagram (A). Now notice that there is an energy hill for electrons to climb in order to move from the N to P side of the junction. An applied voltage can either decrease this hill or energy barrier for forward bias (B) or increase it in reverse bias (C). If the hill is made small enough by a forward voltage about equal to two-thirds (67%) of the band gap energy, Eg, then current starts to flow. This corresponds to the knee in the diode current vs voltage curve shown at the top right in this figure. In reverse bias, no current flows because the barrier just gets bigger. Thus a diode is a rectifier allowing current flow in only one direction.

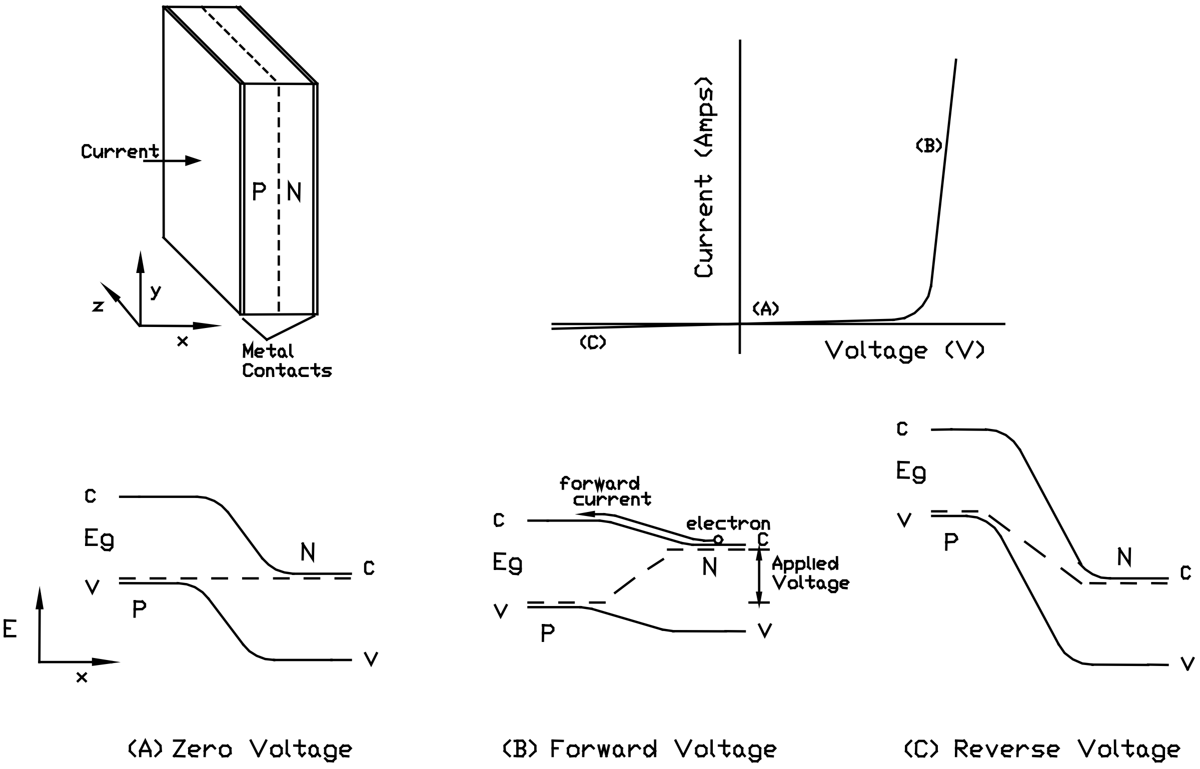
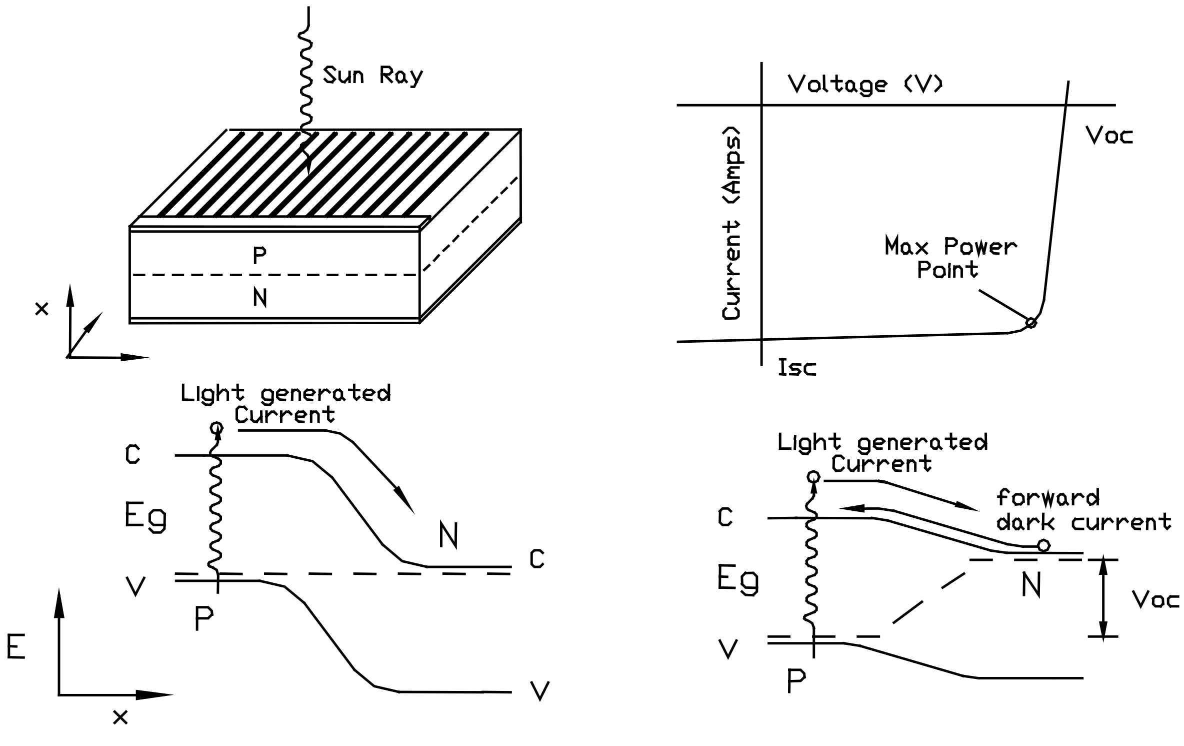


