

# CHAPTER 1

## INTRODUCTION

### 1.1 General Background

The conversion of sunlight directly into electricity using the electronic properties of suitable materials is the most elegant energy conversion process. Being a laboratory curiosity for more than a hundred years, the solar cell technology has seen enormous development during the last four decades, initially for providing electrical power for spacecrafts and more recently for terrestrial applications. The driving force for this technological development is the realization that the traditional fossil energy resources such as coal, oil and gas are not only rapidly depleting, but also contribute to unpredictable and possibly irreversible climate changes in the near future through the high emission levels of greenhouse gases (e.g. CO<sub>2</sub>, CO, SO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub>). Furthermore, the increasing concern for environmental pollution problems in industrialized countries has discredited nuclear power as a long term alternative energy concept. The population growth, which is particularly large in rural areas, not connected to the electrical network (2.5 billion worldwide), is another factor favoring the development of a solar energy industry.

The interest in solar cells as an alternative energy source for terrestrial applications awoke in the mid 1970's after the political crises in the Middle East, the oil embargo and the realization of the limitations in fossil fuel resources. The increased research resulted not only in the further improvement of the efficiencies of silicon solar cells and considerable reduction of the energy cost, but also in the development of new photovoltaic materials and devices. The increase in production volume and new cost

efficient solar cell technologies rendered this achievement possible. In the early 1980's new solar cell materials and innovative device concepts have been evaluated at the pilot production stage and currently a number of promising options for future developments are available. The commercialization of these technologies has been hindered by the high cost per peak watt for solar cell modules. Even though researchers have made extraordinary progress over the years, improved performance, lower costs and reliability still remain major considerations [Stone, 1993]. Policy goals by some governments such as improved energy security and diversity, reduced emissions of greenhouse gases and increased levels of technology growth have spawned several photovoltaic technologies in the past two decades.

## 1.2 The Sun and Solar Radiation

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  $1.99 \times 10^{30}$  kg and a radius of  $6.96 \times 10^8$  m [Wielder, 1982]. The earth-sun distance,  $R$ , is approximately  $1.5 \times 10^{11}$  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. As a result 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.

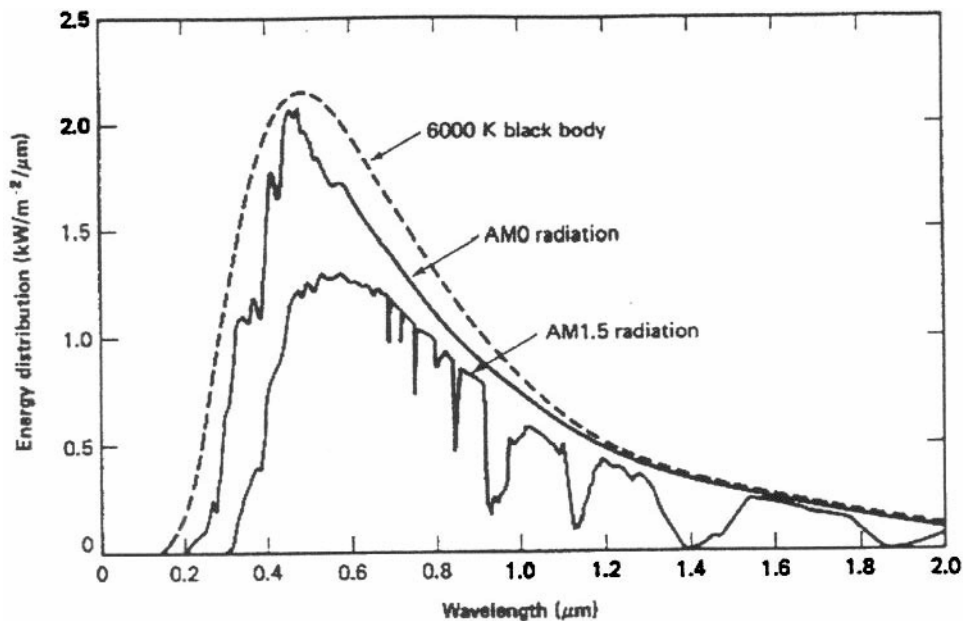


Figure 1.1: Spectral distribution of sunlight. Shown are the radiations outside the earth's atmosphere (AM0) and at the surface (AM1.5). The dashed line indicates the radiation distribution expected from the sun if it were a black body at a temperature of 6000 K [Backus, 1980].

