CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1 An Overview of Solar Energy

One of the main factors for the sustenance of life is energy whether being purely functional for day-to-day requirements such as electricity, gas or vehicle fuel or for larger scale industrial applications. Traditional sources of energy such as petroleum, natural gas and coal are predicted to be depleted with present and foreseeable rates of use projected into the near future. Bearing this predicament in mind, much research and development has been put into developing alternate sources of energy over the last few decades. The conversion of solar energy via photovoltaics appears to be a very promising way of meeting the increasing energy demands of the future since it is practically inexhaustible and freely available to everyone.

The media or device for converting solar energy into usable power is known as a solar cell and the mechanism behind its operation is known as the photovoltaic effect. Photovoltaic (PV) systems convert light energy into electricity. The term "photo" originates from the Greek word "phos," which means "light." "Volt" is named after Alessandro Volta (1745-1827), a pioneer in the study of electricity. "Photo-voltaics," then, could literally mean "light- electricity." Photovoltaic (PV) systems are already an important part of our lives in small applications for calculators and wrist watches, as well as more complicated systems to provide electricity for pumping water, powering communications equipment, and even lighting homes and running appliances. In a surprising number of cases, PV power is the cheapest form of electricity for performing these tasks.

1.2 The Objectives of This Research

In selecting the current area of study, various goals and targets were set to achieve. The idea behind research in photovoltaics and electrodeposition is to blend fundamental research on **Cadmium based photovoltaic conversion materials with a commercial**

application which is the utilisation of waste silicon wafers from the numerous wafer producing industries in Malaysia . Some of the objectives are outlined below:

- **Development of Electrodeposition**

The technique of choice in the fabrication of solar cells in this piece of research is Electrodeposition. Much work has been done in recent years to develop various photovoltaic materials, such as $CuInSe_2$, CdS, ITO, CdSe and CdTe [1-6], utilising this technique. Being a low temperature process, it is capable of tremendously reducing costs in a mass production atmosphere. As a point of comparison, solar coatings were also deposited by electron beam sputtering to study the fundamental differences between the two techniques.

- **Commercial Feasibility and Usage of Waste Silicon**

Another goal of this research is to utilise waste silicon wafers from the semiconductor industry for the fabrication of solar cells. Over the last two decades, many semiconductor giants from the United States of America and Japan have made large investments in Malaysia. From the cutting and encapsulation of integrated circuits, the primary investment has been shifted into the dicing and polishing of silicon wafer for supply to high end device manufacturers who pattern them. The advancement in technology has brought the advent of sub-micron level devices such as microprocessors and EDO-RAMS, thus the current industrial requirement of contamination control is high. Allowable contamination in these industries are in the region of 10^9-10^{12} atoms per cm^2. Any contamination beyond this level is considered inappropriate for patterning and these wafers are scrapped. These levels of contamination are negligible for solar cell manufacturing, providing an avenue for utilising waste wafers for solar cell fabrication as an associated industry.

Silicon wafers are often discarded due to defects in the manufacturing process. The defects normally encounterd are as follows [7] :

- **Process induced defects** - oxidation induced stacking faults, saucer pits etc.
- **Slicing defects** - Chips (surface chips, exit chips and indent chips), saw marks, thickness defects.
- **Edge profiling defects** - Bad grind (One sided grind, uneven grind and incomplete grind) and Dings (tiny chips due to insuficient grinding pressure)
- **Lapping defects** - Lapping scratches and fractures
- **Etching defects** - Bad etch, dull centre, roller mark, white stain
- **Polishing defects** - Polishing scratches, dimple, streaks and syton spots
- **Light point defects** - Particles, haze, microscratches
- **Flatness defects**
- **Metallic contamination** - metallic impurities from all the above processes

If any of these defects are detected, the silicon wafer is normally scrapped as they are deemed unsuitable for device manufacturing but it can however, be used for solar cell fabrication. In a normal process line, the losses of materials in processing is usually about 30% on kerf loss and about 10.4% from removal processes such as lapping, etching and polishing. What is actually useful for solar cell production is the performance losses, which is normally about 9.6%, because these losses are in the form of ready silicon wafers.

This provides an opportunity for a lucrative industry, as well as solves waste disposal problems for the wafer manufacturers. Crystalline silicon wafers are indeed advantageous with conversion efficiencies of up to 23% under laboratory conditions, but the manufacturing of such wafers purely for solar applications is becoming less popular due to the advent of polycrystalline and amorphous silicon which are relatively inexpensive (but less efficient). Therefore the utilisation of waste wafers is a cost effective option. Without doubt, it is extremely practical and commercially viable to use silicon wafers as the substrate material in the following research upon which cadmium based materials are coated to obtain the p/n heterojunction which is required for solar energy conversion. This adds a practical dimension to the research involved for this thesis.

- **Producing Ternary Compounds of Higher Efficiency**

Of the current cadmium based materials used for solar coatings, cadmium telluride and cadmium selenide have been the most widely researched, the former being the more popular of the two. The criteria of solar cell efficiency in terms of material choice is based on the energy gap of the coating. It has been established that a material, which has an energy gap which most closely matches the peak energy of solar radiation (about 1.5eV), will be the most efficient. Cadmium telluride and cadmium selenide have a direct bandgap of 1.45eV and 1.74eV. It is therefore hypothesised that a certain combination of these two materials may yield a band gap which best matches that of the solar spectrum. The targeted compound would therefore be $CdTe_xSe_{1-x}$ (Cadmium Telluride-Selenide). Films of cadmium telluride, cadmium selenide and cadmium telluride-selenide were coated and physically characterised and their subsequent solar performance was studied individually.

Electrodeposition is a technique that is capable of accurately depositing materials [8] of choice, by varying the core parameters such as the electrolyte and electrodes and other conditions such as the deposition voltage, electrolyte concentration, bath temperature, pH and others. This gives an exciting avenue for research as it is now possible to alter the stoichiometry of materials in a very simple manner.

- **Initiate a Precedent for Further Research**

One of the major reasons behind this area of research is to initiate an area of study concerning photovoltaics and the technique of electrodeposition in the Materials Science laboratory in University Malaya. This would set the foundation for further research into this aspect of materials science.

1.3 The Advantages of Solar Energy

Some of the significant advantages of solar energy as an energy source is as follows [9]:

- ***Environmental Benefits***

Because they burn no fuel and have no moving parts, PV systems are clean and silent. Solar power generation produces neither residue nor exhaust gasses and is therefore non-polluting - hence it can be known as 'clean energy.' This is especially important where the main alternatives for obtaining power and light are from diesel generators and kerosene lanterns.

- ***High Reliability.***

PV cells were originally developed for use in space, where repair is extremely expensive, if not impossible. PV still powers nearly every satellite circling the earth because it operates reliably for long periods of time with virtually no maintenance. In photovoltaic cells, there are no moving parts as in generators and turbines which are part of thermal power, wind power and atomic power generation process implying low maintenance and automation and unmanned operation feasible. These factors make solar power highly suitable for isolated power requirements such as satellites, unmanned lighthouses and in desert locations.

- ***Modularity.***

A PV system can be constructed to any size based on energy requirements so the owners of a PV systems can enlarge or move it if their energy needs change. Electricity can be generated where it is needed in amounts ranging in low power applications such as wrist watches and calculators to medium scale applications such as private homes and water pumps up to very large scales in the range of hundreds of kilowatts, without needing power transmission lines. With localised power generation at the place of consumption, the need for power distribution transmission lines and all its associated costs disappear.

- ***Long Lifespan***

Solar cells have been known to have a useful life in excess of twenty years and therefore can be considered to be long life devices.

- ***Low Operating Costs***

PV cells use the energy from sunlight to produce electricity as the fuel is free. The life of the sun is infinite and therefore solar energy is in inexhaustible supply and is effectively free to be obtained by all. With no moving parts, the cells require little upkeep. These low-maintenance, cost-effective PV systems are ideal for supplying power to communications stations on mountain tops, navigational buoys at sea, or homes far from utility power lines.