Figure 4.4: UPPER LEFT: P / N junction diode; UPPER RIGHT: Current vs voltage for P / N diode. LOWER LEFT: Conduction band minimum and valence band maximum positions through P / N junction at zero applied voltage. LOWER MIDDLE: Forward voltage band diagram = reduced barrier for high current flow. LOWER RIGHT: Reverse voltage = barrier blocks current flow.

Solar Cell band diagrams and power curves

Referring now to figure 4.5, a solar cell is just a large P / N junction diode with a metal grid on its front side facing the sun. A solar cell converts the energy in sunrays to electric power. Now we shall refer to the sunrays as photons. In figure 4.5, the now familiar band edge diagrams are shown at the bottom. These band edge diagrams show how a solar cell works. First, a photon is absorbed exciting an electron from the ground state or valence band in the P material to an excited conduction band state. It is mobile in the conduction band and if it lives long enough in this excited state, it can diffuse to the junction and fall down the potential barrier. Another way of thinking about this potential barrier is simply that it represents an electric field region created by the initial separation of electron and holes when the junction was formed. Anyway, when an electron enters a field region, it gains electrical energy. This can be converted to a voltage and current to do work.



Short Circuit Current (Isc) at Zero Voltage

Open Circuit Voltage (Voc) at Zero Current

Figure 4.5: UPPER LEFT: P / N junction solar cell with metal grid on top. LOWER LEFT: Photon absorption excites electron into conduction band. Electron then falls through junction potential. UPPER AND LOWER RIGHT: Current vs voltage curve for solar cell is diode I vs V curve moved down by light generated current.

High Efficiency and Multijunction Solar Cells

How efficient can a solar cell be and how do we achieve these high efficiencies? Theoretically, a solar cell efficiency of 70% is possible. However, no one believes that, in practice, this can be achieved. Still, a 35% efficient solar cell has been demonstrated and 40% is probably an achievable target.

