1 Introduction

Ever since Becquerel discovered the first photovoltaic effect in 1839, harvesting solar energy has been a goal in the scientific world. The earth’s atmosphere absorbs more energy in one hour from the sun than the amount of energy consumed in one year for the entire world. For this reason, research in the last few decades has exploded to find the most efficient and cost effective solar cell so the world does not remain oil dependant.

Solar cells need to absorb a range of energy, which corresponds to the solar spectrum to be efficient. The solar spectrum has a range of 100 nm to 1 mm, but as Figure 1 shows, most of the irradiance occurs between 250 and 2500 nm with the maximum in the visible region of light (400 to 700 nm) for air mass (AM) 0, which means that solar cells should strive to absorb as much in the visible region of the solar spectrum as possible.

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Air mass is the relative path length of light through the earth’s atmosphere in relation to the zenith point (Figure 2); the zenith point is the path length vertically upward at 90° and is defined as AM 1. Air mass 0 is above the atmosphere at the zenith point. Solar cells are tested at AM 1.5, which corresponds to the sun at a 48.2° angle from the zenith point, with a temperature of 25 °C.

Figure 1: Solar irradiance spectrum at AM 0. Adapted from M. Pagliaro, G. Palmisano, and R. Ciriminna, *Flexible Solar Cells*, John Wiley, New York (2008).

Figure 2: Illustration of various air mass (AM) positions and the zenith point. Adapted from M. Pagliaro, G. Palmisano, and R. Ciriminna, *Flexible Solar Cells*, John Wiley, New York (2008).

Solar cells are characterized in categories called generations, and these are usually defined as being in one of three generations. First generation solar cells are made of silicon wafers. This type of solar cell is the most widely used and manufactured in the world; they also have the highest reported single cell efficiencies.
Silicon solar cells are expensive to produce, so research led the next generation of solar cells away from silicon. Second generation solar cells are called thin film solar cells. These solar cells are made of thin film semiconductor materials such as copper indium gallium selenide (CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\), CIGS) and cadmium telluride (CdTe); they are lower in cost compared to the silicon cells, but they have environmental issues and the efficiencies are lower. Third generation solar cells are much cheaper than all of the other cells, but their efficiencies are much lower than all other cells available. These solar cells are made of materials that do not have a strict p-n junction like first and second generation cells. Examples of third generation solar cells are dye-sensitized solar cells and organic or polymer solar cells. Table 1 shows the highest reported efficiencies of each kind of solar cell along with a tandem cell. Tandem solar cells are cells, which have more than one p-n junction and more than one cell; they are generally used for space due to their high cost and efficiencies.

<table>
<thead>
<tr>
<th>Solar cell</th>
<th>Highest reported efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon (single crystal, single cell)</td>
<td>27.6 ±1.0</td>
</tr>
<tr>
<td>CIGS (thin film, single cell)</td>
<td>20.3 ±0.6</td>
</tr>
<tr>
<td>CdTe (thin film, single cell)</td>
<td>16.7 ±0.5</td>
</tr>
<tr>
<td>Dye-sensitized (single cell)</td>
<td>11.2 ±0.3</td>
</tr>
<tr>
<td>Organic polymer (single cell)</td>
<td>8.3 ±0.3</td>
</tr>
<tr>
<td>InGaP/GaAs/InGaAs (tandem cell)</td>
<td>42.3 ±2.5</td>
</tr>
</tbody>
</table>

Table 1: Solar cell efficiencies.

2 First generation silicon solar cells

Bell Laboratories developed the first silicon solar cell in 1954 with an efficiency of 6%. Since then, research on improving the efficiency and cost of these solar cells has been abundant. Silicon solar cells are the most widely used of all solar cells, and they are also the most efficient in terms of single cell photovoltaic devices, and it is the most abundant element on earth, only second to oxygen. Silicon has an indirect band gap (Figure 3) of 1.12 eV, which allows the material to absorb photons in the visible region of light. An indirect band gap occurs when the valence and conduction band edges are not aligned in \( k \) space. \( k \) space is a coordinate system, which is used for counting quantum states and describing band gaps.
There are three types of silicon used in first generation solar cells: single crystalline silicon, multicrystalline silicon, and amorphous silicon. Single crystalline silicon has the highest efficiency at about 28%, but it is the most expensive. Multicrystalline silicon has a lower efficiency at about 21%, but it is slightly less costly to produce. Amorphous silicon has a much lower efficiency at 16%, but it is much less expensive to make. Multicrystalline silicon is the most widely used commercially due to the efficiency and lower cost.