The attenuation mechanisms, are wavelength dependent which explains the strong adsorption bands in the spectral distribution measured at the earth's surface and which are also depicted in Fig. 1.1. The degree of attenuation is highly variable because of the constantly changing position of the sun and the corresponding change of the light path through the atmosphere. These effects are conveniently described by defining an air mass number (AM<sub>m</sub>). Air mass according to IEEE Standard Dictionary of Electrical and Electronics Terms [Jay, 1977] is the mass of air between a surface and the sun that affects the spectral distribution and intensity of sunlight. AM0 is the spectral distribution and intensity of sunlight outside the earth's atmosphere. For any given angle,  $\theta$ , with respect to the overhead position the air

mass takes the value  $AM_m$ , in which the air mass number,  $m$ , is represented as  $m = 1/\cos\theta$  and thus measures the atmospheric path length relative to path length when the sun is directly overhead. Hence AM1 is the spectral distribution and intensity of sunlight on earth at sea level with the sun directly overhead and passing through a standard atmosphere. AM2 is the solar radiation at ground level when the sun is  $30^\circ$  above the horizon. The most widely used terrestrial standard at the time of writing is the AM1.5 spectral distribution (for  $\theta = 48^\circ$ ), which is plotted as the terrestrial curve in Fig. 1.1. This terrestrial standard allows a meaningful comparison of different solar cells tested at different locations.

### **1.3 Types of Solar Cells**

The first solar cell was developed at Bell laboratories in 1954 [Chaplin et al., 1954 and Chaplin et al., 1957]. At that particular point in time, solar cells were made from semiconductor grade single crystalline silicon and were the power source for space applications such as on satellites. The systems were very reliable, and cost was of little concern with regard to huge space program budgets. At present, solar cells can be categorized into three main groups:

- Single-crystalline and polycrystalline silicon
- III-V Group single crystals
- Thin films

#### **1.3.1 Single-crystalline and polycrystalline silicon**

Silicon is still the most popular solar cell material for commercial application because it is so readily abundant (it is actually the second most abundant element in the earth's crust second only to oxygen). Another reason why silicon is a popular choice for PV energy generation is the large technology base that has built up over the past

50 years for silicon used in the semiconductor industry. However, to be useful in a solar cell, it must be refined to 99.9999% purity; standard purification techniques have already been developed [Runyan, 1965]. The source material for extraction of silicon is silicon dioxide, the major constituent of sand. Single-crystalline and polycrystalline silicon have an indirect band gap of 1 eV and low absorption coefficient. This means over a large range of the visible spectrum, light absorption occurs only with the assistance of phonons. The phonon provides the additional wave vector needed for momentum conservation in any energy transition in an indirect band gap semiconductor.

Silicon devices have attained an efficiency of 23% [Green M. A., 1993a] on laboratory scale. The molecular structure of the material is uniform since the entire structure is grown from the same or a "single" crystal. This uniformity is ideal for efficiently transferring electrons through the material. The efficiency can be increased to 28% when a concentrator system is used [Green and Emery, 1993b]. This performance achievement can be attributed to the substantial understanding of the material properties and improved design of the solar cell. Commercial silicon solar cell modules are available with conversion efficiencies as high as 18%. The major disadvantages of single-crystalline silicon solar cells are the requirements of high grade material and the problems associated with producing single crystals over large areas. Recently, there have been some imaginative attempts to make single crystal ribbon silicon, which is lower in cost than high quality single crystals. However, to date the efficiencies of these apparently low-cost materials have been relatively low.

The production of polycrystalline cells is more cost-effective than single-crystalline silicon. Silicon is poured into blocks that are subsequently sawed into plates. During solidification of the material, crystal structures of varying sizes are formed.

Polycrystalline silicon has the disadvantage that large grain sizes are required to reduce the negative influence caused by grain boundaries. In polycrystalline silicon the several smaller crystals or “grains” introduce boundaries and these boundaries impede flow of electrons and encourage them to recombine with holes thereby reducing the power output of the cell. However, polycrystalline silicon is much cheaper to produce than single-crystalline silicon; hence researchers are working on new innovative ways of minimizing the effects of grain boundaries.