- ***Low Construction Costs.***

PV systems are usually placed close to where the electricity is used, requiring much shorter power lines than if power is brought in from the utility grid. In addition, using PV eliminates the need for a step-down transformer from the utility line. Less wiring means lower costs, shorter construction time, and reduced permitting paperwork, particularly in urban areas.

1.4 Problems and Solutions

Some of the drawbacks faced and the steps taken to overcome them has been outlined below:

1. Photovoltaic generation only takes place where there is light: This is fundamental to solar cells. Even though they are commonly known as cells, they do not store electricity.

Solution: Recent development in technology has brought on the advent of high power storage batteries which can not only store the necessary charge accumulated but also remove all traces of glitches and instability of the supplied power.

2. Generation of large amounts of power requires a large area. For example, if a solar cell generating capacity is 100W/m^2, a power station would require a space of 1 km^2 for a 100,000 kW power station. Therefore the construction of such a large scale power station in a city centre, for example, is not feasible. Therefore the building sites would have to be in suburbs, wastelands and deserts.

Solution: Recent advances in science has enabled higher efficiency solar cells to be developed. Along with this advancement, improvement in architecture and solar cell design and layout can minimise the utilised space. Today we can even find applications whereby solar cell arrays are computer controlled on their movement axis and thus the array can be angled and tilted accordingly to maximise the utilisation of the suns rays with respect to the time of day. These are known as tracking solar concentrators.

In the search for a suitable source of an alternative energy to meet the demands of the future, many forms of energy sources have been explored and even used commercially. The following table depicts the profile and the pros and cons of current and future energy sources [10].

Table 1.1: Present and Future Energy Sources

Energy Source	*Types of Processes*	*Advantages*	*Disadvantages*
Petroleum	Drilling, oil shale	Convenient, low pollution	Limited supply, nonrenewable (20-year supply)
Natural Gas	Drilling	Convenient, low pollution	Very limited supply, nonrenewable (5-10 year supply)
Coal	Deep or strip mining, solvent refining, pyrolysis, gasification, magnetohydrodynamic usage	Easy to handle, provides source of hydrocarbons in gaseous or liquid form as well as normal solid form	Atmospheric pollution, nonrenewable, much research needed for production of power by unconventional means, nonrenewable (200-300-year supply)
Nuclear Fission	Light-water reactors	Existing technology, compact	Limited fuel supply, thermal pollution, operating and transport hazards, storage of wastes
Breeder Reactors	Liquid-metal-cooled reactors	Reduces limitation of fuel availability	As for nuclear fission, but generally more severe
Nuclear fusion	Magnetic containment, laser initiated	Unlimited fuel supply	Much materials research needed, radiation leakage problems
Solar thermal	Direct heating and cooling via absorption of solar radiation	Pollution-free unlimited energy source	Need for extensive architectural changes, storage required
Solar thermal: electric	Use of solar energy to operate a steam turbine	Pollution-free unlimited energy source	Research needed on collection, focusing and storage
Solar photovoltaic	Photovoltaic effect in semi-conductor junction devices	Pollution-free unlimited energy source	Present high cost of cells, energy storage, and operating lifetime
Hydroelectric	Fall of water under gravity used to generate electricity	Renewable, inexpensive, can be used as storage processes, large potential in Third World	Limited to special locations, most of which in U.S. have been developed
Tidal energy	Motion of water under gravitational pull of moon used to generate electricity	Pollution-free, renewable	Limited number of exploitable sites
Wind	Force of the wind used to generate electricity	Pollution-free, renewable	Limited to special locations, large-scale effect on weather unknown, storage required
Ocean thermal	Uses thermal gradients to drive heat engine and generate electrical energy	Pollution-free, renewable	Special materials problems in resisting corrosion , costly transmission
Geothermal	Decay of radioactive materials within the earth produce heat	Inexpensive	Limited to special locations,corrosion problems, non-renewable
Biomass	Conversion of solid organic matter into synthetic fuel	Ready supply, could utilize wastes	Uses arable land if deliberately planted, cost uncertain, sludge disposal

1.5 The Photovoltaic (PV) Effect

The photovoltaic effect was described by the french physicist, Edmond Bacqueral, in 1839 who found that certain materials could produce small amounts of electric current when exposed to light but it remained a curiosity of science for the next three quarters of a century. The effect was first studied in solids such as selenium by Heinrich Hertz in the 1870s. Selenium PV cells were found to convert light to electricity at 1-2% efficiency and was soon adopted in the emerging field of photography for use in light measuring devices. When the Czochralski process was developed in the 1940s for producing highly crystalline silicon, major steps were taken towards commercialisation of PV cells. In 1954, Bell laboratories had developed the first crystalline silicon PV cell which had an efficiency of 4%.

The "photovoltaic effect" is the basic physical process through which a PV cell converts sunlight into electricity. Sunlight is composed of photons, or particles of solar energy. These photons contain various amounts of energy corresponding to the different wavelengths of the solar spectrum. When photons strike a PV cell, they may be reflected or absorbed, or they may pass right through but only the absorbed photons generate electricity. The energy of the photon is transferred to an electron in an atom of the cell (which is actually a semiconductor) and the electron is able to escape from that atom to become part of the current in an electrical circuit. By leaving this position, the electron causes a "hole" to form. The special electrical property of the PV cell is a built-in electric field that provides the voltage needed to drive the current through an external load. This is schematically shown in figure 1.1.

When light falls on the active surface of a solar cell, photons with energies exceeding the bandgap interact with the valence electrons and elevate them to the conduction band. These electrons leave 'holes' behind, so this process is called 'electron-hole pair' generation. A bandgap of 1.12 eV (in the case of silicon) results in a minimal required wavelength of ($hc/E_g =$) 1100 nm. Electron-hole pairs are generated throughout the thickness of the wafer and they depend in concentration on the intensity and spectral distribution of the light. If an electron-hole pair is generated within the minority carrier

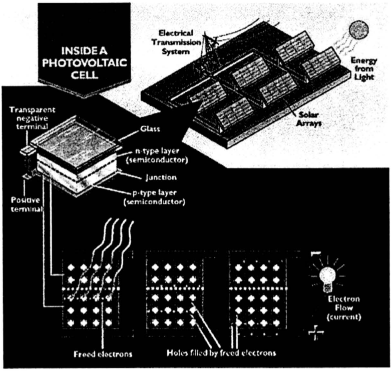


Figure 1.1: The Photovoltaic Conversion Process

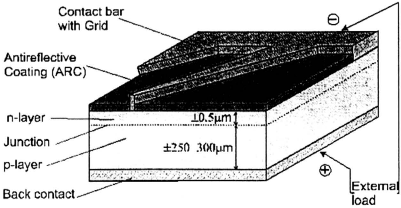


Figure 1.2: Cross Section of a Typical Photovoltaic Cell

diffusion length of the depletion region, the electric field, associated with the p-n junction, will cause the electron and the hole to separate.

The generated electrons will be accelerated to the negative contact and the less mobile holes to the positive contact. In this way, a potential difference is generated across the cell. This potential difference is called 'open circuit voltage(OCV)' and is capable of driving a current through an external load. The generated current depends on the irradiance, the active area of the cell and its spectral response.

1.5.1 Theory of Photovoltaic Cells

Photovoltaic cells, also commonly known as solar cells, has the function of converting light from the sun directly into electrical current using the electronic properties of semiconductors. For this purpose, the most commonly used semiconductors are: Si (Single crystal, polycrystalline and amorphous), GaAs(gallium arsenate), $CuInSe_2$ (copper-indium-diselenide), CdTe(cadmium telluride) and CdSe(cadmium selenide). New materials such as organic materials consisting of macro molecules are also being developed. Below, a simplified example on the working of a solar cell is given using a typical n-on-p structured crystalline silicon cell [11]. Figure 1.2 illustrates a section of such a cell.

To induce the electric field within a PV cell, two separate semiconductors are sandwiched together. The "p" and "n" types of semiconductors correspond to "positive" and "negative" because of their abundance of holes or electrons. The extra electrons make an "n" type because an electron actually has a negative charge. This is shown in figure 1.3. Although both materials are electrically neutral, n-type silicon has excess electrons and p-type silicon has excess holes. Sandwiching these together creates a p/n junction at their interface, thereby creating an electric field.