The cost of fabricating single crystalline silicon solar cells is due to the purification process of bulk silicon into single crystals. To purify silicon, quartzite gravel, high purity silica, is melted and reduced using a carbon bed at a temperature above 1800 °C; this process makes the silicon 98 - 99% pure and is called metallurgical grade silicon (MGS). MGS is then ground and reacted with hydrochloric acid at 300 °C to make trichlorosilane (TCS). The TCS is heated to 1100 °C in a hydrogen atmosphere to make electronic grade silicon (EGS); this final process makes the silicon 99.9999999% pure.

A process is known as the Czochralski process is used commercially for single crystal silicon production. In the Czochralski process, a small single crystalline silicon seed is inserted in to molten EGS at a temperature above 1700 °C. The seed is continually twisted and slowly drawn out of the melted silicon, which allows the silicon atoms to attach to the seed and arrange in a single crystal lattice; this forms a uniform single crystalline ingot of silicon. Silicon wafers are sliced from the ingot. These wafers are then made smooth from the slicing by polishing them chemically and mechanically.

Multicrystalline silicon and amorphous silicon are much less pure than the single crystalline silicon, and their efficiencies reflect that. Amorphous silicon is prepared as a thin film not as a crystal and will be discussed in the next section. Multicrystalline silicon is made by pouring molten silicon in a mold and allowing it to cool, and this process is called casting. The resulting silicon has no overall lattice structure, but the ingot produced has large column grains of crystallinity. The ingot is still sliced and treated as the single crystalline silicon ingot is treated except that the bottom and top of the ingot are removed before slicing due to poor crystallinity at the edges. The casting process is much cheaper and simpler than the Czochralski method used for single crystal growth.

Silicon solar cells typically have two layers: a positive layer (p-type) and a negative layer (n-type). The positive layer is usually made by doping silicon with boron to create extra holes in the silicon lattice, and
the negative layer is usually made by doping silicon with phosphorus to have extra electrons available in the silicon lattice. The two types of silicon are put into contact with each other and a p-n junction is formed at the boundary between them. Figure 4 illustrates what happens when electrons and holes are generated near the p-n junction of the solar cell; the electrons and holes diffuse into the n-type and p-type silicon respectively and form a neutral depletion region. Once the solar cell is exposed to light, or photons, of greater energy than the band gap of silicon \((1.12 \text{ eV})\), an electron-hole pair is generated, and the cell starts converting solar energy into electricity.

**Figure 4:** Schematic of a p-n junction and the depletion region of a silicon solar cell. Adapted from T. Soga, *Nanostructured Materials for Solar Energy Conversion*, Elsevier, New York (2006).

Several issues affect the efficiency of solar cells (Figure 5):

1. The energy of the photons hitting the solar cell is less than the band gap, so the light cannot be converted into electricity and is lost.
2. The energy of the incoming photons is greater than the band gap, so the excess energy is lost as heat.
3. The Fermi levels of both n-type and p-type silicon are always inside the band gap of silicon so the open-circuit voltage is smaller than the band gap.
4. The series and shunt resistors generated from the contacts and lattice defects in the silicon consume some of the electricity that is generated.
5. Electron-hole pair recombination instead of conversion to electricity.

http://cnx.org/content/m41217/1.1/
The cell also has an aluminum backing for energy transfer, an anti-reflective coating on top of the silicon to maximize use of the photons hitting the cell typically made of SiN$_x$ or TiO$_2$, silver conductor strips for energy transfer, followed by glass on the top of the cell for protection from the elements. Figure 6 illustrates the basic structure of a silicon solar cell.

Today, the highest efficiency reported for terrestrial solar cells is around 28%, which is relatively low; however, Shockley and Quissier reported the maximum efficiency of a single silicon cell is only 31%. The
efficiency of these solar cells is slowly reaching the theoretical maximum, which leaves little room for improvement, and because of this, different approaches to solar cells are investigated.

3 Second generation thin film solar cells

Thin film solar cells emerged due to their lower production costs and minimal material consumption, which makes these cells attractive to industry. There are three types of thin film cells: amorphous silicon, copper indium gallium diselenide (CuIn_{x}Ga_{1-x}Se_{2}, CIGS), and cadmium telluride (CdTe). Amorphous silicon is the most commercially used of these due to the fact that they can use existing silicon solar cell technology for manufacturing, but these cells have a couple of disadvantages. One disadvantage is that they do not absorb as efficiently as other silicon solar cells, and the other is that these cells photodegrade over time. Because of these disadvantages, CIGS and CdTe thin film cells were developed due to their stability and efficiencies. These cells are also much less expensive to produce than amorphous silicon thin film cells.