What needs to be done to achieve high efficiencies is a more interesting question. In fundamental terms, three things need to be done. First, for each photon absorbed, the excited state carrier generated needs to last long enough to be collected at the junction. Second, while the sun’s spectrum contains photons of different energies, the energy available in each photon must be used as wisely as possible. And third, the voltage a cell generates should be as close as possible to the bandgap energy. We will discuss each of these requirements in succession in the following paragraphs.

The first requirement of one electron collected for every photon absorbed implies single crystal material and high purity material. The measure of electrons collected per photon absorbed is called quantum efficiency. Anyway, figure 4.6

provides a semi-quantitative answer to the semiconductor purity question. To understand figure 4.6, let's go back to the crystal channels shown in figure 4.3. First, how far will an electron move through one of these crystal channels. The answer is about one hundred atomic spacings. This is because the atoms are not really stationary but are vibrating small distances around their home positions because they have thermal (heat) energy. This vibration energy is small, however, so that the excited electron does not return to the valence band but just gets deflected into another channel. We think of this deflection as a step in a random-walk diffusion problem. This brings us back to figure 4.6.

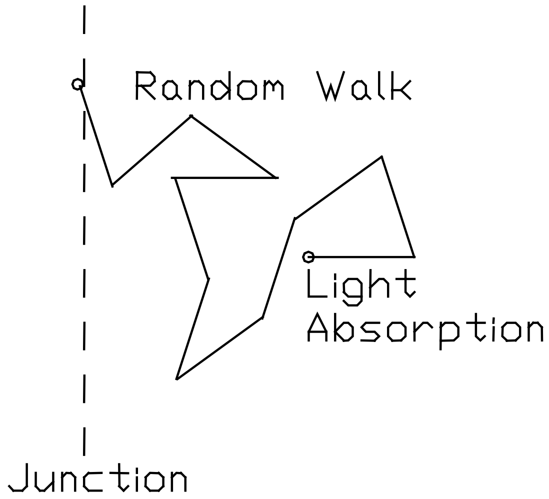


Figure 4.6: A light generated carrier diffuses to the junction in a random walk sequence.

The next question is how far is the excited state carrier away from the junction. This depends on the photon absorption distance. This absorption distance depends on the material and the rules for photon absorption. Now we shall divert for a minute to the rules for photon absorption. This will be important because, as we will see, silicon is fundamentally different from the III-V semiconductors in its photoelectric properties.

Let's return quickly to the hydrogen atom in figure 4.1. A rule for photon absorption is that the wave functions involved have to have different symmetries. For example, note that the S and D wave functions are symmetric around the position of the nucleus while the P functions are anti-symmetric. Thus, absorption between S to P and P to D are allowed but S to D is not allowed. Now let's look at the wave functions for silicon and gallium arsenide (GaAs) in figure 4.2. Note that both wave functions for silicon are symmetric around the point between two silicon atoms. This means that photon absorption in silicon is not allowed to first order. In GaAs, however, photon absorption is allowed.

So the photon absorption length in GaAs is about 10,000 atomic spaces. In reality, photons are also absorbed in silicon but in about 100,000 atomic spaces. This second order absorption in silicon results because of atomic thermal vibrations.

Now, we can return to the purity question and the random walk diffusion problem. Remember that a step length is about 100 atomic spaces. So a carrier in GaAs will be about 100 steps away from the junction and a carrier in silicon will be about 1000 steps away. However, in a random walk problem, the number of steps required to move N steps away from the start is N x N steps. So the distance an excited electron must travel to the junction in GaAs will be 10,000 steps or 1 million (1,000,000) atomic spaces. If it were to see a large impurity in a channel on this path, it could return to the valence band and be lost. So the purity requirement for GaAs is about 1 part per million. The analogous argument for silicon suggests a purity requirement of 10 parts per billion. In fact, silicon solar cells lose performance given transition metal impurities in the range of several parts per billion. The above argument has been a little tedious but the goal is to impress the reader with this purity requirement. By analogy, it should also be clear that good single crystal quality without defects is as important as purity.

