Chapter 1

Introduction

1.1 Overview

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 increase in 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. 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. 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.

Some of the renewable energy technologies have been in development for a few decades. In spite of this, they have failed to emerge as a prominent component of the energy generation because the power obtained from these technologies is still expensive, when compared to that obtained from traditional technologies. The traditional technologies may produce cheap power in term of cost to the consumer, but environmental, political, and health costs are not reflected in this cost. An important thing in developing renewable energy technologies is the desire to avoid fossil fuels because of their adverse effect on the environment. Solar energy is the Earth's major renewable energy resource, therefore, the exploitation of the energy irradiated by the Sun is the potential key to a sustainable energy production in the future.

1.2 Types of Solar Cells

The first solar cell was developed at Bell laboratories in 1954 [1, 2]. At that time, solar cells were made from semiconductor grade single crystalline silicon and were the power source for space applications such as on satellites. At present, solar cells can be categorized into three main groups:

single-crystalline and polycrystalline silicon;

III-V group single crystals; and

thin films.

1.2.1 Single-crystalline and Polycrystalline Silicon

Silicon is still the most popular solar cell material for commercial applications because it is the second most abundant element in the earth (second only to oxygen) and its technology base has built up over 50 years for use in the semiconductor industry. However, silicon used in solar cell must be refined to 99.9999% purify. Single-crystalline and polycrystalline silicon have an indirect band gap of 1.1 eV and low absorption coefficient. A considerable thickness (about 100 μm) of silicon is needed to absorb the light, thus, increasing the material cost.

Silicon solar cells have attained an efficiency of 23% [3] on laboratory scale. The efficiency can be increased to 28% when a concentrator system is used. Commercial silicon solar cell modules are available with 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 are some attempts to make a single crystal ribbon silicon which the cost is lower than that of the high quality single crystals. The cost of production of polycrystalline silicon is lower than single-crystalline silicon. However, the polycrystalline silicon has disadvantage in solar cell fabrication. The large number of grains in polycrystalline silicon introduce boundaries that impede flow of electrons and encourage them to recombine with holes thereby reducing the power output of the cell.

1.2.2 III-V Group Single Crystals

The most important solar cells in this group are gallium arsenide (GaAs) and indium phosphide (InP). Some advantages for use GaAs in solar cell applications are its direct band gap of 1.43eV, nearly ideal for single junction solar cells, and high absorption coefficient causing sufficient absorption of photons in only a few microns of material and resistance to radiation damage. To date, the efficiency of GaAs solar cell has reached 25.1% and increased to 27.6% using concentrator. The major disadvantage of GaAs cells is a high cost of single crystalline GaAs substrate. InP has a direct band gap of 1.34 eV, close to the optimum for solar energy conversion. The efficiency of InP crystalline solar cell has been reported to be 21.9% [4]. Moreover, a 31.8% multijunction InP/GaInAs cell, operating at 50-suns concentration has been achieved [5, 6]. The major disadvantage of InP crystalline solar cells is the high cost due to limited resources for indium and purification of phosphorous.

1.2.3 Thin Film Solar Cells

In order to reduce the fabrication cost of single-crystalline solar cells, materials for thin film solar cell have been intensive research. Three types of materials which are the most promising candidates for the next generation solar cells consist of hydrogenated amorphous silicon (a-Si:H), cadmium telluride (CdTe) and copper indium gallium diselenide ($CuIn_{1-x}Ga_xSe_2$).

Amorphous silicon (a-Si:H)

The hydrogenated amorphous silicon exhibits a band gap that can be varied from approximately 1.6 to 1.8eV depending on deposition conditions. This material can be doped either p-type by introducing of boron or n-type by introducing phosphorous during the deposition. a-Si:H solar cells are based on a p-i-n structure. Doping process generates the electric field across junction that causes high defect density, thus reducing carrier lifetime. Hence, the deposition of an insulating intrinsic layer between p-type and n-type layers circumvents this problem. In this structure, the intrinsic layer becomes the absorber layer. The important problem of a-Si:H solar cells is a photo-induced increase in defect density resulting in degraded device performance from the initial value.

Cadmium telluride (CdTe)

CdTe-based thin film solar cell is promising candidates for terrestrial applications [7, 8]. CdTe has a direct band gap of 1.5 eV which match to the solar spectrum for a photovoltaic absorber. For the complete of devices, a small area cell efficiency of 16.5% has been achieved [9]. The major disadvantage of CdTe solar cell is the toxicity of the material used and both Cd and Te are considered to be heavy metals. Thus, CdTe-based solar modules need to be recycles or specially handled to prevent improper disposal of this heavy metals at the end of their lifetime.