When the p-type and n-type semiconductors are sandwiched together, the excess electrons in the n-type material flow to the p-type, and the holes thereby vacated during this process flow to the n-type. Through this electron and hole flow, the two semiconductors act as a

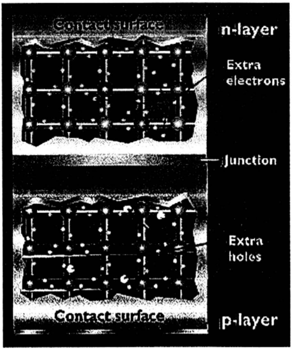


Figure 1.3: Sandwiched p- and n- type Materials to Form a junction

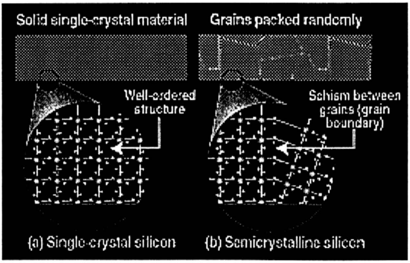


Figure 1.4 : Comparison Between Single Crystal and Polycrystalline Silicon

battery, creating an electric field at the surface where they meet (known as the "junction"). It is this field that causes the electrons to jump from the semiconductor out toward the surface and make them available for the electrical circuit. At the same time, the holes move in the opposite direction, toward the positive surface, where they await incoming electrons.

1.6 Role of Silicon

Silicon is still the most popular solar-cell material for commercial applications because it is the second most abundant element in the Earth's crust (next to oxygen). To be useful in solar cells, it is refined to 99.9999% purity. Silicon is explained here in greater detail because crystalline silicon is the semiconductor material most widely used for PV applications, and also the key substrate material in this research. Although other PV materials and designs exploit the PV effect in slightly different ways, knowing how the effect works in crystalline silicon gives a general understanding of how it works in all devices. The most common way of making p-type or n-type silicon material is to add an element that has an extra electron or is lacking an electron in a process called "doping."

In single-crystal silicon, the molecular structure of the material is uniform because the entire structure is grown from the same or a "single" crystal. This uniformity is ideal for efficiently transferring electrons through the material. To make an effective PV cell, silicon is "doped" to make it n-type and p-type. Semicrystalline silicon consists of several smaller crystals or "grains," which introduce "boundaries" which impede the flow of electrons and encourage them to recombine with holes and reduce the power output of the cell. Semicrystalline silicon is however, much cheaper to produce than single-crystalline silicon, therefore there is much ongoing research to minimise the effects of these grain boundaries.

1.6.1 Preparing Single Crystal Silicon

Polycrystalline material contains many single crystals about 1/1000 the size of the crystals in semicrystalline material. To change it into the single-crystal state, the high-purity silicon has to be melted. It is then allowed to reform and grow very slowly in contact with a single crystal "seed." The silicon adapts to the pattern of the single crystal seed as it cools and solidifies gradually. Several specific processes can be used to accomplish this, namely the Czochralski method and the floating-zone (FZ) technique.

In the Czochralski process, the seed of single-crystal silicon contacts the top of molten silicon. As the seed is slowly raised, atoms of the molten silicon solidify in the pattern of the seed and extend the single-crystal structure. In the FZ process, a silicon rod is set atop a seed crystal and lowered through an electromagnetic coil. The coil's magnetic field induces an electric field in the rod, heating and melting the interface between the rod and the seed. Single-crystal silicon forms at the interface, growing upward as the coils are slowly raised.

Although single-crystal silicon technology is well developed, the Czochralski, FZ, and ingot-casting processes are complex and expensive. The single-crystal ingots are then sawed into thin wafers for further processing into PV cells. After the wafers are produced, they are doped to produce the necessary electric field, treated to reduce reflection, and coated with electrical contacts to form functioning PV cells.

A group of new crystal-producing processes called 'shaped-ribbon growth' could reduce processing costs by forming silicon directly into thin, usable wafers of single-crystal silicon. These methods involve forming thin crystalline sheets directly, thereby avoiding the slicing step required of cylindrical ingots.

1.6.2 Conversion Efficiencies

The conversion efficiency of a PV cell is the proportion of sunlight energy that the cell converts to electrical energy and this is an important parameter consideration to make PV energy competitive with more traditional sources of energy like fossil fuels. If one efficient solar panel can provide as much energy as two less-efficient panels, then the cost of that energy and the space required will be reduced by 50%. The earliest PV devices converted about 1-2% of sunlight energy into electric energy, but modern PV devices have an efficiency of 7-17%. The manufacturing costs have been improved over the years as well and today, PV systems produce electricity at a fraction of the cost of earlier systems.

There are three main categories [12-14] of Silicon Solar Cells:

1.Monocrystalline or single crystal cells

- Excellent conversion rate (12 - 16%) (23% under laboratory conditions)
- Manufacturing the silicon wafers is an expensive process
- Much energy is required to obtain pure crystal

2.Polycrystalline cells

- Lower production costs, requiring less energy to make
- 11 - 13% conversion efficiency (18% under laboratory conditions)

3.Amorphous

- Lower production costs
- Lower efficiency (8 - 10%) (13% under laboratory conditions)

1.6.3 Amorphous Silicon

The atoms of amorphous silicon are not arranged in any particular order, thus not forming crystalline structures. They also contain large numbers of structural and bonding defects. Amorphous silicon can be used in PV devices by properly controlling the conditions under which it was deposited and by carefully modifying its composition. Today, amorphous silicon is commonly used for solar-powered consumer devices that have low power requirements (e.g., wrist watches and calculators). Its flexibility enables it to be even made into a roof shingle [15].

Amorphous silicon absorbs solar radiation 40 times more efficiently than single-crystal silicon. So, a 1µm film can absorb 90% of the usable solar energy [16]. This is one of the most important factors affecting its potential for low cost. Other principal economic advantages are that amorphous silicon can be produced at lower temperatures and can be deposited on low-cost substrates. These characteristics make amorphous silicon the leading thin-film PV material. Amorphous panels need about twice the surface area to produce the same amount of electricity, and their output deteriorates more quickly over time, but they react better to diffuse and fluorescent light and work better at higher temperatures.

1.6.4 Polycrystalline Thin Films

The computer semiconductor industry has developed the PV industry in terms of thin-film technology. Polycrystalline thin-film devices require very little semiconductor material and have the added advantage of being easy to manufacture. Rather than growing, slicing, and treating a crystalline ingot, thin layers of the required materials are deposited sequentially. The deposition techniques available is potentially cheaper than the ingot-growth techniques required for crystalline silicon. These deposition processes can be scaled up easily so that the same technique used to make a 2-inch x 2-inch laboratory cell can be used to make a 2-foot x 5-foot module. Like amorphous silicon, the layers can be deposited on various low-cost substrates, like glass or plastic, in virtually any shape, even flexible plastic sheets. Figure 1.4 shows the comparative structure between single crystal and polycrystalline silicon.

Single-crystal cells have to be individually interconnected into a module, but thin-film devices can be made monolithically. Layer upon layer is deposited sequentially on a glass substrate, from the antireflection coating and conducting oxide, to the semiconductor material and the back electrical contacts.

1.7 Other Semiconductor Materials

Like silicon, all PV materials must be made into p-type and n-type configurations to create the necessary electric field that characterizes a PV cell. But this is done in a number of different ways, depending on the characteristics of the material. For example, amorphous silicon's unique structure makes an intrinsic layer (or i layer) necessary. This undoped layer of amorphous silicon fits between the n-type and p-type layers to form what is called a 'p-i-n' design.

