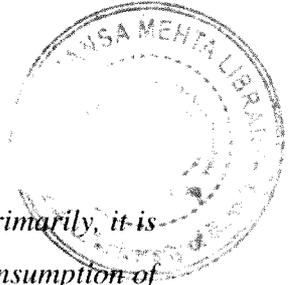




CHAPTER 1

Introduction



1. Introduction

Energy is the key input to drive and improve the life cycle. Primarily, it is the gift of the nature to the mankind in various forms. The consumption of the energy is directly proportional to the progress of the mankind. With ever-growing population, improvement in the living standard of the humanity and industrialization of the developing countries, the global demand for energy is expected to increase rather significantly in the near future. The primary source of energy is fossil fuel. However the finiteness of fossil fuel reserves and large scale environmental degradation caused by their widespread use, particularly global warming, urban air pollution and acid rain, strongly suggests that harnessing of renewable and environment “friendly” energy resources is vital for steering the global energy supplies towards a sustainable path. A brief description of various renewable energy sources is given in this chapter.

Compared to other renewable energy sources such as wind power, hydro power, and solar thermal power, photovoltaic (PV) solar power holds obvious advantages. Whereas wind and hydro electrical power generation, relies on turbines to turn generators with moving parts, are noisy and require maintenance, PV systems, with no moving parts, require virtually no maintenance, and have cells that can last for decades.

In addition, the exclusive modular nature of PV enables designers to build PV systems with various power output in a distributed fashion, and allowing the power generation to keep in step with growing needs without having to overbuild generation capacity as is often the case with conventional large-scale power systems. Since its first commercial use in powering orbital satellites in the 1950s, PV has been widely used in space and on the earth for several decades. Crystalline silicon was first used to produce PV cells (also known as solar cells), and still dominates the PV market today. This is mostly due to a well-established knowledge on silicon material science and engineering, an available abundant supply of silicon raw material, and the advantages of low ecological impact but

high efficiencies. However, the relatively high price of crystalline silicon material, and additionally, its too low optical absorption ($\sim 10^2 \text{ cm}^{-1}$), due to an indirect transition, requiring a much larger raw material consumption and a complicated manufacturing process lead to a high installation cost for crystalline silicon-based PV technology. From this point of view, the PV power generation is not competitive in most urban areas where conventionally generated power is readily available. A substantial reduction of PV production costs is expected from the development of thin film solar cells, in which highly absorbing layers with a few micrometer thickness can be produced by economical, high-volume manufacturing techniques. This lays down the background for the extensive research interest in materials suitable for thin film solar cells.

At present, several manufacturing facilities based on thin film semiconducting materials such as amorphous silicon, cadmium telluride, and copper indium diselenide are in the pilot-line stage. A brief summary of these thin film solar cells with their present status is given in this chapter. The present thesis is dealing with fabrication and characterization of copper indium diselenide (CIS) based thin film solar cells. The structure of CIS thin film solar cell device is discussed in this chapter. The thesis overview is also included here for the sake of the completion and convenience.

1.1 Renewable Energy Sources

To meet the future energy demands and to give quality and pollution free supply to the growing and today's environment conscious population, the present world attention is to go in for natural, clean and renewable energy sources. These energy sources capture their energy from on-going natural processes, such as geothermal heat flows, sunshine, wind, flowing water and biological processes.

Most renewable forms of energy, other than geothermal and tidal power ultimately come from the Sun. Some forms of energy, such as rainfall and wind power are considered short-term energy storage, whereas the energy in biomass is accumulated over a period of months, as in straw, and through many years as, in wood. Fossil fuels too are theoretically renewable but on a very long time-scale and if continued to be exploited at

present rates then these resources may deplete in the near future. Therefore, in reality, renewable energy is energy from a source that is replaced rapidly by a natural process and is not subject to depletion in near future.

Renewable energy sources may be used directly, such as solar ovens, geothermal heating, and windmills or indirectly by transforming to other more convenient forms of energy such as electricity generation through wind turbines or photovoltaic cells, or production of fuels (ethanol, etc.) from biomass. A brief description of these renewable energy resources is given here for the sake of comparison.

1.1.1 Wind Energy

The origin for wind energy is the sun. When the sun rays fall on the earth, its surface gets heated up and consequently uneven winds are formed. Kinetic energy in the wind can be used to run wind turbines but the output power depends on the wind speed. Turbines generally require a wind in the range 5.5 m/s (~20 km/h). In practice, relatively few land areas have significant prevailing winds. Otherwise, wind power is one of the most cost competitive renewable energy today and this has been the most rapidly growing means of electricity generation at the dawn of the 21st century and provides a complement to a large-scale base-load power stations. Its long-term technical potential is believed to be five times the current global energy consumption or forty times the current electricity demand.

The Indian wind energy sector has an installed capacity of 11,807 MW (as on March 31, 2010). In terms of wind power installed capacity, India is ranked fifth in the World. Today India is a major player in the global wind energy market [1]. Indian Wind Energy Association has estimated that with the current level of technology, the 'on-shore' potential for utilization of wind energy for electricity generation is of the order of 65,000 MW. The unexploited resource availability of wind energy sector in India has the potential to sustain the growth in the years to come.

1.1.2 Water Power

Energy in water can be harnessed and used, in the form of motive energy or temperature differences. Since water is about a thousand times heavier than air is, even a slow flowing stream of water can yield great amounts of energy. There are many forms of water energy usage:

- Hydroelectric energy, a term usually reserved for hydroelectric dams.
- Tidal power, which captures energy from the tides in horizontal direction. Tides come in, raise water levels in a basin, and tides roll out. The water is made to pass through a turbine to get out of the basin. Power generation through this method has a varying degree of success.
- Wave power, which uses the energy in waves. The waves will usually make large pontoons go up and down in the water. The wave power is also hard to tap.

The large hydro power projects of millions of megawatts are available with the developing countries of the world but major bottleneck in the way of development of these large hydro power projects is that each site calls for huge investment. As a result, micro/small hydro power projects described underneath are another option to generate electricity.

➤ **Micro/Small Hydro Power**

This is renewable energy source and is easy to tap. Quantitatively small volumes of water, with large falls (in hills) and quantitatively not too large volumes of water, with small falls (such that of canals), can be tapped. The force of the falling and flowing water is used to run water turbines to generate energy.

In India, during the 12th Five Year Plan (2012-2017), the Government has identified hydro power benefits of 38,242 MW. During the same period the National Hydroelectric Power Corporation Ltd., a government of India enterprise, is targeting to install 5,837 MW of hydro power in India. In the approach paper on power and energy to the 11th Five Year Plan-2007-2012, the government of India is anticipating in hydro capacity addition of 16,553 MW, out of which Central Sector will add 9,685 MW, State Sector 3,605 MW and Private Sector 3,263 MW. From 1,061 MW in 1st Five Year Plan (1951-1956), the hydro power has grown to 34,131 MW at the end of 10th Five Year Plan. In fact, installed capacity of hydro power plant has increased at a compound growth rate of 4.35 % per annum since 1991, higher than all other power sub-sectors [2].