### **1.3.2 Group III-V technologies.**

Photovoltaic technologies based on group III and V elements in the Periodic Table show very high efficiencies under either normal or concentrated sunlight. Although expensive, their cost can be compensated for by using concentrators, which increase the energy conversion efficiency under higher illumination. Concentrators focus light from a large area to a small area thereby increasing illumination to many times the terrestrial sunlight. The most important solar cells in this category are gallium arsenide (GaAs) and indium phosphide (InP).

#### **1.3.2.1 Gallium Arsenide**

Gallium Arsenide (GaAs) is a compound semiconductor; i.e. a mixture of two elements, gallium (Ga) and arsenic (As). Gallium arsenide use in solar cells has been developing synergistically with its use in light emitting diodes, lasers, and other optical devices. It has a direct band gap of 1.43 eV, nearly ideal for single junction solar cells. The absorption coefficient of GaAs is relatively high and causes sufficient absorption of photons in only a few microns of material. It is also very resistant to radiation damage. This, along with its high efficiency, makes GaAs very desirable for space applications. The most efficient solar cell to date has been based on this

material and cells of 25.1% efficiency have already been confirmed [Green and Emery, 1993b]. When used in concentrator application, the efficiency increases to 27.6% [Vernon et al., 1991]. The greatest barrier to the success of GaAs cells has been the high cost of single crystalline GaAs substrates. For this reason, GaAs cells are used primarily in concentrator system. For mass production of GaAs solar cells, gallium element availability and the toxic nature of the arsenic are considered as major limitations of this technology.

### **1.3.2.2 Indium Phosphide**

Indium phosphide (InP) has a direct band gap of 1.34 eV, close to the optimum for solar energy conversion. Research on InP heterojunctions did not start until about 1974, probably because of the unavailability of high quality single crystals of p-type InP. InP crystals are grown by the Czochraski method at high pressures or by using a liquid encapsulation technique to preserve the stoichiometry. A 21.9% efficient InP crystalline solar cell has already been reported [Keavney et al., 1990]. When 99-suns concentration is used, the efficiency increases to 24.3% [Ward et al., 1991]. A 31.8% multijunction InP/GaInAs cell, operating at 50-suns concentration has been achieved [Wanlass et al., 1990]. The major limitation of this technology is the high cost due to limited resources for indium and purification of phosphorous.

### **1.3.3 Thin film solar cells**

In an effort to reduce the fabrication costs of the present technology based on Si, and to increase material utilization, thin film materials have been the subject of intensive research. Three main types of materials have emerged as the most promising candidates for the next generation of solar cells. These are hydrogenated

amorphous silicon (a-Si:H), cadmium telluride (CdTe) as well as copper indium diselenide (CuInSe<sub>2</sub>) and its related alloys.

### **1.3.3.1 Amorphous silicon (a-Si:H)**

Amorphous silicon films exhibit very different characteristics than crystalline silicon. The main difference between the two materials is that there is no long-range order in the amorphous film. There is also a large number of dangling bonds in amorphous films that create trap states throughout the band gap region. In order to remove the dangling bonds, amorphous silicon films are hydrogenated during deposition. This results in the occupation of dangling bonds by hydrogen atoms. Hydrogenated amorphous silicon (a-Si:H) exhibits a band gap that is not well defined. Its value may vary from approximately 1.6 to 1.8 eV depending on deposition conditions. For plasma chemical vapor deposited a-Si:H, the variation depends on the deposition conditions including substrate temperature, RF power and gas pressure [Hishikawa et al., 1993]. This material can be doped either p-type or n-type by introduction of boron or phosphorous during deposition, respectively.

Solar cells fabricated from a-Si:H are based on a p-i-n structure rather than a p-n junction. This is because the doping necessary to generate the field across the junction results in a very high defect density, greatly reducing carrier lifetime. The deposition of an insulating intrinsic layer between thin p-type and n-type layers circumvents this problem. A nominally 100 nm thick p-type layer and a 20-30 nm thick n-type layer generate a field across the 100-400 nm intrinsic layer. The intrinsic layer becomes the absorber in this configuration, with the collection of the generated carriers enabled by the externally generated field. Textured surfaces are typically used in this type of device to induce light trapping, thereby effectively increasing the optical path length within the device. This results in an increased probability of



collecting each photon and generating an electron-hole pair. A primary problem associated with these devices is a photo-induced increase in defect density resulting in degraded device performance. This effect was reported by Staebler and Wronski in 1980 [Staebler and Wronski, 1980]. The effect can be reversed by annealing the device after degradation, but the process repeats when the device is again illuminated. Elimination of this effect is a topic of current research.