Polycrystalline thin films, like copper indium diselenide ($CuInSe_2$) and cadmium telluride (CdTe), show great promise for PV cells [17-24]. These materials cannot be doped to form n and p layers, but instead layers of different materials are coated. For example, a "window" layer of cadmium sulfide or similar material is used to provide the extra electrons necessary to make it n-type. $CuInSe_2$ can itself be made p-type, whereas CdTe benefits from a p-type layer made from a material like zinc telluride (ZnTe). Gallium arsenide (GaAs) is similarly modified with indium, phosphorous or aluminium, to produce a wide range of n- and p-type materials.

1.7.1 Gallium Arsenide (GaAs) Photovoltaic Cells

GaAs is suitable for use in multijunction and high-efficiency solar cells for several reasons:

- The GaAs band gap is 1.43 eV, nearly ideal for single-junction solar cells.
- GaAs has an absorptivity so high, it requires a cell only a few microns thick to absorb sunlight. (Crystalline silicon requires a layer 100 microns or more in thickness.)
- Unlike silicon cells, GaAs cells are relatively insensitive to heat. (Cell temperatures can often be quite high, especially in concentrator applications.)
- Alloys made from GaAs using aluminium, phosphorus, antimony, or indium have characteristics complementary to those of gallium arsenide, allowing great flexibility in cell design. A cell can be made to have several layers of different composition to precisely control the generation of electron and holes.
- GaAs is very resistant to radiation damage. This, along with its high efficiency, makes GaAs very desirable for space applications.

1.7.2 Multijunction Photovoltaic Cells

The common PV cells use a single junction, or interface, to create an electric field within a semiconductor, where only photons, whose energy is equal to or greater than the band gap of the cell material, can free an electron for an electric circuit [9]. The photovoltaic response of single-junction cell is limited to the portion of the sun's spectrum, which energy is above the band gap of the absorbing material, and lower-energy photons are not used. To circumvent this limitation, 'Multijunction Cells' are used, whereby two or more different cells are used with more than one band gap (and junction), to generate a voltage. Multijunction devices can achieve a higher total conversion efficiency because they can convert more of the energy spectrum of light to electricity. A multijunction device is a stack of individual single-junction cells (figure 1.5) in descending order of band gap (E_g). The top cell captures the high-energy photons and passes the rest of the photons on to be absorbed by lower-band-gap cells.

Research in multijunction cells today focuses on gallium arsenide as one (or all) of the component cells. Such cells have reached efficiencies of around 35% under concentrated sunlight. This multijunction device uses a top cell of gallium indium phosphide, "a tunnel junction," to aid the flow of electrons between the cells, and a bottom cell of gallium arsenide. Other materials studied for multijunction devices have been amorphous silicon and copper indium diselenide.

1.8 Electrical Contacts

An essential part of a PV cell is the electrical contacts because they connect the active semiconductor to the external load. The back contact of a cell usually consists of a layer of aluminium or molybdenum metal but the front contact is complicated. When the cell generates current, attaching contacts at the edges of a cell would not be adequate because of the excessive electrical resistance of the top layer in this configuration, thus the contacts must be made across the entire surface to collect the most current. This is normally done with a metal "grid." But if a large grid is placed on the top of the cell, it shades the active parts of the cell from the sun effectively reducing the cell's conversion efficiency.

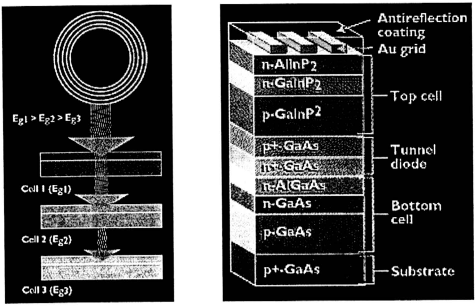


Figure 1.5: Operational Principle of a Multijunction Solar cell

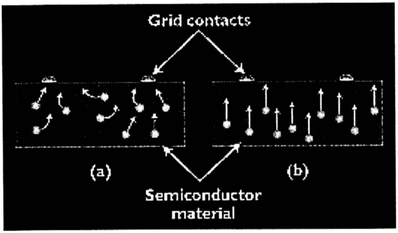


Figure 1.6 a: Crystalline Si Conducts Well Horizontally - Metallic grids are Used
Figure 1.6 b: Amorphous Silicon - Poor Horizontal Conductivity - TCO is Used

In designing grid contacts, a balance between electrical resistance losses against shading effects must be obtained. The usual approach is to design grids with many thin, conductive fingers spreading to every part of the cell's surface. The fingers of the grid must be thick enough to conduct well but thin enough to block a minimum of incoming light. An efficient grid keeps resistance losses low, while shading only about 3-5% of the surface.

1.9 Transparent Conductors

A transparent conducting oxide (TCO), such as tin oxide (SnO_2) is an alternative to grid contacts. The advantage of TCOs is that they are nearly invisible to incoming light, yet form a good bridge from the semiconductor to the external circuit. TCOs are very useful in manufacturing processes when a glass "substrate" is used for depositing layers of thin films such as amorphous silicon and cadmium telluride. The TCO is generally deposited as a thin film on the glass substrate before the semiconducting layers. These layers are then deposited, followed by a metallic contact that will actually be the bottom of the cell. In this manner, the cell is actually "built" upside down, from the top to the bottom.

The 'sheet resistance' of the semiconductor is an important factor when deciding if a TCO or grid contact is suitable. In crystalline silicon the semiconductor carries electrons well enough to reach a finger of the metallic grid (figure 1.6a). Since metal conducts electricity better than a TCO does, shadowing losses are less than the losses encountered in TCOs. Amorphous silicon conducts poorly in the horizontal direction and therefore benefits from having a TCO over every bit of its surface (figure 1.6b).

1.10 Theory of I-V curves

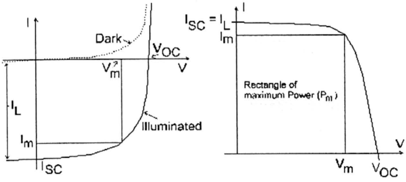
A single solar cell produces a voltage of approximately 0.3-0.5 volts, regardless of its size. However, the larger the solar cell, the greater the current generated. For increased voltage applications, individual cells are connected in series and for higher current applications, the cells can be connected in parellal. The most common solar panels are for 12 V applications. To reach that voltage, 24 cells would normally be sufficient, but for charging batteries and in order to compensate for voltage drops, a PV panel normally contains between 28 and 40 cells for a higher voltage.

Voltage can drop due to several reasons as stated below:

- High temperatures. Unlike thermal solar energy, PV works less well when it is very hot. Therefore in tropical climates, higher voltage panels are chosen.
- As a result of long wires. It is important to keep wiring between panels and other parts of the installation as short as possible.
- Diodes can cause small voltage losses.

The typical current-voltage characteristics under illumination is given in figure 1.7. The illuminated characteristics are the dark characteristics of a p-n junction (diode), shifted down by the photon generated current (I_L) [11]. This gives a region in the fourth quadrant and shows power can be extracted. I_{SC} is the short-circuit current and OCV is the open-circuit voltage of the cell. A more common IV-curve is represented in figure 1.8, which is an inversion of figure 1.7 about the voltage axis. I_m and V_m, which represent the current and the voltage at maximum power output, Pm, are important quantities. The fill factor (FF) is a quantity that assists in determining the maximum deliverable power from a solar cell. The larger the FF value, the closer the maximum power rectangle is to the maximum deliverable power. The fill factor is given by formula 1.

$$(1) \quad FF = \frac{I_m V_m}{I_L V_{oc}}$$



(a) (b)

Figure 1.7 & 1.8 : Typical Current-Voltage Characteristics Under Illumination

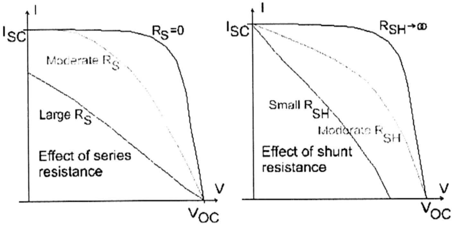


Figure 1.9 : The Effect of Series and Shunt Resistance on The I-V Curve

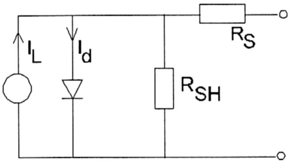


Figure 1.10 : The Equivalent Circuit of a Solar Cell

A solar cell in operation may be represented by a constant current generator with an ideal diode across it to simulate the effect of the p-n junction. The internal characteristics of the cell are better described with a series resistor (R_S) and a shunt resistor (R_{SH}). The effect of these parasitic resistance is illustrated in figure 1.9. In figure 1.10, the equivalent circuit of a solar cell is visualised. The series resistance of a solar cell is controlled by sheet resistance of the diffused layer, the metal-semiconductor contacts and resistance of the substrate. Shunt resistance effects arise from leakage paths around or through the junction.