There are a few fundamental differences between second generation solar cells and first generation solar cells. The most notable difference is the semiconductor material used in the cell has a direct band gap as opposed to the indirect band gap of silicon, but these cells still rely on a p-n junction design. Thin film cells have a top layer called the window layer made of a large band gap material that absorbs the higher energy photons and a bottom layer called the absorber layer made of a smaller band gap material that absorbs the lower energy photons, which are not absorbed by the window layer. This design allows for an inherently better efficiency. CIGS cells have the highest efficiencies of thin film cells at 20%; CdTe cells have an efficiency of 17%, and amorphous silicon has an efficiency of 16%.

CIGS has a direct band gap which is tunable depending on the ratio of Cu to (In + Ga) and the ratio of In to Ga; CuInSe_{2} has a band gap of 1.0 eV while CuGaSe_{2} has a band gap of 1.7 eV. The CIGS layer is the absorber layer of the thin film cell. Cadmium sulfide (CdS), with a larger direct band gap of 2.4 eV, is the window layer of this cell. CdS has been determined as the best window layer material, but ZnS, ZnSe, In_{2}S_{3}, ZnO, and MgZnO could also be used as window layer material.

The basic structure of a CIGS thin film solar cell is illustrated in Figure 7. The glass substrate is typically soda lime glass due to the fact that the sodium diffuses into the CIGS layer and increases conductivity and reduces the formation of lattice defects. Molybdenum (Mo) is used as a back contact for energy flow. The CIGS layer is deposited on the Mo by physical vapor deposition (PVD). A thin CdS layer is then deposited into the CIGS layer by chemical bath deposition (CBD). Both PVD and CBD must be performed at temperatures above 350 °C to ensure crystallinity. A high resistance and low resistance bilayer of ZnO is sputtered onto the cell as transparent conductive oxides. Finally, nickel/aluminum (Ni/Al) contacts are added for energy flow. An anti-reflective coating of MgF_{2} is added to maximize the absorption of the photons hitting the cell.
CdTe thin film cells are very similar to CIGS solar cells. CdTe has a direct band gap of 1.45 eV, and it is used as the absorber layer material. These cells also use CdS as the window layer material. Figure 8 illustrates the basic structure of a CdTe solar cell. The glass substrate for this solar cell is typically soda lime glass coated with a thin conductive layer of tin oxide (SnO) or indium tin oxide (ITO). A thin film of CdS is deposited on the glass using the CBD method. The CdTe layer can then be deposited using several different methods; closed-space sublimation (CSS), PVD, electrodeposition, or spray pyrolysis are all methods of CdTe deposition and all require temperatures greater than 400 °C to ensure crystallinity. Finally, a back contact of Mo or W (tungsten) is deposited for conductivity.
Although these thin film solar cells have a competitive edge on the first generation solar cells because of lower costs and good efficiencies, they have some drawbacks. Most of the material that these cells are made of are either becoming increasingly rare and more expensive (indium) or are highly toxic (cadmium). To mass produce these solar cells would also require new facilities, which would greatly increase the cost of production. Because of these drawbacks, a different generation of solar cells has been inspired.

4 Third generation solar cells

Due to high costs of first generation solar cells and toxicity and limited availability of materials for second generation solar cells, a new generation of solar cells emerged. Third generation solar cells are inherently different from the previous two generations because they do not rely on the p-n junction design of the others. There are a couple of popular models for third generation cells, which include dye-sensitized solar cells (DSSC) and organic or polymer solar cells.

Dye-sensitized solar cells are also frequently called Grätzel cells named after the developer. DSSCs separate the absorption of photons from the energy generation. An organometallic dye, which absorbs photons in the visible range, direct injects the electrons generated from absorption into the band gap of a wide bandgap semiconductor, and charge separation occurs at the interface of the dye and the semiconductor. The cell also contains an electrolyte to assist in hole transport.