1.1.3 Geothermal Energy

Geothermal energy comes from radioactive decay in the core of the earth, which heats the earth from the inside out and thus energy/power can be extracted owing to the temperature difference between hot rock deep in the earth and relatively cool surface air

and water. This requires that the hot rock should be relatively shallow, so it is site - specific and can only be applied in geologically active areas. It can be used in two ways: one is Geothermal heating and the other is Geothermal electricity.

As stated above, the geothermal energy from the core of the earth is closer to the surface in some areas than in others. Where hot underground steam or water can be tapped and brought to the surface it may be used directly to heat and cool buildings or indirectly, it can be used to generate electricity by running steam/gas turbines. Even otherwise, on most of the globe, the temperature of the crust a few feet below the surface is buffered to a constant 300-310 K, so a liquid can be pre-heated or pre-cooled in underground pipelines, providing free cooling in the summer and heating in the winter by using a heat pump.

India has several geothermal provinces characterized by high heat flow and thermal gradients. Subsequent to the oil crisis of the 1970s, the Geological Survey of India generated data of resource assessment for over 300 hot springs in the country. The National Geophysical Research Institute and the IITs, especially at Puga valley in Ladakh and Tatapani in Chhattisgarh, carried out subsequently detailed geological, geophysical and tectonic studies on several thermal provinces, geochemical characteristics of the thermal discharges and reservoir temperature estimations.

It is estimated that there is a technical potential to produce about 10,000 MW of geothermal power in India. From the point of view of electrification of rural and remote areas, there is even greater potential in terms of the impact of geothermal power where even small projects of 5 kW can significantly change the economic situation and living standards. The Himalayan region is one of the most promising geothermal areas. It contains about 100 thermal springs and falls in one of the most tectonically active zones. In the year 1980, the first pilot binary 5 kW power plant was successfully operated by the Geological Survey of India at Manikaran in Himachal Pradesh which proved the power producing capability there. The Puga Valley geo-thermal field in Jammu and Kashmir has been estimated to have a temperature of 513 K at a depth of 2000 meters [3].

1.1.4 Biomass

Plants use photosynthesis to store solar energy in the form of chemical energy. The easiest way to release this energy is by burning the dried up plants. Solid biomass such as

firewood or combustible field crops including dried manure is actually burnt to heat water and to drive turbines. Field crops may be grown specifically for combustion or may be used for other purposes and the processed plant waste then used for combustion. Most sorts of biomass, including Sugarcane residue, wheat chaff, corn cobs and other plant matter can be, and is, burnt quite successfully. Currently, biomass contributes 15 % of the total energy supply worldwide. A drawback is that all biomass needs to go through some of these steps: it needs to be grown, collected, dried, fermented and burned. All of these steps require resources and an infrastructure.

The government of India strongly encourages the utilization of biomass energy. All renewable energy matter is under jurisdiction of Ministry of New and Renewable Energy (MNRE). MNRE estimated the biomass power potential in the entire country as 19,500 MW. To obtain the maximum utilization of such high potential energy source MNRE has been conducting various researches such as technologies, resource assessment and system modeling on biomass energy sector. As a result, India now becomes one of the leading countries of biomass energy utilization. The commissioned biomass power capacity reached 290 MW (52 projects) and the commissioned co-generation capacity installed mainly at sugar mills reached 437 MW.

1.1.5 Solar Energy

The sun, our closest star, is the origin of most of the energy maintaining life on earth and produces the necessary gravitational attraction to keep our planet in a nearly circular orbit. It has a mass of 1.99×10^{30} kg and a radius of 6.96×10^8 m. The earth-sun distance, R , is approximately 1.5×10^{11} m. A simple model assumes that the sun is circular and behaves as a black body whose surface is maintained at $T = 6000$ K. This surface temperature is kept constant by energy generated through continuous nuclear fusion of hydrogen into helium in the interior. The interior temperature is, approximately 10^7 K. Because of interior temperature, the surface (photosphere) radiates electromagnetic radiation in all directions of space. The spectral distribution is changed considerably when the sunlight penetrates through the earth's atmosphere. Even for a clear sky the light intensity is attenuated by at least 30 % due to scattering by molecules, aerosols and dust particles and adsorption by its constituent gases like water vapor, ozone or carbon dioxide.

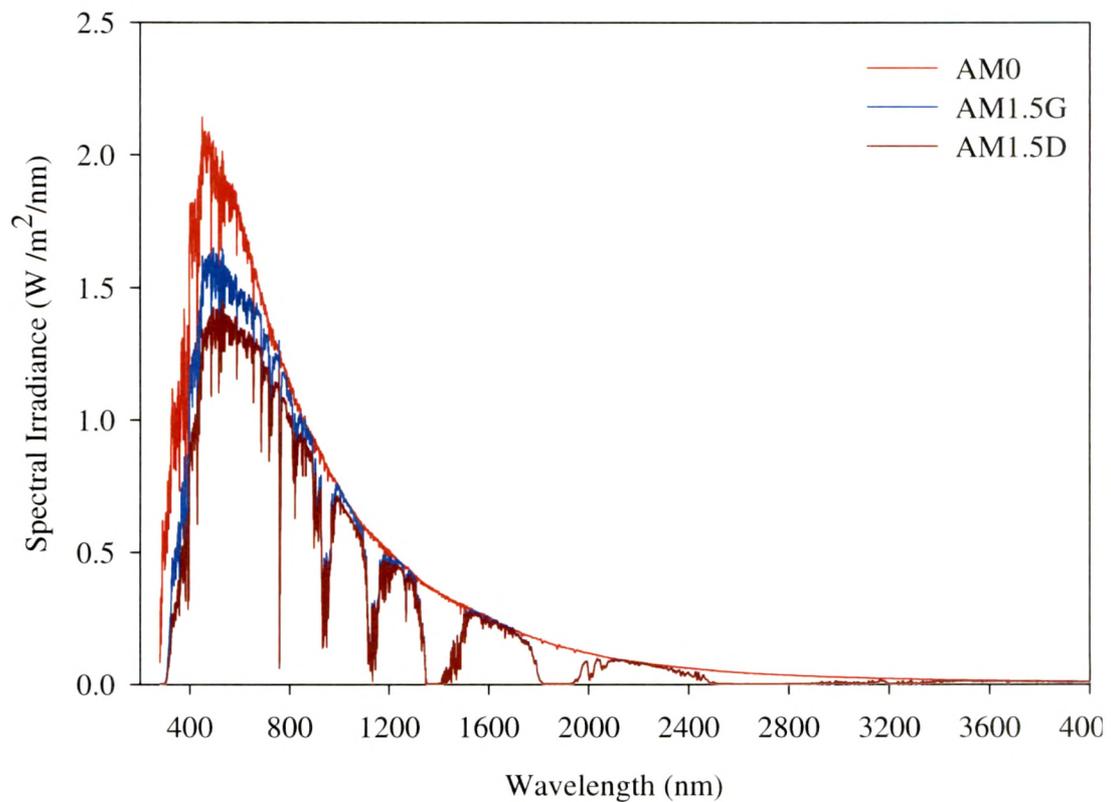


Figure 1.1: Spectrum of solar radiation.