Series and shunt resistance may be lumped together as effective resistance to give the following equation for a solar cell:

$$(2)\ I = I_L - I_O[\exp(AkT) - 1] - \frac{V + IR_S}{R_{SH}}$$

Where:

A = diode ideality factor lying between 1 and 2, depending on cell-type

I = output current of the cell (A)

T = temperature (K)

I_L = light generated current (A)

k = Boltzmann's constant (1.3810-23 J/K)

I_0 = diode saturation current (A)

q = elementary charge (1.60210-19 C)

V = voltage across cell terminals (V)

R_S = series resistance ()

e = base for natural logarithm (2.71828)

R_{SH} = shunt resistance ()

1.10.1 Theory of Transient Effects

In a solar cell, the difference in charge density between the p- and the n-layer, leads to a junction capacitance and an electric field.

$$(3)\ C_j = \frac{\varepsilon_r A}{W}$$

Where:

C_j = junction capacitance (F)

ε_r = relative permittivity (F/m)

A = area of junction (m^2)

W = width of depletion region (m)

Equation (2) is only correct for an abrupt junction like a parallel plate capacitor. In forward bias, many carriers are injected across the junction and it takes time for the carriers to recombine. The expression for this phenomenon, the diffusion capacitance (C_d), consequently includes the carrier lifetime.

$$(4)\quad C_d = \frac{eE\,t}{kT}$$

Where:

C_d = diffusion capacitance (F)
e = electron charge (1.60210-19 C)
E = irradiance (W/m^2)
t = carrier lifetime (s)
T = Temperature
k = Boltzmann's constant (1.3810-23 J/K)

1.11 Junction Theory

To fully understand and describe the properties and use of solar cells, it is helpful to consider the sequence of the phenomenons involved: from the radiation of the sun, through the process of absorption of the radiation, generation and transport of the charge carriers in the semiconductor, separation of charge carriers by the junction, collection of these carriers at the contact to the device and finally to the various types of power conditioning and storage that may be needed and the utilization of power generated. In the final product, where the device is applied to terrestrial use, every stage of this sequence depends critically on others. For example, photovoltaic generation of electricity must be coupled with an effective storage process in order to compensate for the intermittent nature of solar radiation.

In general, a solar cell consists of a potential energy barrier within a semiconductor material that is capable of separating the electrons and the holes that are generated by the absorption of light within the semiconductor. The four most common types of design (figure 1.11) and the respective energy barriers are as follows [10]:

- ***Homojunction:*** p/n junctions within the same semiconductor material
- ***Heteroface structures*:** similar to homojunctions but with a window layer of a larger band gap semiconductor added to reduce surface recombination loss

- ***Heterojunctions:*** p/n junctions between two different semiconductor materials
- ***Schottky barriers:*** metal/semiconductor junctions

It can be noted that in each case a layer type structure is apparent. In homojunctions, the light is incident through a contact grid on a thin layer of one conductivity type, which is usually n-type. In heterojunctions, two possibilities of configuration exists. Firstly, the light is incident through a grid on the larger band-gap material which is known as the *backwall* configuration and secondly, through a grid on a thin layer of the smaller band gap material called the *frontwall* mode. In Schottky barriers , it is possible to have the light incident either through the semi transparent metal forming the barrier (*frontwall*) or through the semiconductor (*backwall*).

Six domains can be distinguished from the various electronic processes occurring in a solar cell and are described below:

- The metal contact to the p-type semiconductor introducing a contact resistance, R_{cp}
- The bulk of the p-type region where most of the electron - hole pairs are generated by absorption of the light and where the minority carriers (electrons) are transported by diffusion and are partially lost by recombination.
- The junction region itself with the associated depletion regions, where carriers are separated by the junction electric field.
- The bulk of the n-type region, which contributes mainly a series resistance.
- The contact to the n-type semiconductor, introducing a contact resistance, R_{cn}
- The front surface, where surface recombination loss of minority carriers can occur

Therefore the total series resistance of a cell can be expressed as :

$$\mathbf{R_s = R_{cp} + R_{bp} + R_{bn} + R_{cn}}$$

Where : R_{bp} and R_{bn} are the series resistance of the bulk p- and n- type regions.

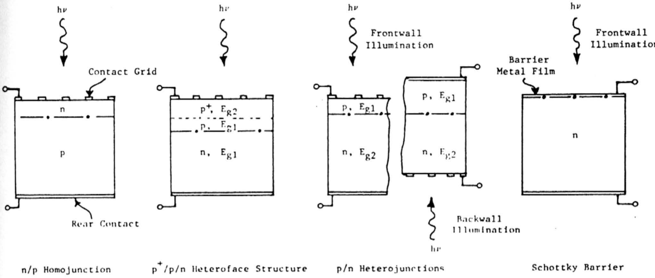


**Figure 1.11 : Illustrations of different types of solar cells. In each the junction barrier is indicated by _._._._.
For the heteroface and heterojunction structures, $E_{g1} < E_{g2}$**

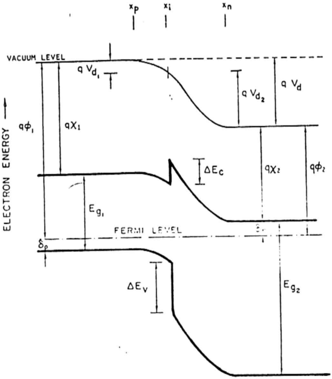


Figure 1.12 : Schematic of a heterojunction with $\Delta E_c > 0$ and $\Delta E_v > 0$

1.12 Heterojunction Model and the SIS Structure

Emphasis will be placed in this particular junction type as the solar cells fabricated in this research would have the heterojunction (HJ) interface with a SIS type structure.

1.12.1 The Heterojunction Model

The Anderson model forms the basis for most HJ theories. The model incorporates the discontinuities in material properties, ε, χ and E_g, across an abrupt metallurgical surface into the Shockley diode theory. The discontinuity in the relative dielectric constants, $\varepsilon_s/\varepsilon_o$, is dealt with by requiring that the electric displacement be continuous across the interface:ie., $\varepsilon_{S1}\,\xi_1 = \varepsilon_{S2}\,\xi_2$. The differences in E_g and the electron affinities, χ, require discontinuities in the conduction and valence band edges, ΔE_c and ΔE_v. The result of bringing the two semiconductors together and lining up the Fermi levels under thermal equilibrium is shown in figure 1.12. Anderson's model assumes that no interface states are present and that current transport is via injection into the quasi-neutral regions or by recombination/generation in the depletion layer. The relation between the various quantities is given as:

$$\Delta E_C = (\chi_1 - \chi_2)q\,, \qquad \Delta E_v = (\chi_1 - \chi_2)q + E_{g2} - E_{g1}$$

$$qV_d = qV_{d1} + qV_{d2} = E_{g1} - \delta_n - \delta_p + \Delta E_C$$

$$V = V_1 + V_2\,, \qquad V_{d2}/V_{d1} = V_2/V_1 = (V_{d2} - V_2)/(V_{d1} - V_1)$$

Here V_{d1} and V_{d2} are the diffusion voltages and V_1 and V_2 are the portions of the applied voltage dropped on either side of the junction. The values of δ_n, δ_p, χ_1 and χ_2 permit a wide range of other profiles to be obtained which represent the usual configuration for a solar cell. We want $E_{g2} > E_{g1}$ to maximise the band gap window so that in most cases the transport of one of the carrier types across the interface dominates.