Copper indium gallium diselenide ($CuIn_{1-x}Ga_xSe_2$: $Cu(In,Ga)Se_2$)

The development of $CuInSe_2$ cells started in 1974, when the single crystalline solar cells with an efficiency of 12% were reported [10]. The thin film solar cells with 6.6% conversion efficiency were prepared by evaporating the $CuInSe_2$ compound and adding Se from a separate source by Kazmerski *et al.* in 1997 [11]. The conversion efficiency of $CuInSe_2$ thin film solar cells was increased to 10.6% in 1982 by the research group at Boeing [12]. Their $CuInSe_2$ thin films were prepared by the co-evaporation (physical vapor deposition) of the three elemental sources. Using this technique, "bi-layer" recipe, combining Cu-rich films and Cu-poor films developing by Boeing, the films with desired compositions and suitable electronic properties can be obtained [13].

The $Cu(In,Ga)Se_2$ does not suffer from light-induced degradation as that of the a-Si:H. The performance of $Cu(In,Ga)Se_2$ -based thin film solar cells has even shown some improvement after illumination under normal operating conditions [14]. The $Cu(In,Ga)Se_2$ -based thin film solar cells with stacked layer sequence, Ni-Al/ZnO(Al)/i-ZnO/CdS/$Cu(In,Ga)Se_2$/Mo/glass, exhibit the highest efficiencies among thin film solar cells. An additional advantage of the $Cu(In,Ga)Se_2$ -based absorber materials is that they do not have the acceptability problems like the CdTe. Nevertheless, the Cd issue is shared also by the $Cu(In,Ga)Se_2$ technology in the CdS buffer layer fabrication process. However, the CdS is very thin, the amount of Cd used in the $Cu(In,Ga)Se_2$ technology are much less than those in CdTe technology. Another advantage is that they are direct band gap materials that have high absorption coefficients as shown in Fig 1.1. The band gap of $Cu(In,Ga)Se_2$ can be varied from 1.04 eV of $CuInSe_2$ to 1.7 eV of $CuGaSe_2$ by substituting Ga for In [15]. At present, the most promising thin film solar cell is based on $Cu(In,Ga)Se_2$ absorber layer because of its optimum opto-electronic properties. The details of material properties of these compounds are summarized in Chapter 2. Recently, the national renewable energy laboratory (NREL) group has reported on a new world record conversion efficiency of $Cu(In,Ga)Se_2$ -based thin film solar cells with 19.2% [16, 17]. Their $Cu(In,Ga)Se_2$ absorber layers were prepared using a "three-stage" process multi-source evaporation technique. The details of this technique are described in Chapter 4. Not only small devices of this type show high performance, but also solar modules from industrial pilot lines show the efficiency close to 13% [18].

Recent trends in $Cu(In,Ga)Se_2$ research and development are focused on the fabrication of large area modules with conversion efficiencies above 15%, the improve of open-circuit voltage of the cells by using wide band gap $Cu(In,Ga)Se_2$ with Ga content above 50%, as well as the fabrication of tandem structure solar cells having more than one junction with conversion efficiencies above 20% [19]. However, the successful production of commercial $Cu(In,Ga)Se_2$ -based modules is slow because of the complexity of the process. Furthermore, most of the research activities were driven by the need to improve performance and not to develop the fundamental scientific of material.