Figure 1.1 shows three curves related to solar spectral irradiance. The upper curve, which represents the solar spectrum outside the earth's atmosphere, is the air mass zero condition (AM0). This condition can be approximated by a 5800 K black-body radiation. For a typical cloudless atmosphere and zero zenith angle, the irradiance reaching the outer atmosphere is reduced to approximately 1050 W/m² direct beam radiation (AM 1.5D), or 1120 W/m² global irradiation (AM 1.5G), on a horizontal surface at sea level [4] as shown in figure 1.1. Some key technologies for harnessing the power from the sun are briefly reviewed in the following subsections.

1.1.5.1 Solar Heating

The best-known technology for active solar heating is the solar domestic hot water systems. Another technology in the building sector is solar space heating system. Such a system can be sized for single houses or for collective buildings and district into low-temperature heat (up to 373 K). In general, two classes of technologies can be distinguished, namely passive and active solar energy conversion. Active conversion relies on a solar collector, and the heat is transported to the process by a medium, often heating. Similar technologies can be applied in the industrial and agricultural sector for

low-temperature heating and drying applications. Finally, there are technologies to use thermal solar for cooking purposes.

1.1.5.2 Photovoltaics-State of Art

Photovoltaic energy conversion is the direct conversion of sunlight into electricity. This can be done by flat plate or concentrator systems. An essential component of these systems is the solar cell, in which the photovoltaic effect takes place. In photovoltaic effect, the energy of light generates free electrons and an electric current. Today's commercially available photovoltaic devices are fabricated from semi-conducting materials. The most commonly used material is silicon, to which small amounts of impurities, typically boron and phosphorous, are added. In this process, which is called doping, one region with excess of free electrons (called n-type) and one region with excess of holes (called p-type) are created. In the junction between these regions (the p-n junction) a static internal electric field is formed. This field, which is directed from the n-type region towards the p-type region, separates the electrons and holes that are produced when the material is illuminated. At wavelengths where the photons have energies above a certain threshold energy (the bandgap energy) the light will be absorbed in the semiconductor material and an electron-hole pair is created. If the electron-hole pair is generated close enough to the p-n junction the carriers can be separated by the internal electrical field and contribute to the generated current.

The efficiency of conversion from sunlight to electricity in a photovoltaic solar power system is typically 10-15 %. Hence, substantial areas are required to capture and convert significant amounts of solar energy to fulfill the energy needs relative to today's energy use. For instance, at a plant efficiency of 10 %, an area of 3–10 km² is required to generate an average power of 100 MW, resulting in a yearly electricity generation of 0.9 TWh [5]. Some of the more provocative solar energy experts, however, claim that this is not a problem - there are desert areas more than enough to supply the world with solar electricity. Covering an area of 5,00,000 km², corresponding to approximately 5 % of the Sahara desert, with 10 % efficient solar panels would provide sufficient amounts of electricity to meet the total global energy needs [6]. In this scenario, photovoltaic systems would be placed in many desert areas around the world and connected in a worldwide solar energy grid.

In densely populated countries with a well-developed infrastructure, there is an emphasis on applications of grid-connected photovoltaic systems in the built environment. These systems are necessarily small or medium sized, typically between 1 kW and 1 MW. The electricity is generated close to the place where electricity is also consumed. In less densely populated countries, there is a considerable interest in ground-based power plants, generally larger than 1 MW. In countries or rural regions with a weak grid infrastructure, small standalone systems and modular electric systems may be used for electrification of houses or village communities. Grid connected systems here account for only a small fraction, while the majority are small standalone systems used for water pumping, communication, leisure, consumer products, etc. This shows that the photovoltaic technology has the potential to give a substantial input to the energy supply in the future, and to be part of creating a sustainable energy system.

Figure 1.2 shows efficiency of solar cells prepared from different semiconducting materials, as reported by industrial manufacturers and world's leading photovoltaic research laboratories. It can be seen that the development of multi-junction and thin film photovoltaic devices are areas of active research in the 21st century.

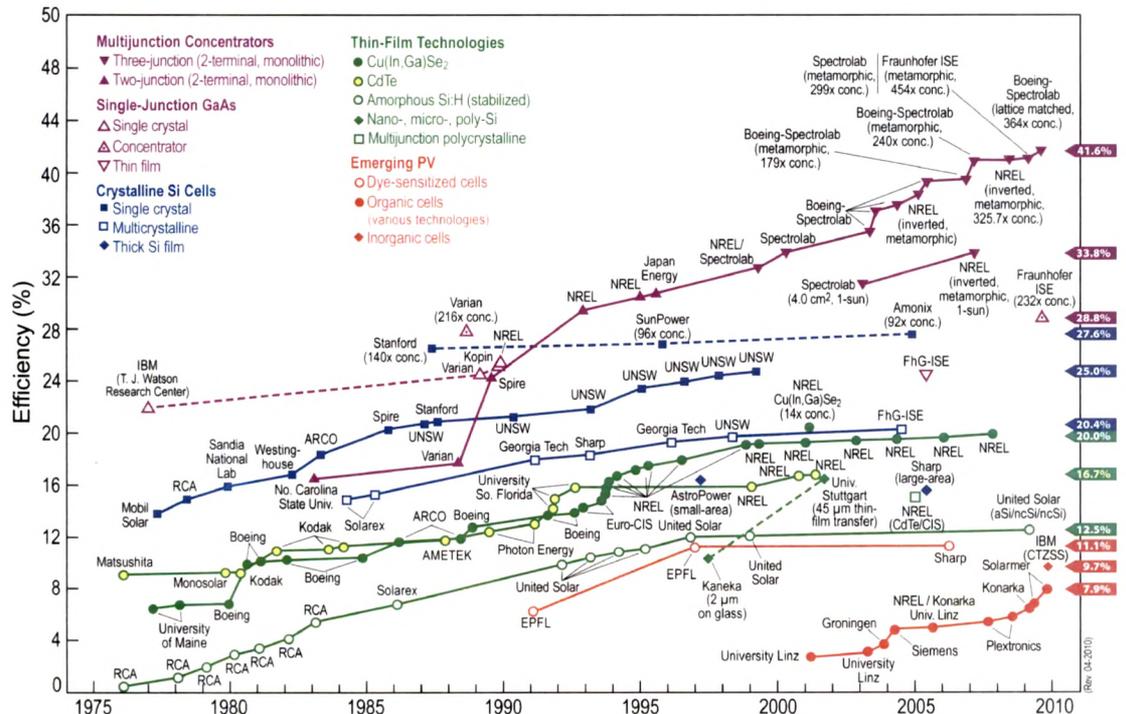


Figure 1.2: Solar cell efficiency records [7].

Due to complexities involved in the fabrication of multi-junction solar cells and low efficiency of modules, thin film solar cells based on cadmium telluride (CdTe) and

copper indium diselenide (CIS) are useful alternatives to crystalline silicon cells. The up scaling of this technology from the single solar cell to the large area module is a challenge. Three major thin film materials used for large-scale production of photovoltaic devices are amorphous silicon (a-Si) and CdTe and CIS based multi-crystalline compounds.