- The current voltage characteristics of a Heterojunction may contain components due to three principal current mechanism:
- Diffusion current due to injection of minority carriers from each side of the junction similar to a p-n junction
- Generation-recombination current arising within the space charge region
- Current arising from tunneling

With the front layer heavily doped to reduce series resistance and its much lower intrinsic carrier concentration, it is possible to use a step junction approximation for diffusion current. The current for a n-p heterojunction is then given by:

$$J = J_{OH}[\exp(V_D)-1]$$

Where: V_D = Voltage across the junction
J_{OH} = Saturation current

1.12.2 The Semiconductor-Insulator-Semiconductor (SIS) Structure

The SIS junction is a variation of the semiconductor- semiconductor junction where a thin layer of insulation, such as an oxide, is sandwiched in the junction. The photovoltaic behaviour of the SIS structure [10] is complex and restrictive assumptions have to be made. It was found when the collection takes place in the more heavily doped semiconductor, the insulating layer is disadvantageous, but when collection takes place in the weakly doped semiconductor, the insulating layer should have a favourable effect if the band discontinuity has the appropriate sign. In other cases, the layer has no influence whatsoever.

In this research, silicon wafers were used as the substrate upon which semiconducting materials such as CdTe and CdSe and a combination of the two are coated. Silicon wafers almost immediately form an SiO_2 oxide layer when exposed to air. Steps were taken in the experimental approach whereby the wafer is immediately used for coating after the HF etching bath to minimise the oxide formation but it cannot be avoided all together. However electrons can tunnel through this layer. The SIS junction has a similar limitation as Schottky barrier devices which is described below:

- The layer acts as a passive dielectric separation between the semiconductors, thus lowering the potential barrier height.
- The flow of carriers may be limited through the insulating layer, reducing the current for a given bias voltage.
- The applied bias is sustained partially by the insulating layer, thus the barrier height is not constant
- Trapped charge within the insulator or at the insulator/semiconductor interface, acts either to increase or decrease the potential barrier.

Since the photogenerated minority carriers must tunnel through this layer, it must not be thicker than 20 - 30 Angstroms to maintain high quantum efficiency. The presence of the insulating layer can be detected by Capacitance - Voltage measurements which would give a shift in capacitance towards more negative bias compared to its ideal curve. Hence a C^{-2} versus V would yield a curve instead of a straight line when there is no insulating layer between the heterojunction. Here, C is the capacitance and ,V is the biasing voltage across the junction. This is called the Mott-Schottky effect and is due to the charges trapped within the insulator. These trapped charges will influence the capacitance of the junction.

1.13 From Cells to Arrays

The PV cell is the basic unit in a PV system. An individual PV cell typically produces between 1 and 2 watts but it can be increased by connecting cells together to form larger units called modules. Modules, in turn, can be connected to form even larger units known as arrays (figure 1.13). In this way, a PV system can be built to meet almost any power need, no matter how small or great. Modules or arrays do not constitute a PV system and there must also be structures on which to put them and point them toward the sun, and components that take the direct-current (dc) electricity produced by the modules or arrays, and condition the electricity so it can be used in the specific application. These structures and components are referred to as the balance of system (BOS).

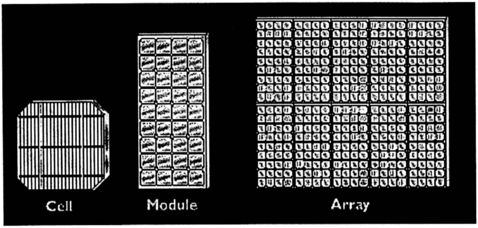


Figure 1.13 : The Cell, Module and Array Arrangement of Solar Cells

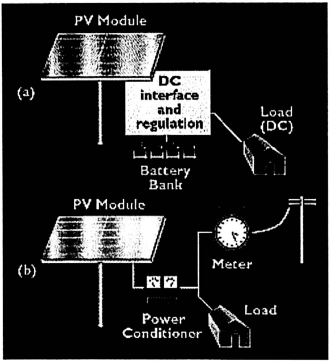


Figure 1.14 : The Elements Required to get PV Power to a Load (BOS)

1.13.1 Balance of System

A complete PV system comprises of three subsystems. The PV devices (cells, modules, arrays, etc.) that convert sunlight into direct-current (dc) electricity, the load or the application for which the PV electricity is intended and a third subsystem to enable the PV electricity to be properly applied to the load. This third subsystem is generally referred to as the "balance of system" or BOS.

The illustration in figure 1.14 shows the elements required to get the power created by the PV system to the end load. The stand-alone system (a), uses battery storage to provide dependable dc electricity day and night. For a home connected to the utility grid (b), PV can produce electricity during the day and the extra electricity can be sold to the utility. The utility can in turn provide electricity at night or during poor weather. The BOS typically consists of structures for mounting the PV arrays or modules and the power-conditioning equipment that adjusts and converts the dc electricity to the proper form and magnitude required by an alternating-current (ac) load. The BOS can also include storage devices such as batteries, for storing PV-generated electricity, to be used during cloudy days or at night.

1.13.2 Flat-Plate Systems

Flat-plate collectors use large numbers of cells that are mounted on a rigid, flat surface. These cells are encapsulated with a transparent cover that lets in the sunlight and protects them from the environment. Figure 1.15 shows one typical flat-plate module design which uses a substrate of metal, glass, or plastic to provide back structural support; encapsulant material to protect the cells; and a transparent cover of plastic or glass.

The advantage flat-plate collectors have over concentrator collectors is, they are simpler to design and fabricate and do not require special optics, specially designed cells, or mounting structures that must track the sun precisely. Flat-plate collectors can use all the sunlight that strikes them - both the direct sunlight and the diffuse sunlight that is reflected from clouds, the ground, and nearby objects.

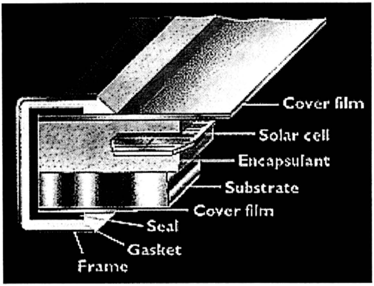


Figure 1.15 : Arrangement of a Flat Plate Module Solar Cell

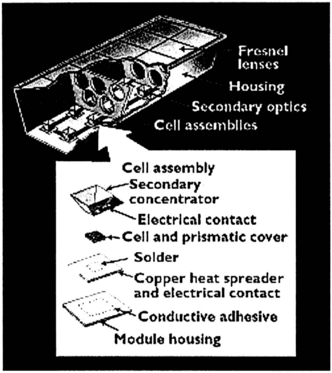


Figure 1.16 : A Solar Cell Concentrator Assembly

1.13.3 Concentrator Systems

The performance of a PV array can be improved by employing concentrating optics, which gather sunlight with lenses, thereby increasing the intensity of sunlight striking the PV cell. Figure 1.16 shows a typical basic concentrator unit, consisting of a lens to focus the light, a cell assembly, a housing element, a secondary concentrator to reflect off-center light rays onto the cell, a mechanism to dissipate excess heat produced by concentrated sunlight, and various contacts and adhesives.

The primary reason for using concentration is to decrease the area of solar cell material being used in a system, as the solar cells are the most expensive components of a PV system, on a per-area basis. A concentrator uses relatively inexpensive materials (plastic lenses, metal housings, etc.) to capture a large area of solar energy and focus it onto a small area, where the solar cell resides. One measure of the effectiveness of this approach is the concentration ratio which is how much light concentration the cell is receiving.

1.14 Light, The Sun and Solar Insolation

The sun's energy is vital to life on Earth and determines the Earth's surface temperature and supplies virtually all the energy that drives natural global systems and cycles. Although some other stars are enormous sources of energy in the form of X-rays and radio signals, our sun releases 95% of its energy as visible light and the rest as infrared and ultraviolet rays. The sun emits virtually all of its radiation energy in a spectrum of wavelengths that range from about $2x10^{-7}$ to $4x10^{-6}$ m (figure 1.17). The majority of this energy is in the visible region. Each wavelength corresponds to a frequency and an energy; the shorter the wavelength, the higher the frequency and the greater the energy (expressed in eV, or electron volts). In the invisible portions of the spectrum, photons in the ultraviolet region, have more energy than those in the visible region and photons in the infrared region, have less energy than the photons in the visible region [25].