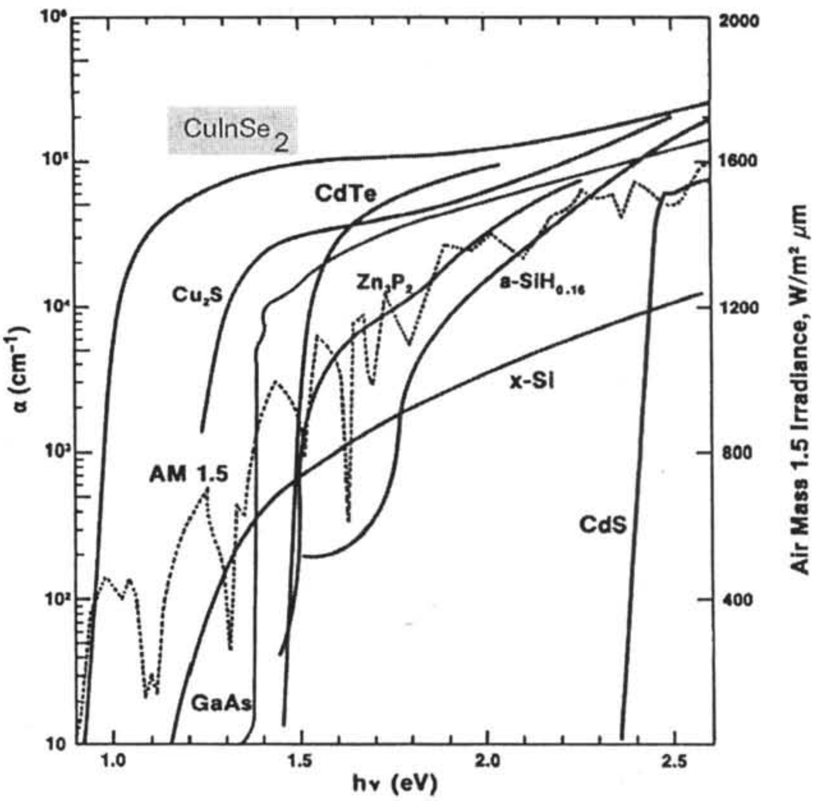

Figure 1.1: Absorption coefficient spectrum of $CuInSe_2$ compared with that of other photovoltaic semiconductors [20].

1.3 Motivation of the Research

Since the highest conversion efficiency of $CuIn_{1-x}Ga_xSe_2$-based thin film solar cell can be achieved with material of low band gap ≈ 1.2 eV corresponding to Ga ≈ 25%, while the possibility of designing devices yielding high output voltage, is driving the attention towards wide band gap materials. In this case, $CuGaSe_2$ shows interesting properties for PV applications. With a wide band gap of 1.7 eV, well matched to the solar spectrum, and a high absorption coefficient, this material promises high output voltages, low efficiency losses and low resistance losses in solar modules. The combination of $CuGaSe_2$ and $CuInSe_2$ in a tandem solar cell device, each material absorbs in different ranges of the solar spectrum. The theoretically calculated energy conversion efficiency closes to 40% in this tandem structure. However, at present, conversion efficiency by $CuGaSe_2$ absorber lag far behind those achieved by $Cu(In,Ga)Se_2$ or even $CuInSe_2$. This is due to some fundamental differences between the low band gap and wide band gap materials.

The degree of fundamental knowledge of $CuGaSe_2$ lag well behind those of related compounds such as $CuInSe_2$, $CuInS_2$ and the alloys $Cu(In,Ga)(Se,S)_2$. Hence, the research on the material properties of wide band gap $Cu(In,Ga)Se_2$ and the dependence on the different growth process parameters are necessary.

In this work, the molecular beam deposition method approach for growing high quality polycrystalline wide band gap $Cu(In,Ga)Se_2$, focused on $CuGaSe_2$ thin films for PV application will be assessed.

1.4 Objectives of the Research

The objectives of this research were:

- To investigate the characteristics of molecular beam epitaxy (MBE) system used to fabricate the $Cu(In,Ga)Se_2$ polycrystalline thin films.
- To observe the effect of gallium incorporation into $CuInSe_2$ and related influences on film growth and phase formation.
- To investigate the influence of growth conditions on the material properties of wide band gap $Cu(In,Ga)Se_2$ thin films.
- To prepare high quality wide band gap $Cu(In,Ga)Se_2$ absorber layers using molecular beam deposition (MBD) with *in situ* monitoring technique.
- To fabricate and evaluate completed device-structures based on wide band gap $Cu(In,Ga)Se_2$ absorber films.

1.5 Thesis Organization

This thesis is organized into six chapters. In Chapter 2, a literature survey is presented on the theoretical relevance of Cu-In-Se material system. The fundamental principles of solar cell devices are reviewed as well as the important advantages of $Cu(In,Ga)Se_2$ chalcopyrite thin films for photovoltaic applications. In Chapter 3, the basic principle and the characteristics of the molecular beam deposition system are described including to the calibration of parameters involved the polycrystalline $Cu(In,Ga)Se_2$ thin films. The experimental procedures followed during the preparation of $Cu(In,Ga)Se_2$ absorber layers as well as the deposition techniques used for CdS, ZnO and front contacts for solar cells are discussed in details in Chapter 4. The details of the growth process, the calculation of temperature profiles, the structural and optical characterization techniques used in this work, are thus discussed in this chapter. The experimental results that followed from the detailed observation of the influence of variation of growth processes such as two-stage, three-stage including with *in situ* monitoring signals during growth are presented and discussed in Chapter 5. The investigation of material properties of $Cu(In,Ga)Se_2$ film using SEM, AFM, including EDS measurements of composition and x-ray diffraction patterns to determine the presence of crystalline phases are pointed out. Finally, completed solar cells were fabricated and their I-V characterizations are discussed and evaluated. In Chapter 6, the most significant results are summarized and the conclusions are drawn, with suggestions for future research.