1.2 Thin Film Photovoltaic Technology

Currently, a-Si, CdTe, and CIS based material are considered the mainstream thin-film technologies. Out of these, a-Si currently has the highest market share [8]. Due to the involvement of several industries worldwide during the last two decades, this technology has attained a significant level of maturity for large volume production. In addition, CdTe and CIS have proven their potential to become leading technologies but they lacked adequate research, development, industrial, and investors' support to make a mark. However, recently several companies have started production-related activities and production volume is expected to increase during the next few years. Recent developments on a new technology for organic and dye-sensitized solar cells appear to be quite interesting with their low-temperature processing and cheaper processing cost on flexible substrates [9,10]. However, there are potential issues of instability and degradation. They are in the infancy of their development now and would require considerable efforts and time to see them become a commercially viable option. The front-line thin-film technologies such as a-Si, CdTe, and CIS based solar cells are discussed here.

1.2.1 Amorphous Silicon (a-Si)

Hydrogenated amorphous silicon was introduced as a material with a potential for semiconductor devices in the mid 1970s [11] and is the first thin-film solar cell material that has reached the stage of large-scale production. Amorphous silicon has a higher optical absorption coefficient than crystalline silicon and, thus, can be efficient at much less thickness. In order to reduce recombination losses, amorphous silicon solar cells are based on a p-i-n structure, consisting of a thin p-type doped layer, a central intrinsic i-type layer as the photon absorbing layer, and a thin n-type doped layer. The electrical transport in i-type layer is assisted by an electric field.

Amorphous silicon solar cells are commonly deposited on glass coated with a transparent front contact of either tin oxide (SnO_2) or zinc oxide (ZnO). The most widely used deposition technique is plasma enhanced chemical vapor deposition (PECVD). At present, industrial fabrication processes for large-area amorphous silicon are limited by rather low deposition rates, and the devices suffer from low efficiencies. One of the main reasons for the limited efficiencies is the light induced degradation [12], due to which the efficiency decreases after extensive illumination. Typically, for commercial amorphous silicon modules, an initial efficiency drop of about 25 % followed by stabilization and mild oscillation around the stabilization point can be expected. Amorphous silicon cells in a tandem- or triple-junction structure have the potential for improved efficiencies by better utilizing the solar spectrum. Typically, efficiencies of stabilized triple-junction laboratory cells reach the 13 % level, while commercial triple-junction modules have stabilized efficiencies in the 4-8 % range [13]. The price of amorphous silicon solar modules is still today, for a given stabilized power output, only marginally lower than that of crystalline silicon modules.

1.2.2 Cadmium Telluride (CdTe)

Thin films of cadmium telluride (CdTe) receive much attention as absorber materials for efficient, low-cost solar cells. CdTe devices are commonly based on a CdS/CdTe heterojunction, and laboratory cell efficiencies as high as 16.7 % and large area modules at the 10.9 % have been reported [14]. Their advantages include direct bandgap with nearly optimum value for photovoltaic applications, and good match of the electron affinity to the cadmium sulfide window.

Based on predictions of optimum bandgap for solar conditions, CdTe was suggested as a photovoltaic compound in 1959 [15]. The first efficient devices based on the CdS/CdTe structure was accomplished in 1972 [16], and soon devices with conversion efficiencies exceeding 10 % were fabricated by screen-printing. The first commercial product was released in 1982, but withdrawn again because of stability problems related to degradation of the electrical contact to the CdTe film [17].

CdTe films have been deposited by a variety of methods, including electrodeposition, screen-printing, and high-rate evaporation, but the best performing CdTe-based devices are fabricated using closed-space sublimation [14]. The raw materials, cadmium and tellurium, are relatively inexpensive and available in reasonable

quantities. Cadmium is classified as an environmentally hazardous material, but the compound CdTe itself is reported to be very stable [18]. Advances in process development at the laboratory scale have been gradually transferred to large-scale deposition and module fabrication. The most important players within commercialization of the CdTe technology are Matsushita in Japan, Antec in Germany, and First Solar and BP Solar in the USA [19].

1.2.3 Copper Indium Diselenide (CIS)

Copper indium diselenide (CIS) is a p-type multi-crystalline semiconductor with high optical absorption coefficient. For thin film solar cell applications, this compound is used in a heterojunction structure, commonly with a very thin n-type cadmium sulfide layer. The optimal bandgap for a single-junction solar cell with respect to the solar spectrum is around 1.4 eV [20]. Pure CIS has a bandgap of 1.04 eV. To increase the bandgap, indium can be partially replaced by gallium, thus obtaining copper indium gallium diselenide (CIGS). An indium to gallium ratio of 20–40 % will result in a bandgap of approximately 1.1–1.2 eV, which has been shown empirically to give the best cell results. The bandgap of pure copper gallium diselenide (CGS) is 1.67 eV. A further degree of freedom is achieved by the partial substitution of S₂ for Se₂ (CIGSS). The direct bandgap and the high absorption coefficient of CIGS relaxes the requirements on minority carrier lifetime and facilitates thinner absorber layers since the photo-excited carriers are generated close to the depletion region [21]. This makes CIGS a suitable compound for thin film solar cells.

CIS based thin film solar cells have been fabricated by several research groups with efficiency over 15 %, and the efficiency record obtained for a small laboratory cell is reported as high as 20.3 % for CIGS solar cell [22]. Laboratory mini-modules have reached 16.6 % efficiency [23]. In terms of stability, CIS based solar cells do not have the problem of light-induced degradation. CIGS devices have shown promising results in outdoor long-term performance tests but at the same time they are more sensitive than crystalline silicon solar cells to hot and humid environments [24].

CIS is one of the most promising materials for large-scale fabrication of low-cost high-efficiency thin film solar cells, and as device results are approaching two of the important milestones on the route to commercialization – the 15 % efficient module and the 20 % cell – several research institutes have announced their plans for CIGS

production lines. Siemens Solar Industries [25] released the first commercial CIS based thin film module in 1998, but the US-based production is still on a limited scale. It is expected that CIS based modules in mass production will be substantially cheaper than wafer based crystalline silicon modules. Module production costs of less than 1 USD per watt peak is commonly forecasted [26]. Much of the current research activities in the CIS based thin film solar cells are directed towards manufacturability issues such as technology scale up, module design, packaging, and long-term stability. Other hot research topics are the possibilities to reduce the amount of indium used, and to remove or to find a less hazardous replacement of the thin cadmium sulfide layer.

1.3 Present Status of Thin Film Photovoltaic

A high potential for cost reduction is expected for the production of thin-film solar cell modules as compared to conventional silicon-wafer-based methods. Regardless of the material, all thin-film techniques have advantages because of their low active material consumption and costs, the monolithic integration of cells, and independence from shortages in solar-grade silicon supplies. Thin-film module production involves fewer processing steps than silicon, and allows a higher degree of automation. Industrially produced modules attain efficiencies between 8 and 12 % on the square meter scale with individual modules exceeding 50 Wp (watts peak), and expected long-term stability over more than 20 years - all requirements to successfully gain long-term acceptance in the power market. The estimated production of thin film photovoltaic modules by leading photovoltaic manufacturers is shown in table 1.1. As apparent from table 1.1, rapidly growing production volumes are dominated by the amorphous silicon and CdTe approaches.