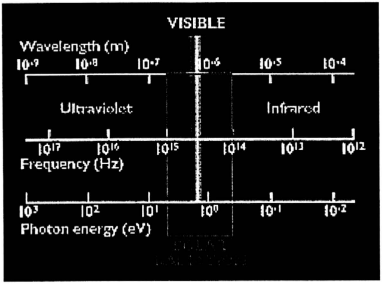


Figure 1.17 : The Solar Energy Distribution in the Visible Region

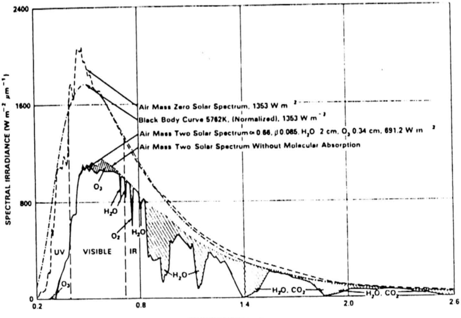


Figure 1.18 : Comparison of AM0 and AM2 Solar Spectra, Showing the various atmospheric absorption bands in AM2

Each second, the sun releases an enormous amount of radiant energy into the solar system of which the Earth receives a fraction of it at an average of 1367 W m^{-2} at the outer edge of the atmosphere. This value is known as the **'solar constant'**. The atmosphere absorbs and reflects some of this radiation, including most X-rays and ultraviolet rays and the thickness of the layer of the atmosphere is known as **'Air Mass.'** Therefore , an air mass is the path traversed by the direct solar radiation, expressed as a multiple of the path traversed to a point at sea level with the sun directly overhead.Thus, the path length at sea level with the sun at the zenith is 'Air Mass 1' or (AM1), while above the earth's atmosphere is (AM0). Air mass depends on the time of day, time of year, altitude and latitude of a certain place. Figure 1.18 shows the solar radiation at various air mass. The Earth's atmosphere and cloud cover, absorb, reflect, and scatter some of the solar radiation entering the atmosphere, but still enormous amounts of direct and diffuse sunshine energy reaches the Earth's surface and can be used to produce photovoltaic electricity.

1.15 Band Gaps In Photovoltaic Cells

The band-gap energy is defined as the amount of energy required to dislodge an electron from its covalent bond and allow it to become part of an electrical circuit. Photons from incident light with an energy higher than the band-gap energy, will expend the extra energy as heat when freeing the electrons. Therefore, it is important for a PV cell to be "tuned" through slight modifications to the semiconductor's molecular structure to maximize the photon energy.

An important consideration when dealing with photovoltaics and radiation is the energy gap response. It is important to note from the solar spectrum that the energy gap of CdTe and CdSe lies on either side of the peak of the solar spectra (figure 1.19). It is one of the goals of the research here to attempt to modify the energy gap of CdTe with CdSe to obtain a semiconductor with an optimal energy gap. Combining CdTe (E_g=1.45eV) and CdSe (E_g=1.74eV) could form a new compound which has a band gap somewhere in between to closer match the peak energy of the solar radiation. Figure 1.19 shows the theoretical solar efficiency versus semiconductor band gap for ideal cells. Curves for two

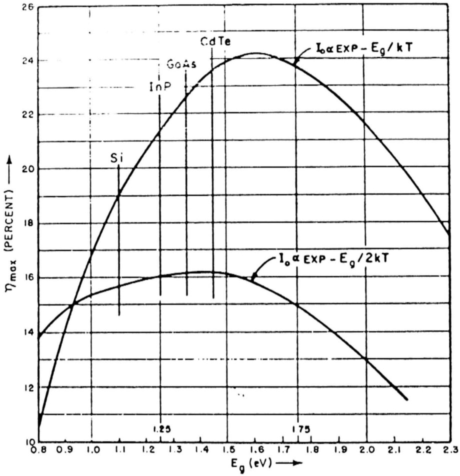


Figure 1.19 : Theoretical Solar Efficiency vs. Semiconductor Band Gap. For ideal junction cells with no surface recombination loss. Curves for two different diode mechanisms are shown: (top) A=1 for injection dominated current and (bottom) A=2 for recombination in the depletion layer. The positions of CdTe and CdSe are indicated clearly.

different diode mechanisms are noted: (top) A=1, for injection current and (bottom) A=2, for recombination in the depletion layer.

Effective PV semiconductors have band-gap energies ranging from 1.0 to 1.6 eV, because this level of energy is good for freeing electrons without causing extra heat. The entire spectrum of sunlight, from infrared to ultraviolet, covers a range of about 0.5 eV to about 2.9 eV. Red light has an energy of about 1.7 eV and blue light has an energy of about 2.7 eV. About 55% of the energy of sunlight cannot be used by most PV cells because this energy is either below the band gap or carries excess energy.

Table 1.2 Criteria for Band Gap Choice of a Heterojunction System for Photovoltaic Solar Cells

Property	**Criteria**
Band gap of smaller band-gap material	Band gap near 1.5-1.55eV to maximize absorption of solar radiation, while minimizing diode current that limits OCV. Direct optical absorption so that carriers are generated close to the junction. Long minority-carrier diffusion length
Band gap of larger band-gap material	As large as possible while maintaining low series resistance
Conductivity type	Smaller band-gap material should usually be *p*-type because of longer electron diffusion lengths
Electron affinities	Materials should be chosen such that no potential spike occurs at the junction for the minority photoexcited carriers
Diffusion voltage	As large as possible, since the maximum OCV is proportional to the diffusion voltage
Lattice mismatch	As little mismatch in lattice constant between the two materials as possible (this appears to minimize interface state density and recombination losses through such states)
Deposition methods	Suitable deposition methods for thin-film formation and control should be available
Electrical contacts	It should be possible to form low-resistance electrical contacts to both *n*- and *p*-type materials
Material availability	Supplies of the material should be sufficient to allow large-area cell protection
Material cost	Cost of the material should be competitive with alternative systems
Material toxicity	Materials should be nontoxic, or control of toxicity should be possible
Cell stability and lifetime	Cell must have an operating lifetime sufficient to pay back economic and energy costs required to produce it

1.16 Thin Films

In recent years, research on thin films have been expanded into a wide field of scientific and technical applications [26] such as antireflection coatings, protective layers, electrical capacitors, where they act as passive components, solar coatings, high temperature superconductors, modelling and circuit simulation, devices and circuits and flat panel displays and many others. As active devices, they may offer an advantage where large areas are to be coated. For example, thin film solar cells are potentially less expensive than bulk ones of the same area. In other situations, thin film active devices offer a unique solution, such as in the development of 'active matrix' high resolution liquid crystal displays for graphic and TV application, where only a macroelectronic approach is viable.

In all cases, the material properties of these thin films are very different from the bulk due to their polycrystalline nature and the high surface to volume ratio which enhances the importance of usually detrimental surface properties. This characteristic has an important role in the electronic and related industries because when the film becomes thinner, the surface properties become more important than the bulk properties. When the surface properties and energy levels are better understood, this would lead to a far better utilisation of thin films. For example, thin film technology holds the key to the miniaturisation of electronic components and which could lead to a great savings in terms of material costs and power consumption.

Thin film solar cells are one of the most cost effective method of photovoltaic generation for terrestrial application. Two of the major advantages of thin film solar cells is as follows:

- The cells can be deposited over large area, continuous flow process onto a variety of substrates such as glass, silicon and indium tin oxide.
- Since the required thickness of the active layers is in the order of two to three times the optical absorption length, material cost becomes only a small part of the total cell cost and consequent wastage is minimised.