The above purity specification is routinely met in commercial single crystal silicon solar cells today as well as in various other single crystal silicon based devices that have revolutionized our lives over the last 50 years. While the reader is probably not aware of it, various single crystal III-V devices have penetrated our everyday lives as well in the last 10 years. As the above argument about the difference in photon absorption for GaAs vs silicon suggest, the III-V are often a better choice for photoelectric and optical-electronic applications. Referring to the periodic table, there are a large number of III-V materials available including GaAs, InP, InSb, and GaSb. Additionally, alloys of these materials are available including AlGaAs, GaAsP, InGaAsP, etc. This makes a large set of band gaps and electron mobilities available. Single crystal III-V devices can now be found in cell phones, satellite receivers, CD music players, CD-ROMs in personal computers, taillights in cars, traffic stoplights, and military weapon systems. Single crystal III-V devices are also key components in fiber optic phone communication and the internet.

In fact, the most efficient solar cells are made using III-V materials. This brings us back to our second requirement for making high efficiency solar cells. We need to use the energy in the sun's varied colored rays as efficiently as possible. A problem with sunlight is that the photons come in different colors with different associated energies. If we wanted to maximize the efficiency of a photodiode, we would illuminate it with only photons with a single energy with an energy equal to the bandgap energy, Eg. Then if the crystal quality and purity were sufficient, all of the excited carriers would be collected at the junction with 67% of the photon energy being delivered as a voltage. The energy conversion efficiency would be roughly 67%.

However referring to figure 4.7, photons from the sun come with different energies. Some of the photons have too little energy to be absorbed and some of the photons have energy considerable in excess of the bandgap energy. For the sun's spectrum, this limits the single junction solar cell efficiency to less than 30%. However, the III-V's offer a solution because various materials with various bandgap energies are available. Specifically, one can stack a visible light sensitive GaAs solar cell with metal grids on its front and back on an infrared sensitive GaSb solar cell to arrive at the two color or two junction solar cell shown at the right in figure 4.7. In this way, one absorbs the high-energy photons first in the top material generating a high voltage while the low energy photons pass through the top cell to be converted in the bottom cell. More photons are used and they are used more wisely. This then is the world record 35% efficient GaAs/GaSb two color or two junction solar cell.