Table 1.1: Thin Film PV Capacity (2007-2010) [27].

| Group | Material | Present (MW) | Additional (MW) | Total (MW) | Group | Material | Present (MW) | Additional (MW) | Total (MW) | Material | Present (MW) | Additional (MW) | Total (MW) | Total | Grand Total | | | | |
|----------------|----------------------|---------------|-----------------|------------|--------------------|--------------|--------------|-----------------|------------|----------|--------------|-----------------|------------|-------|-------------|----|----|--|--|
| USA | First solar | 90 | | 90 | AVA solar | CdTe | 3 | | 3 | | | 20 | 23 | 1127 | 3704 | | | | |
| | Uni- solar | 60 | 240 | 300 | Nano PV | a-Si | - | | | | | 4 | 4 | | | | | | |
| | Miasole | 5 | 50 | 55 | Optisolar | a-Si | - | | | | | 40 | 40 | | | | | | |
| | Global solar | 3 | 60 | 63 | Primestar solar | CdTe | - | | | | | 20 | 20 | | | | | | |
| | EPV | 2 | 25 | 27 | Solo power | CIS | - | | | | | 20 | 20 | | | | | | |
| | Daystar technologies | CIS | 1 | 10 | 11 | ISET | CIS | - | | | | 3 | 3 | | | 3 | | | |
| | | a-Si | 1 | 10 | 11 | MWOE solar | a-Si | - | | | | 3 | 3 | | | 3 | | | |
| | Power film | 1 | 10 | 11 | | | | | | | | | | | | | | | |
| | Ascent solar | 2 | 25 | 27 | | | | | | | | | 20 | | | 20 | | | |
| | Nano solar | CIS | - | 430 | 430 | Heliovolt | CIS | - | | | | | 20 | | | 20 | | | |
| | JAPAN | Kaneka | 20 | 50 | 70 | MHI | a-Si | 14 | | 14 | | | 56 | | | 70 | | | |
| | | Showa Shell | 20 | 60 | 80 | Kanto sanyo | a-Si | 7 | | 7 | | | | | | 7 | 7 | | |
| | | Sharp | 15 | 100 | 1015 | Honda | CIS | 3 | | 3 | | | 27 | | | 30 | 30 | | |
| | | Fuji | 15 | 25 | 40 | | | | | | | | | | | | | | |
| First solar | | 120 | 100 | 220 | AMI | a-Si | - | | | | | 160 | 160 | 160 | | | | | |
| CSG solar | | 10 | 15 | 25 | Johanna solar Tech | CIS | - | | | | | 30 | 30 | 30 | | | | | |
| EUROPE | Wurth solar | 3 | 15 | 18 | Brilliant | a-Si | - | | | | | 25 | 25 | 25 | | | | | |
| | Antec solar | 10 | - | 10 | Solisbro | CIS | - | | | | | 30 | 30 | 30 | | | | | |
| | Schott solar | 3 | 27 | 30 | Global solar | CIS | - | | | | | 30 | 30 | 30 | | | | | |
| | ICP Solar tech | 3 | - | 3 | Hello Grid | a-Si | - | | | | | 50 | 50 | 50 | | | | | |
| | Solar cells | 1 | - | 1 | Sunfilm | a-Si | - | | | | | 60 | 60 | 60 | | | | | |
| | Free energy | 1 | - | 1 | T.J.Solar | a-Si | - | | | | | 40 | 40 | 40 | | | | | |
| | Solar Plus | - | 5 | 5 | Signet Solar | a-Si | - | | | | | 20 | 20 | 20 | | | | | |
| | Sulfur Cells | 5 | - | 5 | Clyxco | CdTe | - | | | | | 25 | 25 | 25 | | | | | |
| | Aleo Solar | - | 30 | 30 | Avancis | CIS | - | | | | | 20 | 20 | 20 | | | | | |
| | Ersol | - | 40 | 40 | Odersun | CIS | - | | | | | 5 | 5 | 5 | | | | | |
| | | | | | Scheuten solar | CIS | - | | | | | 10 | 10 | 10 | | | | | |
| | ASIA | First solar | - | 220 | 220 | GET | a-Si | - | | | | | 40 | 40 | 40 | | | | |
| | | Bangkok solar | 7 | - | 7 | Nanowin Tech | a-Si | - | | | | | 35 | 35 | 35 | | | | |
| | | Simonar | 3 | - | 3 | Moser Baer | a-Si | - | | | | | 20 | 20 | 20 | | | | |
| T.J.Solar Cell | | 2 | - | 2 | Solar Morph | a-Si | - | | | | | 20 | 20 | 20 | | | | | |
| Soltech | | 15 | - | 15 | Topray solar | a-Si | 20 | | 20 | | | - | - | 20 | | | | | |
| Suntech Power | | - | 50 | 50 | CMC | a-Si | - | | | | | 40 | 40 | 40 | | | | | |

1.4 Trends in CIS-based Devices

CIS was first synthesized by Hahn and co-workers in 1953 [28], but not until 1973 it was proposed as a photovoltaic material by Wagner and co-workers, who reported on a single-crystal based cell with an efficiency of 12 % [29]. Large progress in the development of multi-crystalline CIS solar cells was made by Boeing Corporation during the early 1980s, when an efficiency higher than 10 % was achieved with a three-source co-evaporation process [30]. By using a different process, based on selenization of stacked metal layers, Arco Solar achieved cell efficiencies as high as 14.1 % in 1987 [31]. Arco had the intention of commercializing their technology, but due to poor reproducibility and low production yield, the envisaged pilot production was considerably delayed. Not until 1998, long after Arco Solar had become Siemens Solar Industries, the first commercial product was introduced to the market [32]. Initially, Siemens released a series of 5 and 10 watt modules produced at the pilot plant in California, USA. The Siemens plant is fabricating up to 40 watt modules [58]. Another important player in this field is Würth Solar, GmbH & Co. KG, who is operating a 3 MWp pilot production facility in Marbach, Germany, aiming at scaling up to 30 MWp [33]. Global Solar Energy Inc. has a slightly different approach to take market shares by aiming at niche applications where lightweight, flexible solar cells are valued. Global solar is the only manufacturer in a full-scale production of CIGS PV modules on a flexible substrate [34]. In addition to the organizations mentioned above, there are a number of companies, which are at early stages of commercialization. These include Showa Shell Sekiyu K.K. in Japan [35] and the three American companies Solopower [36], International Solar Electric Technology Inc (ISET) [37] and Heliovolt [38].

1.5 Structure of CIS Solar Cell

CIS devices in this study are typically fabricated in a substrate configuration as shown in figure 1.3. The substrate is an important part of the device - not only does the quality of the substrate influence the properties of the device, but also the reproducibility of the fabrication process [39]. CIS solar cell device fabrication involves several processing steps. The process used for each of the layers in the device fabrication is discussed in the following sections.