Constant work is also done to obtain the best possible electrical and optical properties for materials such as cadmium telluride(CdTe) and cadmium selenide(CdSe), for improving the conductivity and mobility and hence to establish good ohmic contact between materials in the construction of a solar cell.

1.17 Thin Film Coating Techniques

1.17a Chemical Deposition Techniques

The commonly used techniques for chemical deposition of films are electrodeposition, chemical vapour deposition and spray pyrolisis. These techniques will be elaborated in the following:

1.17.1. Electrodeposition

Since electrodeposition is one of the key techniques of film preparation in this study, greater emphasis will be placed on describing the technique. Electrodeposition is used to deposit elements, alloys and compounds on a conducting or semiconducting substrate. The apparatus involved is basically simple, consisting of a conducting anode and cathode, immersed in a suitable electrolyte. A reference electrode is sometimes used to determine the exact voltage across the anode and cathode. The deposition could either be anodic or cathodic (depending on the system) and is influenced by parameters such as deposition voltage, current density, electrode separation, temperature, bath concentration, deposition time and pH.

The electrodeposition method has been successfully used to fabricate materials for practical uses such as photovoltaic solar cells, fast ionic conductors as shown in earlier work [27, 28] and numerous electrochemical devices [29, 32]. Some of the reasons why the method of electrodeposition is gaining popularity are as follows [33]:

- Electrodeposition enables the fabrication of thin films in the order of 1μm for certain applications such as solar cells. The thickness of the film can be controlled by the charge passed during deposition and deposition time. Absorption coefficient measurement of electrodeposited CdTe showed that as much as 90% of the solar spectrum can be absorbed by a 1μm film.
- Being a low temperature process, it allows the use of an inexpensive apparatus equipment and instrumentation.
- There is minimal wastage of materials as the deposition is carried out only on the required substrate section and the bath dimensions can be adjusted accordingly.
- Being a simple electrochemical process, it can be scaled up for mass production at a practical cost.
- It is also possible to obtain p- and n- type materials by changing the deposition potential difference.

The method of electrodeposition involves surface phenomena, solid state processes and processes occurring in the liquid state. Electrodeposition may seem simple as it adopts the fundamental process of electrolysis using electrodes and an electrolyte, but in actual fact, it involves a complex and varied nature of interdisciplinary studies as outlined below [34].

Discipline	**Involvement**
Electrochemistry	Electrode processes
Electrochemical Engineering	Transport phenomenon
Surface science	Analytical tools
Solid state physics	Use of quantum mechanical solid state concepts to study electrode processes
Metallurgy and material science	Properties of deposits
Electronics	Modern instrumentation

1.17.2 Chemical Vapour Deposition

The compound of interest is condensed from the gasseous phase onto a substrate where reaction occurs, to produce a solid deposit. The chemical reaction may be activated by application of heat, r.f. field, glow discharge etc. The vapour for reactions are transported either by creating pressure difference or by using a carrier gas, which may or may not participate in the reaction.

1.17.3 Spray Pyrolysis

Spray pyrolysis, as suggested by the name, involves the application of a fine mist of very small droplets, containing the reactants onto a hot substrate. This is a variation of the CVD technique and it is essentially pyrolytically (thermally) stimulated reaction between liquid clusters or vapour atom of different chemical species. A solution of chemical species is sprayed on a hot substrate, where the desired reaction takes place [35-38]. Various types of spray pyrolysis methods have been developed such as substrate rotating method, XY movement of nozzle method, corona spraying method and also improved methods of spray pyrolysis.

1.17b Physical Deposition Techniques

Physical deposition techniques are exemplified by evaporation, sputtering and molecular beam epitaxy.

1.17.4 Vacuum Evaporation

The evaporation of metallic compounds in vacuum and condensation of the vapour onto chemically inert substrate is one of the techniques for the preparations of thin films. Details of various methods used in vacuum evaporation are discussed below.

A. Resistance Heating Evaporation

The material to be deposited is placed in a resistive heater and the substrate over which deposition is desired, are kept enclosed in a vacuum chamber with pressure below 10^{-5} mbar [39]. On heating, the material vaporizes into atoms or molecules. Since the chamber pressure is low, the mean free path of these particles would be large and they can travel towards the substrate placed at a distance which acts as a cold finger where nucleation occurs, leading to ultimate film growth. The common heating elements used are those of tantalum, molybdenum or tungsten depending upon temperature required and reactivity of the material to be heated. This technique is very convenient for metal films or electrodes and thin films of low melting point materials which do not dissociate on heating. Films of refractory materials or oxides are generally not possible.

B. Electron Beam Evaporation

The evaporant in a hearth of electrically conducting material is bombarded with a beam of electrons so that the evaporant is directly heated and vaporized [40]. The portion of the evaporant that is heated, is in the centre of the exposed surface, and there is a long thermal conduction path through the material to the hearth. Therefore, the hearth can be maintained at lower temperatures compared to the melting point of the evaporant without prohibitive heat loss. That means, the reaction between the hearth and the evaporant is virtually inhibited. This technique is particularly suitable for materials that react with the source or require very high evaporation temperatures or both.

C. Reactive Evaporation

It is possible to evaporate oxide films from metal wires or foils under oxygen pressure ($> 10^{-4}$ mbar) [41, 42]. The evaporated material (by resistive or electron beam heating) is transported through a reactive gas (such as oxygen, nitrogen etc) to yield a film of reaction product. This technique is used for depositing single element oxide films as multielement oxides and alloy films are not possible.

1.17.5 Sputtering

If a surface is bombarded with energetic particles, it is possible to cause ejection of the surface atom which is known as sputtering. The ejected atoms can be condensed on to a substrate to form a thin film. The process can be realised by forming positive ions of a heavy neutral gas such as argon, and causing these to bombard the surface of the target material by making the surface as cathode in the electrical circuit.

A. Cathode Sputtering or D.C. Sputtering

The material to be deposited forms the cathode of the system in which a glow discharge is established. The substrate on which the film is to be formed is placed on the anode of the system. Positive ions of the gas created by the discharge are accelerated towards the cathode. Under the bombardment of these ions, particles are removed from the cathode in the form of neutral atoms and ions. The liberated components, then condense on the surrounding areas, including the substrate

B. Radio Frequency Sputtering (RF-Sputtering)

Insulators cannot be sputtered by conventional cathode sputtering techniques, because the accelerating potential cannot be directly applied to the insulator surface. This prevents neutralizing of the positive charge, which would accumulate on the surface during ion bombardment [43]. This problem can be overcome by applying a high frequency potential by a metal eleetrode behind the insulator. The positive charge which accumulates on the surface during the negative portion of each cycle is neutralized by electrons in the positive part of cycle. Uniform deposition from large-area cathode is also possible using this technique.

C. Magnetron Sputtering

It is an RF-sputtering technique in which a magnetic field transverse through the electric field applied at the target surface. Target generated secondary electrons are hence trapped in cycloidal trajectories near the target. Since these electrons do not bombard the substrate, they do not contribute to increased substrate temperature and radiation damage. This allows the use of low temperature substrates (e.g. plastic) and surface-sensitive substrates (e.g. metal-oxide materials) without adverse effects. In addition, this technique offers higher deposition rates to conventional RF-sputtering.

An important advantage of sputtering method is that high quality films with good adhesion can be obtained. On the other hand, its low deposition rate is its main drawback, as long hours of sputtering are required for preparing films of significant thickness.

1.17.6 Molecular Beam Epitaxy (MBE)

This is essentially a layer by layer deposition technique. In this technique, the vapours are derived from an effusion source. The effusion source consists of a metal chamber, with a small orifice, through which the evaporant materiel present in the chamber slowly effuses out. An ultra high vacuum is needed for very large mean free path of effusing particles and for clean ambient. The flux of the vapour coming out of effusing source is controlled by vapour pressure of species, molecular weight, orifice dimension and source temperature. The growth rate is small (1 - 10A/sec) which makes it possible to control film thickness and its crystallinity.

The advantages of MBE technique are used for growing oriented compound semiconductor film and complex interface structures such as quantum well structure and heterostructures. The main disadvantages of this technique are slow deposition rate and high cost.