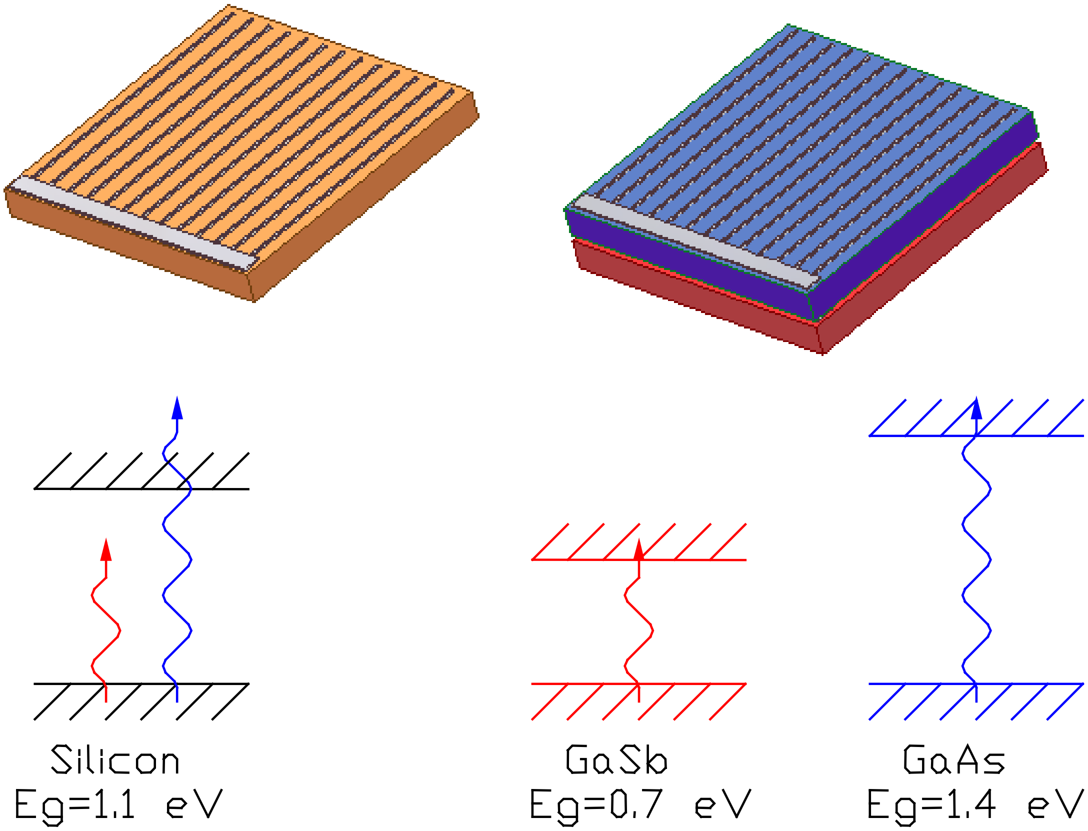


Figure 4.7: LEFT: For single junction solar cell, sunlight contains high energy photons with excess energy and low energy photons with too little energy. RIGHT: Solar spectrum can be more efficiently utilized by stacking two different junctions together.

This brings us to the third way of increasing solar cell efficiency. For a given bandgap energy, we want to generate more voltage. Concentrating the sunlight onto the cell can do this. This is shown in figure 4.8. Sunlight can be concentrated using a lens as is shown at the left in this figure. The resulting currents vs. voltage curves with and without a lens are shown at the right. As is customary for solar cells, the diode curves here have been flipped over. Note that the higher current concentrator cell has a higher efficiency. This is because the diode is being driven harder to a higher current and voltage. In other words, if the light level goes up by 10, the current also goes up by 10 but at the same time, the voltage also goes up. In practice, the open circuit voltage can go up from about two-thirds of Eg to about three-quarters of Eg under concentrated sunlight.

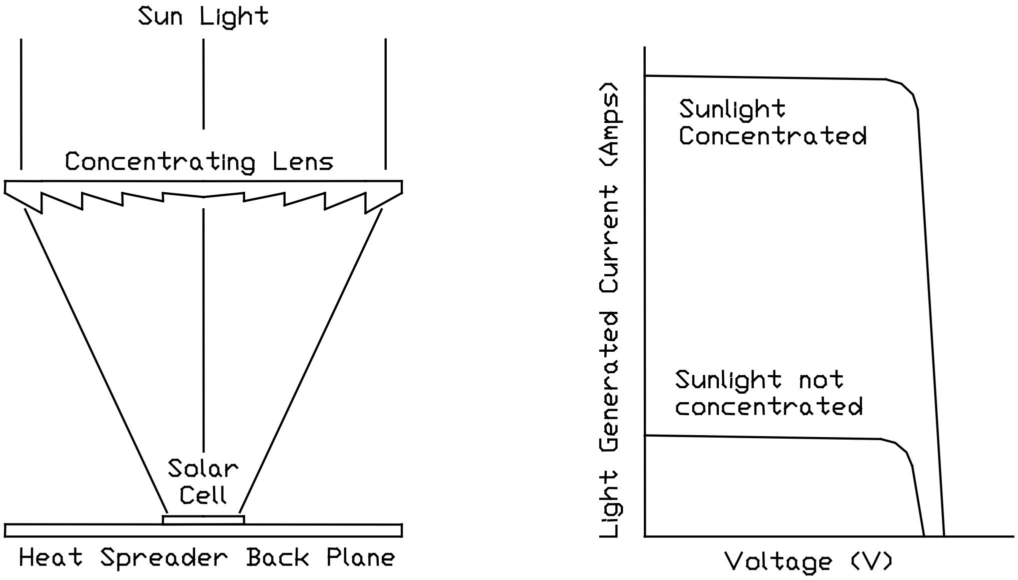


Figure 4.8: Solar cells are more efficient with concentrated sunlight because both current and voltage increase.

Types of solar cells and cost trades

The idea of producing cost competitive electric power using photovoltaic (PV) cells or solar cells in sunlight here on earth has been the dream of the PV community since the oil embargo in the early 1970s. In the decade of the 70s, three approaches to solving this problem were formulated.