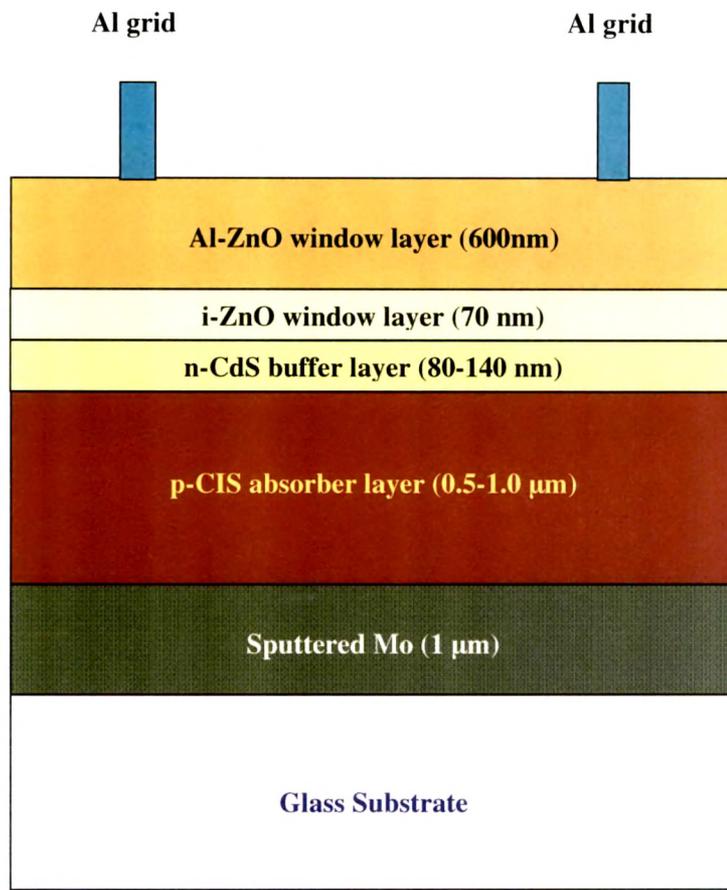


Figure 1.3: Structure of CIS solar cell.

1.5.1 Glass Substrate

CIS thin film solar cell devices are generally fabricated on soda-lime glass substrates. Soda-lime glass substrate affects the CIS formation in a favorable way, resulting in large grains and high film density as sodium diffuses out of the glass, through the molybdenum [40]. In this study, we have used 2 mm thick soda-lime glass slides. The substrates are ultrasonically cleaned using soap solution prepared in warm distilled water, followed by chemical cleaning using methanol, acetone and trichloroethylene to remove contaminants.

1.5.2 Molybdenum (Mo) Back Contact

The first layer deposited on the substrate is the molybdenum back contact, which serves as a conductive path for the photo-generated current and provides a good contact to the p-type CIS absorber. The nucleation and growth of CIS grains are directly influenced by the thermal, morphological and chemical properties of the molybdenum back contact [41]. Molybdenum has proven to have a number of important properties, such as tolerance to the relatively high process temperatures during CIS growth and resistance to alloying with copper and indium

[42]. A considerable effort has been put in this study to establish a good recipe for this process step.

1.5.3 Copper Indium Diselenide (CIS): Absorber Layer

The CIS compound belongs to I-III-VI₂ materials family that crystallizes in the tetragonal chalcopyrite structure. Chalcopyrite is another name for copper iron sulfide (CuFeS₂), a common copper ore, which gave name to these materials. An interesting property of the semiconducting chalcopyrites, in general, and CIS, in particular is, that energy bandgap (E_g) can be varied, for instance by varying the amount of Ga. The optimal energy bandgap for a solar cell with respect to the solar spectrum is around 1.4 eV [43]. The energy bandgap of CIS is 1.04 eV. CIS as an absorber material in solar cells is mainly used in the form of thin films. Conversion efficiencies between 12 and 15 % have already been achieved for devices based on a pure CIS/CdS/ZnO heterojunction [44]. The energy bandgap of CIS can be continuously modified over a wide range (i.e. 1.0-1.65 eV) by partial substitution of In with Ga or substitution of Se for S [45]. Recent trends in CIS research and development focus on these higher energy bandgap chalcopyrite alloys. In this study, CIS thin films are grown using thermal and flash evaporation techniques from synthesized compound material.

1.5.4 Cadmium Sulfide (CdS): Buffer Layer

In earlier years of the development of the thin film CIS solar cell, an evaporated CdS film was used as a partner to create a heterojunction with the CIGS layer [46]. The thickness as well as the deposition method of the CdS layer has a large impact on device properties. During the early days, the device structure consisted of a CIS/CdS junction with a thick (about 1-3 μm) CdS layer [47,48]. The CdS layers of these devices were most often prepared by thermal evaporation technique at substrate temperatures between room temperature and about 473 K. In some cases, a CdS bi-layer was used [49, 50] consisting of a thinner high-resistivity layer, prepared either by evaporation or chemical bath deposition and a thicker low-resistivity layer, doped with 2 % In [49] or Ga [41]. Evaporated CdS has been used also in combination with the transparent conducting oxide layer [51, 52].

Due to a low conductivity and a relatively small bandgap (2.4 eV) of the CdS thin film, the cells had a low quantum response in the blue light region of the solar spectrum [53]. In order to improve these quantities, the thickness of the evaporated CdS was reduced and a ZnO window layer with a better conductivity and a wider bandgap (3.3 eV) was deposited

onto it. Most high-efficiency CIS based solar cells of today have a thin (50 nm or less) CdS buffer layer and an undoped ZnO layer between the absorber and the transparent conducting oxide. The roles of CdS and undoped ZnO are related to some extent [54].

In this work, an attempt is made to study effects caused by evaporated CdS on performance of CIS thin film solar cell. Thin cadmium sulfide buffer layer having thickness in the range of 80-140 nm were prepared using conventional thermal evaporation method. At 373 K substrate temperature on Mo/CIS structure. The thickness of the CdS thin film is optimized to have dark I-V characteristics suitable for solar cell application.

1.5.5 Intrinsic Zinc Oxide (i-ZnO) and Aluminum Doped Zinc Oxide (AZO): Window Layer

Most devices utilize nowadays an oxide bi-layer that consists usually of a thin (50-100 nm) high-resistivity layer, and a thicker (100-1500 nm) low-resistivity layer. The high resistivity layer is most often undoped ZnO. Its role is not completely understood yet, but results of admittance spectroscopy and capacitance voltage measurements indicated that the presence of this resistive layer affects the electronic properties of the heterojunction only to the extent that is expected on the basis of band diagrams. Its benefit to the device performance is the increase of the open circuit voltage (V_{oc}) [55]. The conducting part of the oxide bi-layer is most often ZnO doped with either Aluminum [56,57,58,59] Boron [60,61,62] or Gallium [63,64,65].

RF magnetron sputtering method is the most versatile technique to deposit ZnO films. In this work devices are completed using a bi-layer of high- and low-resistive ZnO. Pure argon is used as sputter gas. The substrate is placed above target and substrate to target distance is fixed at about 50 mm. A base pressure of at least 10^{-5} Torr is obtained before each sputter process. The baseline recipe consists of pre-sputtering and sputtering the films in pure argon. This makes high quality films.