### **1.3.3.2 Cadmium telluride (CdTe)**

The cadmium telluride (CdTe) based thin film solar cell is one of the most promising polycrystalline candidates for terrestrial applications [Zweibel, 1992]. CdTe is typically used in conjunction with cadmium sulfide (CdS) for the formation of p-n heterojunctions. CdTe is a compound semiconductor of II-IV type that has a cubic (sphalerite) structure with a lattice constant of 0.6481 nm. CdTe has a direct band gap of 1.5 eV at room temperature with a temperature coefficient of  $2.3 - 5.4 \times 10^{-4}$  eV/K [De Nobel, 1959]. This band gap is an ideal match to the solar spectrum for a photovoltaic absorber. CdTe films require post deposition treatments in CdCl<sub>2</sub> and O<sub>2</sub> in conjunction with a heat treatment at approximately 400°C to make them suitable for devices. This treatment dopes the CdTe film with oxygen and chlorine and results in recrystallization. For the completion of devices, the contacted surface of the CdTe film requires additional doping to increase conductivity, which is necessary for an ohmic contact [Birkmire and Eser, 1997]. A small area cell efficiency of 17.7% has been achieved [Tuttle et al., 1997] at the National Renewable Energy Laboratory (NREL). A major concern associated with CdTe based devices is the toxicity of the material used. Both Cd and Te are considered to be heavy metals. At the end of their lifetime, CdTe based modules need to be recycled, or specially handled to prevent improper disposal of the heavy metals.

This ultimately impacts negatively on the cost-effectiveness of this technology.

### **1.3.3.3 Copper indium diselenide (CuInSe<sub>2</sub>)**

The most promising thin film solar cell device is based on CuInSe<sub>2</sub> (CIS) absorber films. The relevant material properties of this compound semiconductor are summarized in Chapter 2. Conversion efficiencies of between 12 and 15% have already been achieved for devices based on a CuInSe<sub>2</sub>/CdS/ZnO heterojunction [Verma et al., 1996; Sato et al., 1993 and Hedstrom et al., 1993]. The band gap of CIS can be modified continuously over a wide range (i.e. 1.0-1.65 eV) by substituting Ga for In. Similarly, one can also increase the band gap by the substitution of Se for S. Recent trends in CuInSe<sub>2</sub> research and development focus on these high band gap chalcopyrite alloys, and preliminary results indicated that conversion efficiencies above 18% can be achieved when using these specific absorber films. [Contreras et al., 1999]. Gallium incorporation is also believed to improve adhesion between the CIS and the molybdenum electrical back contact [Jensen et. al., 1993] and also increases the open-circuit voltage of the cell. Beside basic investigations at various university laboratories, commercialization of CIS based solar cell technology has already been realized with Siemens Solar Industries (SSI) believed to be leading in this effort. Other companies in the developmental stages are International Solar Energy Technology (ISET), Energy Photovoltaics (EPV), Solarex Inc. and Global Solar Energy. To compete with silicon solar cells, conversion efficiency above 10% is required on large areas. SSI has manufactured an 11.2% efficient prototype module on 3820 cm<sup>2</sup>. For successful commercialization, conversion efficiency, material utilization, capital cost and process yield have to be taken into account in order to realize this objective. The successful production of commercial CIS-based modules is slow because of the high initial investment and due to the complexity of

the process involved in producing thin film polycrystalline PV modules. Furthermore, most of the research activities were driven by the need to improve performance and not to develop the fundamental scientific and engineering base required to properly engineer manufacturing equipment.