The typical mechanism of a DSSC involves the dye, typically based on ruthenium complexes, gains an electron from the iodide ions in the redox mediator iodide/triiodide (I⁻/I₃⁻) couple electrolyte. The reduction of the triiodide at the cathode, completes the circuit and regenerates the iodide to make the process in this cell regenerative. The electron that the dye obtained from the electrolyte is then direct injected into the semiconductor, which is typically titanium dioxide (TiO₂) or zinc oxide (ZnO) with band gaps of 3.1 eV or 3.3 eV respectively. The injected electrons transfer to the conducting glass where the electrons are collected. Although the process in the DSSCs is reversible and regenerative, the highest efficiency reported for this type of cell is only 11%. These cells are very inexpensive to produce, but they photodegrade in a short period of time and the dyes tend to leak very easily, so other cell designs have been investigated for more ideal properties.
Organic or polymer solar cells were developed to make a more flexible solar cell. DSSCs are not considered organic because they use organometallic dyes and inorganic semiconductors. Organic or polymer cells are classified as such because the active layers of the cell are made of completely organic materials. These cells can either have a bilayer structure or a bulk-heterojunction structure, but the mechanism of both designs is the same. The active layer of organic solar cells is comprised of donor and acceptor materials for charge separation and transportation. Figure 9 illustrates the mechanism of an organic solar cell. The active layer could be made of a few different materials: small organic molecules, conjugated polymers, or combinations of molecules and polymers. The cell is made of an aluminum electrode and conductive ITO glass with the active layer between the two materials with buffers to improve charge transportation. Photons are generally absorbed in the donor material to produce singlet excitons. These excitons migrate towards the acceptor material and separate into electrons and holes at the interface. The electrons and holes diffuse across the acceptor and donor materials respectively until they reach the electrodes. Typical materials for these cells are: phthalocyanines, fullerene (C\textsubscript{60}), oligothiophenes, or polymers.

![Figure 9: Schematic of the mechanism of an organic solar cell. Adapted from T. Kietzke, Adv. Opto-Electron., 2007, 40285, 1.](http://cnx.org/content/m41217/1.1/)

In bilayer cells, electron-hole recombination is much less prevalent due to the fact that the electron and hole are separated at the interface of the material. This design has a flaw, however, because the bilayer only has one active zone, which is the interface. Because the excitons have to diffuse to the interface few of them go the distance, energy conversion is low. Bulk-heterojunction cells take care of this issue by having the donor and acceptor materials mixed throughout the active layer. Figure 10 illustrates the design difference in the two cells. Because the acceptor and donor materials are so well mixed, the active zone for this cell is much larger; therefore, the energy conversion is much higher.
Regardless of the design of the organic solar cell, the efficiency is not competitive with any of the other solar cell design options. The highest reported efficiency for these cells is 8%. They are very inexpensive to build, which is an advantage, but the efficiencies are far too low to make these cells competitive in a commercial market.

5 Multi-junction or tandem cells

A tandem cell, by definition, consists of at least two p-n junctions with cells composed of materials that absorb different photon energies. The top cell would absorb the higher energies while the bottom cell would absorb the lower energies that were not absorbed by the top cell (Figure 11), similar to the principle behind thin film cells. The tandem cell would then have a higher efficiency as it could absorb more photons of the solar spectrum for energy conversion. This technology is already being put to use in solar cells in space. Tandem solar cells are typically made of compounds of elements in the III and V groups of the periodic table. Examples of these compounds are: gallium arsenide (GaAs), indium phosphide (InP), gallium antimonide (GaSb), gallium indium phosphide (GaInP), and gallium indium arsenide (GaInAs). These solar cells have the highest reported efficiency at 43% when using a three cell solar cell, but they use rare metals and are extremely expensive to fabricate, so they are not practical for use on widespread earth.
Figure 11: Schematic of the absorbance of a two cell tandem solar cell where the top cell absorbs higher energy photons and the lower energy photons pass through to be absorbed by the bottom cell.

Increased number of cells in a tandem cell will increase the theoretical maximum efficiency of the solar cell, but there still remains a limit to the efficiency. A single cell has a theoretical maximum efficiency of 31%. A two cell tandem solar cell has a maximum efficiency of 42.5%; a three cell solar cell has a maximum efficiency of 48.6%, and so on. The theoretical maximum efficiencies will continue to increase, but an infinite stack of solar cells has a maximum efficiency of only 68.2%. The efficiency gained by adding another cell decreases with each subsequent addition.

In Australia, Green and coworkers have researched creating a tandem cell using a first generation multicrystalline silicon cell as the bottom cell. The idea of a tandem cell using the original first generation solar cell would make for an easier transition in production. To improve on the existing silicon solar cells, the additions should not be expensive, toxic, or rare. Previous research has suggested that producing uniform silicon quantum dots in a matrix of silica as a top cell for the terrestrial silicon solar cell could improve efficiency by 20% (Figure 12).
Green and co-workers attempted to make the quantum dot cell by using an existing silicon wafer and chemically altering it to produce silicon quantum dots and a silica dielectric matrix. The results of this method are not consistent in terms of quantum dot size or spacing, and they could not determine a way to control either of these parameters effectively using the methods they employed. More recently, arrays of silica coated Si and silica coated Ge quantum dots have been produced using wet methods (Figure 13). These films have successfully shown photoconduction and offer great promise as the key component in a QD-based third generation solar cell.

6 Bibliography