The first approach, the planar crystalline silicon approach, was simply to bring down to earth the silicon solar panels used on satellites with straight forward improvements in manufacturing. In these planar modules, 90% of the illuminated area is single crystal silicon cell area. This approach has come a long way in cost reduction with improvements like large grain size cast polycrystalline silicon ingots, screen-printed grid lines, and wire saws. This approach dominates the terrestrial solar cell market today.

In the second approach, the thin-film PV approach, researchers observed that single crystals, like gemstones, are intrinsically expensive. Wouldn’t it be nice if one could find a thin-film as cheap as paint that could produce electricity in sunlight. They dropped the single crystal cells in search of a thin-film cell material that would generate electricity inexpensively and efficiently. The problem they encounter is that the non-single-crystal materials have reduced cell conversion efficiencies. The National Renewable Energy Lab in the US has led the development of this PV technology.

In the third approach, the solar concentrator approach, researchers observed that one could concentrate the sunlight onto a small single crystal cell with an inexpensive lens or mirror and reduce the impact on cost of the single crystal gemstone. This approach is depicted in figure 4.8. It should be noted that this concentrator approach is most appropriate in sunny locations because the optics need to see the sun and track it in order to keep the sun focused on the cells. In this book, it is argued that this will be the lowest cost approach in the long term.

The status today of module efficiencies under outdoor sunlight measurement conditions is summarized in Table 4.2 for these three approaches.[6] In this table for purposes of comparing these various different technologies, we summarize module efficiencies, not cell efficiencies where the modules are groups of cells wired together with a module solar collector area of at least 100 cm^2. This eliminates the odd small research scale single cell measurement. The first two rows in this table show typical efficiencies for planar large crystal size silicon solar cell modules. The efficiency of 11.7% is for the case when the whole cell is single crystal. The second row efficiency is for the case when a cell has multiple crystals within its area but each crystal is at least 20 times larger than the optical absorption length. In this case, the module efficiency falls off slightly to 11.2%. Planar modules based on single crystal silicon account for over 95% of today's terrestrial commercial solar cell market. These modules will be discussed in more detail in chapter 5.

The efficiency in the third row is for silicon film cells with still smaller crystal sizes. The module efficiencies in the next four rows are for various thin film options. The module efficiency for the amorphous silicon case is only 5.9%.

Table 4.2: Types of Solar Cells and Solar Module Efficiencies [6]

Solar Cell Type	Module Efficiency (Practical Test Conditions)
Mono-Crystalline Silicon	11.7%
Multi-Crystalline Silicon	11.2%
Silicon Film	7.2%
Amorphous Silicon Thin Film	5.9%
Small grain size CIS Thin Film	8.3%
Small grain size CdTe Thin Film	6.7%
Single Crystal Silicon Concentrator	20%
Concentrator III-V	29%

The module efficiencies in the last two rows are for concentrator solar cell systems. These efficiencies are markedly higher than the others at 20% for single crystal silicon cells and 29% for single crystal III-V multicolor cells. These efficiencies are much higher for the reasons described in the last section of this chapter and because using a lens or mirror concentrator allows one to separate the two apparently contradictory requirements for solar modules of lower cost and higher performance into two separate elements. With concentrators, the lens or mirror is the large area low cost collector whereas the small cells are the high efficiency converters. Given this separation of functions, the cells can cost more per unit area for higher performance but their small size relative to the lens area dilutes their cost impact on the total system cost. We shall describe these high power density photovoltaic concentrator cells in more detail in chapter 6.

The importance of single crystals

Given that 35% efficient solar cells were demonstrated in 1989, why are they not commercially available in 2003. One of the reasons is that for the last 25 years, the solar R&D community has spent over 80% of the available R&D funding on thin film solar cells. Why? One answer is that searching for a 20% efficient low cost thin film solar cell is a very attractive dream. However in this chapter, we have talked about electrons as waves and semiconductors as crystals to convey the message that this dream is not well founded on scientific principles. In fact, in graduate school solid-state physics classes, the bandgap in semiconductors is rigorously derived based on the assumption of the perfect periodic single crystal lattice.