## **1.4 Basis and Scope of this Work**

### **1.4.1 Motivation**

At present, the  $\text{CuInSe}_2$  and its alloys ( $\text{CuInS}_2$  and  $\text{Cu(In,Ga)Se}_2$ ) are regarded as promising candidates of thin film solar cells due to its optimum opto-electronic properties. Recent results in literature suggest that a complicated co-evaporation process is required to yield good quality films and high efficiency ( $\eta \geq 18.8\%$ ) solar cell devices. However, poor material utilization and the difficulty of obtaining uniform material fluxes over large area substrates are some of the concerns related to scaling this method to a high production level [Marudachanlan, 1996]. The ultimate aim of this work was to address these technological difficulties. Attention will be therefore be focused on the development of a relatively easily scalable two stage deposition technique, to produce uniform coatings of thin films on large area substrates.

### **1.4.2 Definition of research problem**

In order to produce large area commercial devices, an understanding of the process parameters is of paramount importance. In this regard, it is critical to correlate device performance with the basic material quality of the respective semiconductor thin films in the device structure. Selenization of copper-indium or copper-indium-gallium alloys in elemental Se vapor or in  $\text{H}_2\text{Se}$  appears to be the most feasible from an industrial perspective. The most important advantages of this approach are

composition uniformity over large areas and high throughput. However, the material quality of the absorber films is critically related to the selenization parameters (i.e. reaction temperature and period) and the metallic precursor formation steps. Against this background, the present study systematically quantifies the influence of the above referred to parameters on the material quality of the semiconductor thin films. Attention was also given to the homogenous incorporation of gallium and sulfur into the chalcopyrite lattice, and the corresponding influence on device performance.

### 1.4.3 Objectives of the research

The specific objectives of this study were:

- To investigate the deposition of device quality  $\text{CuInSe}_2$  thin films with a simple and reproducible process technology, and to study the effect of thermal diffusion of sulfur into these films.
- To prepare device quality  $\text{Cu(In,Ga)Se}_2$  absorber layers by controlled selenization of selenium containing precursors in elemental Se vapour.
- To investigate the influence of the GaSe deposition temperature and the selenization temperature on the material properties of  $\text{Cu(In,Ga)Se}_2$  polycrystalline thin films.
- To study the effect of gallium incorporation into  $\text{CuInSe}_2$  and related influences on film growth and phase formation. Specifically, it was intended to experimentally determine the variation in the lattice parameter and band gap with gallium concentration.
- Optimization of the material quality of CdS buffer layers and ZnO window layers.
- Fabrication and evaluation of completed devices structures based on  $\text{CuInSe}_2$ ,  $\text{CuIn(Se,S)}_2$  and  $\text{Cu(In,Ga)Se}_2$  absorber films.

## 1.5 Thesis Organization

This thesis is organized into six chapters. In Chapter 2, a literature survey is presented on the relevant theoretical aspects of present research on CIS thin films. The typical solar cell design is discussed as well as the important advantages of chalcopyrite thin films for photovoltaic applications. Attention is also focused on the critical relationship between the material properties and the growth conditions of these thin films. In Chapter 3, the fundamental principles of solar cell devices are discussed. Attention is given to a mathematical description of a p-n heterojunction diode and solar cell parameters influencing the operation of solar cells. The experimental procedures followed during the preparation of CIS absorber layers as well as the deposition techniques used for CdS, ZnO and front contacts for solar cells are discussed in detail in chapter 4. An important aspect of this study was the accurate characterization of the polycrystalline thin films. A large number of structural and optical characterization techniques were used in this study, and these are thus discussed in this chapter. The experimental results that followed from the detailed study of the influence of growth parameters and selenization conditions on the ultimate CIS material quality are presented and discussed in Chapter 5. These results take the form of SEM micrographs, EDS and XRF measurements of composition as well as x-ray diffraction patterns to determine the presence of crystalline phases. Ultimately, complete solar cells were manufactured and their I-V characterizations are discussed and evaluated. Finally, in Chapter 6, the most significant results are summarized and conclusions are drawn, with suggestions for future research.

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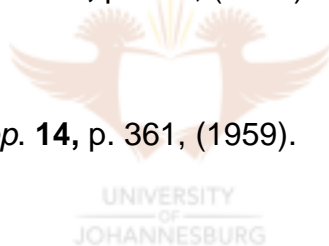
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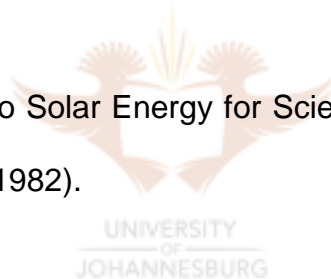
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