1.5.6 Aluminum (Al) Front Contact (Grid)

Thermal evaporation technique is used to deposit $\sim 1\mu\text{m}$ thick aluminum (Al) thin films through a metal mask onto the ZnO window layers. The mask covers only 10 % of the total active cell area. The Deposition of Al grid on prepared CIS solar cell device is carried out without heating the device, at base pressure of 10^{-5} Torr at a deposition rate of 0.4 nm/sec. An oscillating quartz crystal monitors the rate of deposition and the thickness of the film.

1.6 Solar Cell Device Operation

The operation of solar cells in general is thoroughly described in several books, for example Green [43] or Fonash [20]. A short description of solar cell device operation is given here. The electrical performance of a solar cell is normally characterized by current voltage (I-V) measurements. A typical plot for a device under illumination and in dark is shown in figure 1.4.

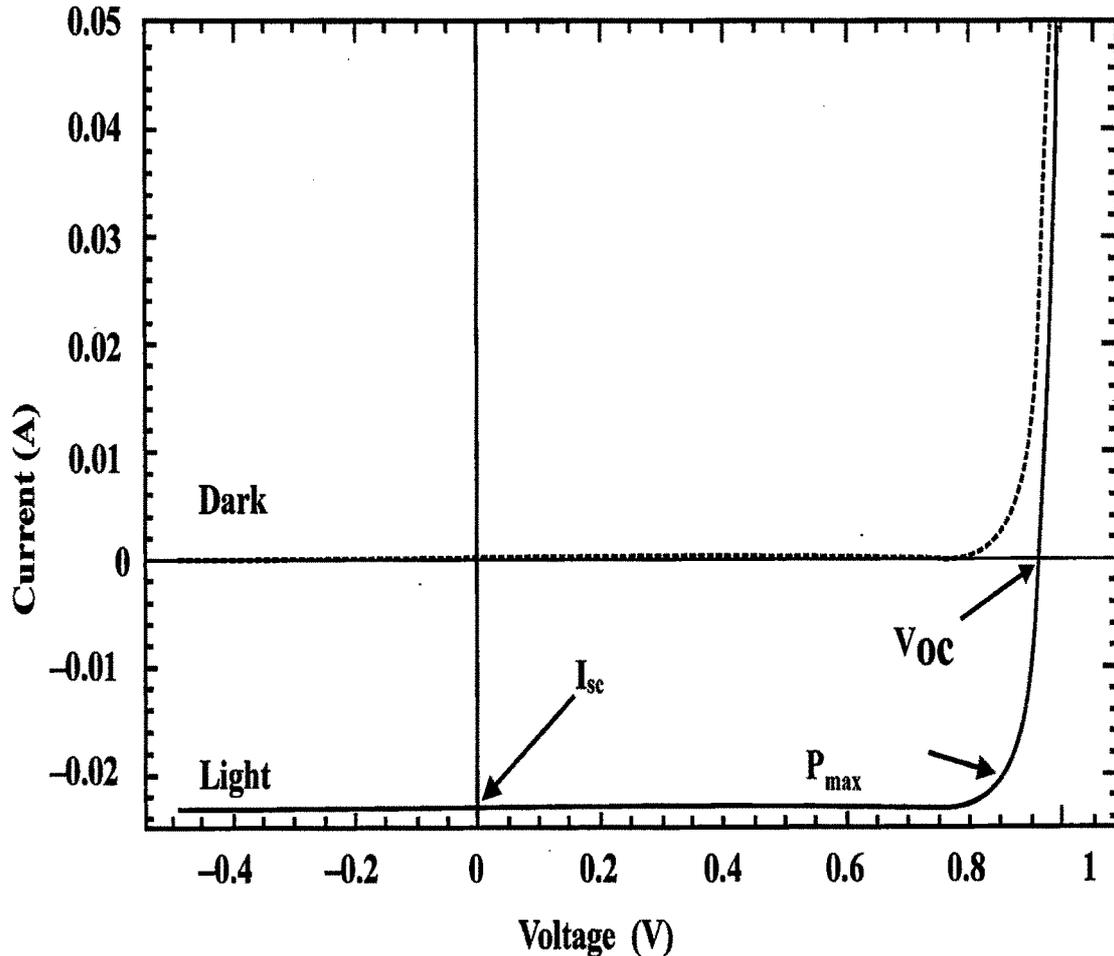


Figure 1.4: I-V characteristics of a solar cell under dark and illuminated conditions, displaying V_{oc} , I_{sc} and maximum power point $P_{max} = V_{mp}I_{mp}$.

From I-V characterization, the open circuit voltage V_{oc} , the short circuit current I_{sc} , the fill factor (FF) and the efficiency (η) at the maximum power working point (V_{mp} , I_{mp}) are extracted. The voltage V , current I , FF, and η are related by,

$$I = I_0 \left(\exp\left(\frac{qV}{nkT}\right) - 1 \right) - I_L \quad (1.1)$$

I_0 is the saturation current in dark, n the diode quality factor and I_L the photogenerated current. From equation (1.1) we get I_{sc} under short circuit conditions ($V = 0$) according to equation (1.2). Setting the current to zero in equation (1.1) gives the V_{oc} according to equation (1.3).

$$I_{sc} = I(V = 0) = I_L \quad (1.2)$$

$$V_{oc} = \frac{nkT}{q} \ln \left[\left(\frac{I_L}{I_0} \right) + 1 \right] \quad (1.3)$$

Fill factor (FF) is defined as,

$$FF = \frac{V_{mp} I_{mp}}{V_{oc} I_{sc}} \quad (1.4)$$

$$\eta = \frac{FF \times V_{oc} \times I_{sc}}{P_{in}} \quad (1.5)$$

1.7 Loss Mechanism in CIS Solar Cell

In a solar cell with no losses each photon striking the surface would transfer its total energy to an electron-hole pair and all carriers would maintain and transfer the absorbed energy to the device contacts and a conversion efficiency of 100 % would be achieved. Losses due to transmittance through the device, relaxation losses due to excess photon energy, and carrier recombination, provide a limit for the achievable efficiency of a single junction device, which is much smaller (about 30 %) [43, 66].

A number of different mechanisms are identified as responsible for recombination losses in a CIS device. The locations of interface recombination (a), recombination due to traps in the depletion region (b) and in the bulk (c) are marked in figure 1.5. The dominating recombination type for CIS solar cells is (b) [67]. Traps in the depletion region reduce V_{oc} and FF. This effect is strongest for traps at an energy level close to the middle of the bandgap.

1.8 Motivation for this Work

1.8.1 RF Sputtering of Mo Back Contact

Molybdenum is currently the most common material used for CIS based solar cell back contacts. Several properties are required to fulfill this role, notably chemical and mechanical inertness during the other deposition processes, high conductivity, low resistance contact with the CIS layer, and commensurate coefficient of thermal expansion [68].



However, the deposition of a molybdenum film as a back contact is not by itself an assurance of a high efficiency solar cell.