However, the importance of single crystals to semiconductor devices is not generally conveyed in a simple understandable way. It is certainly not knowledge available to funding sources or the financial community. Figure 4.9 is an attempt to rectify this situation by making an analogy between an electron traveling in a solid and a car traveling through a forest.

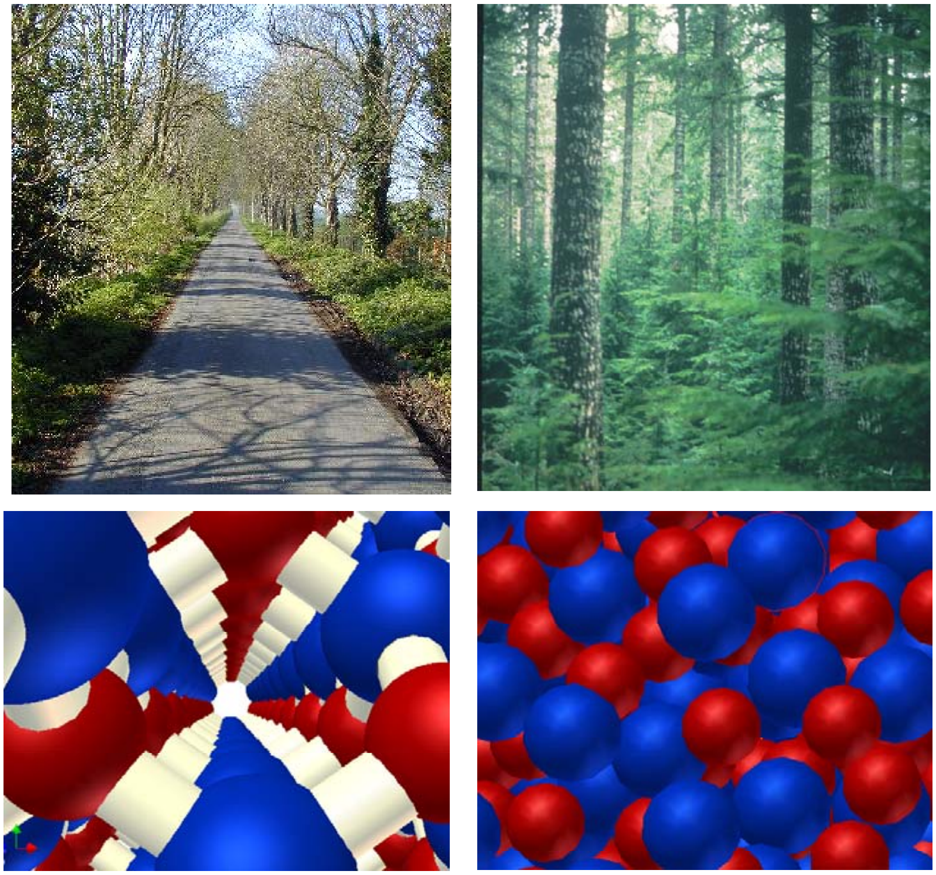


Figure 4.9: Single Crystal vs Thin Film Solar Cells

"If you were a car driving through the national forest, or an electron passing through a solar cell, which path would you rather take?"

Organizing the atoms in single crystals is like removing the trees to make a road through a forest. Atoms out of place or atomic impurities are obstacles for the electron just like trees are obstacles for a car. Collisions with these obstacles force the electron (or the car) to lose energy. Efficiency is dramatically reduced. In any case after 25 years of effort on thin film solar cells, their module efficiencies are still low and they have not penetrated the mainstream electric-power market place.

Concentrator solar cells have not entered the market place either. There are several reasons for this but it is not for lack of performance. The technology for solar concentrators is well founded on established scientific and engineering principles. One of the problems for concentrators is that a larger investment is required. Investment is required both for hardware like lenses and trackers as well as for new solar cell manufacturing facilities.

A problem faced by solar now is that the continued focus on thin films is robbing very limited resource from the solar concentrator alternative. The failure of thin film modules in the market place makes investors think that all solar options are bad generating a negative spiral in funding. A refocus of efforts on concentrators can reverse this spiral with successes in the sunny southwestern US leading to ever expanding markets. Market sales can then support more R&D aimed toward longer-term dreams.