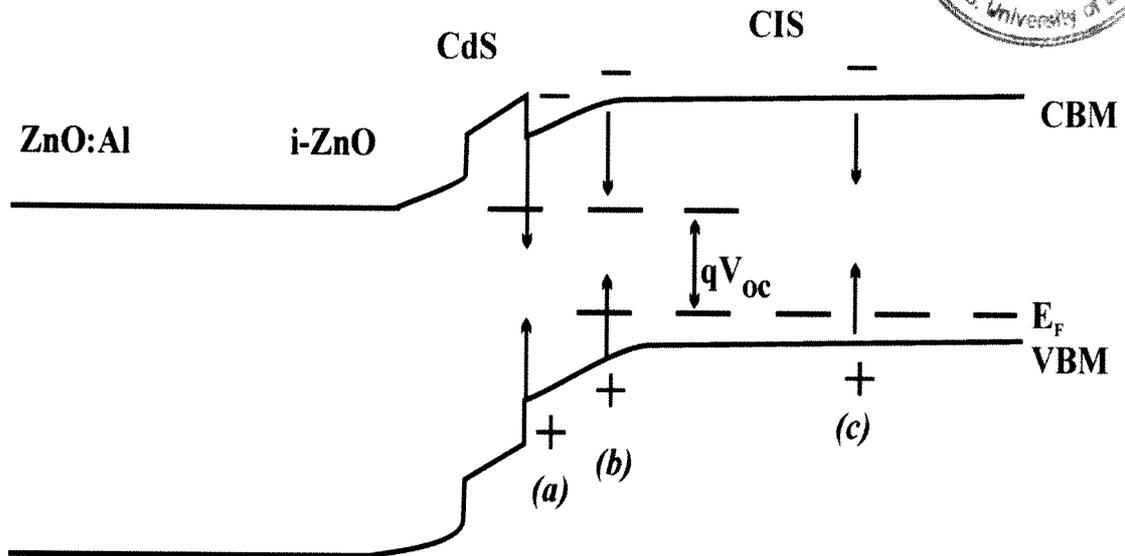


Figure 1.5: Qualitative band diagram for the CIS solar cell under illumination and open circuit conditions. Recombination types are indicated in region of occurrence: interface (a), space charge region (SCR) (b), and bulk recombination (c).

The deposition parameters and process play a key role in obtaining a layer with the appropriate properties. Extensive research has been done on the deposition of molybdenum thin films by dc sputtering [69,70]. However, as the potential portfolio applications of CIS expand, different films' properties may be required to adapt to new requirements. In this work, we therefore used RF magnetron sputtering to deposit Mo thin films on soda-lime glass substrates as little research has been performed on Mo thin films deposited by this method [71,72].

1.8.2 Thermal and Flash Evaporation of CIS Absorber Layer

The chalcopyrite absorber materials of high efficiency CIS devices are generally produced by a single stage growth technique in which all the elements (i.e. Cu, In, Ga and Se) are co-evaporated from individual sources [73]. This technique requires accurate control of all evaporation sources. Therefore, simple one or two-step deposition process to deposit CIS thin films has been proposed and subsequently investigated [74]. Thermal and flash evaporation techniques to deposit CIS thin films from synthesized chalcopyrite compound material onto heated substrates are employed in this study. By accurately controlling, the deposition

parameters these techniques are suitable to deposit CIS thin films well suited for the solar cell applications [75,76].

1.8.3 Thermal Evaporation of CdS Buffer Layer

As the buffer layer is very thin it is of importance that the film is fabricated uniformly and without voids. An inherent property of the thermal process is highly conformal coating even for very thin films. The optimization of thickness and deposition parameters of CdS buffer layer in terms of optical, electrical and structural properties is of paramount interest. The thickness of CdS thin films is optimized to have dark I-V characteristics of Mo/CIS/CdS layer suitable for its application in fabrication of solar cell.

1.8.4 ZnO Window Layer

Bi-layer of very thin highly resistive undoped ZnO (i-ZnO) and aluminum doped zinc oxide (AZO) transparent conductive films are used as window layer in this study. The structural, electrical, and optical properties of this bi-layer thin film are optimized for fabrication of CIS thin film solar cell device.

1.9 Thesis Organization

This thesis is organized into six chapters.

Chapter 2: The deposition methods employed for preparations of the semiconductors layers in fabrication of thin film CIS solar cells that are thermal evaporation and RF magnetron sputtering techniques are described in this chapter. Analyzing methods such as XRD analysis, transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) used for structural and morphological characterization of films are briefly discussed. Optical and electrical parameters measurement techniques of thin films are also discussed.

Chapter 3: CIS is used as an absorber material in the form of thin films. The electrical and optical properties of CIS materials both in thin film and powder form are strongly dependent on their stoichiometric composition, defect chemistry and structure, which in turn are related to the growth parameters. So, synthesis of CIS compound having near stoichiometric composition of elements is the

major concern. Here, we have synthesized CuInSe_x ($x = 2, 2.05, 2.10$) compound material with varying selenium concentrations. Synthesized pulverized material was characterized using XRD analysis, AFM, SEM micrographs and EDAX measurement techniques. CuInSe_x compound having $x = 2.05$ was used as an evaporant source to deposit CIS thin films using thermal evaporation technique. The influence of substrate temperature and thermal annealing on structural, morphological, optical and electrical properties of CIS thin films are discussed. The effect of substrate temperature on properties of flash evaporated films are also investigated

Chapter 4: Cadmium sulphide thin films are deposited using thermal evaporation technique on sodalime glass substrates. The optimization of deposition parameters to deposit film suitable for their application in the solar cell device structure is carried out using structural and optoelectronic analysis of the films. These thin films are characterized using XRD, SEM and TEM techniques. Transmission spectra analysis of thin films is used to measure bandgap while Hall effect measurements is employed for electrical characterization.

Chapter 5: Thin films of undoped (i-ZnO) and aluminum doped ZnO (AZO) are deposited using RF magnetron sputtering technique at different working pressure under Argon ambient. The effect of working pressure on structural, morphological, optical and electrical properties of i-and AZO thin films are discussed.

Chapter 6 This chapter deals with the development and fabrication of CIS thin film solar cells. To investigate the performance of CIS based thin film solar cell, the method of numerical simulation using AMPS-1D is explained in this chapter. The optimized deposition parameters for CIS (absorber layer), CdS (buffer layer) and bi-layer of ZnO (window layer) thin films are used for numerical simulation. Low resistive and highly reflective molybdenum (Mo) back contact is prepared using RF magnetron sputtering method. CIS thin film solar cell having CIS thickness of $0.5 \mu\text{m}$ is fabricated on prepared Mo coated glass substrates using optimized deposition parameters discussed in chapters 3-5. Fabricated CIS solar cell device is characterized by dark and illuminated

current voltage (I-V) measurements. Results of cell having CIS thickness of 0.5 μm are encouraging. Hence, CIS thin film having CIS thickness of 1 μm is deposited on Mo coated glass substrates. As CIS/CdS interface is very important for the optimum performance of CIS based thin film solar cell device, more experiments have been carried out to understand the effect of the thickness of cadmium sulphide buffer layer on dark I-V measurements of Mo/CIS/CdS structure.