# CHAPTER I

# INTRODUCTION

## 1.1  Overview

The photovoltaic (PV) effect was originally discovered by Edmond Becquerel in 1839 with the action of light on an electrode in an electrolyte solution. A material (or solar cell) is said to be "photovoltaic" when it converts sunlight into electricity. For a long time it remained a scientific phenomenon with few device applications. The modern era of semiconductor PV started in 1954 when Chapin, Fuller and Pearson obtained a solar cell efficiency of 6% for a crystalline silicon cell. The value of efficiency was increased to 28% by Verlinden *et al.* in 1988. The all-thin-film cell composed of a $Cu_2S/CdS$ junction was first announced in 1954 by Reynolds and his colleagues with an efficiency of 6%, later increased to over 9% by Bragagnolo *et al.* in 1980. The first GaAs-based solar cell was the 4% p-n homojunction by Jenny *et al.* in 1956; later developments increase the efficiency over 30%. They were soon indispensable for supplying electrical power to telecommunications equipments in remote areas and on satellites [1,2].

In the 1970s, a major reorientation then took place in the general perception of the energy supply problem. The oil crisis in 1973 led to a general public awareness of the limitation of fossil fuels. A few years later, many governments (including those of the United State, Japan, and several European countries) started ambitious programs in the search for alternative energy

sources, including PV solar energy. This trend was reinforced by public controversy over nuclear fusion reactors and by a series of accidents in nuclear power plants (e.g. Three Mile Island in 1979 and Chernobyl in 1986) [3].

Initial efforts were concentrated on thin film solar cells of polycrystalline $Cu_2S/CdS$ and amorphous silicon (a-Si). The $Cu_2S/CdS$ type solar cell displayed severe stability problems and their developments were discontinued by the early 1980s. Instead, the a-Si based solar cell technology has been successful and commercially available products. However, their use is limited to special consumer applications because these products have low conversion efficiencies (about 12.6% stabilized).
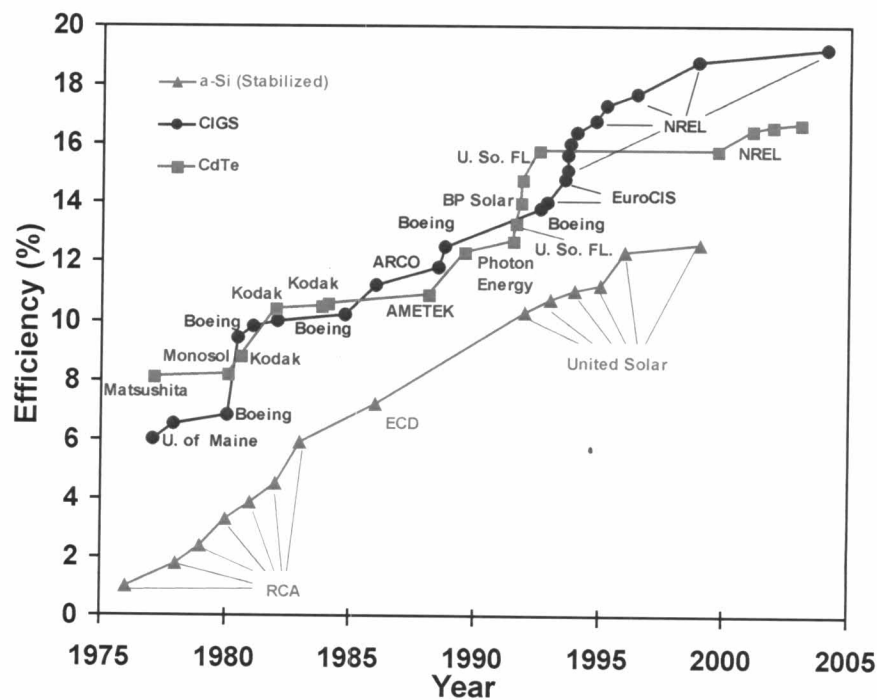


**Figure 1.1:** The evolution of efficiencies of the best thin film solar cells for a-Si, CIGS and CdTe [1,2,5].

Since the beginning of the 1990s, ecology considerations linked with the $CO_2$ global warming problem have been taken over as the main driving force in promoting alternative energy resources based on PV solar energy. The power generation market required module efficiencies in excess of 10%. Most research and development efforts shifted gradually to two other polycrystalline thin film materials: copper indium diselenide ($CuInSe_2$) and cadmium telluride (CdTe) based solar cells [4].

During the past three decades, these research and development efforts resulted in conversion efficiency improvements from 1% to 12.6% for a-Si, from 6% to 19.2% for $CuInSe_2$ (CIS) and other related materials (e.g., $Cu(In,Ga)Se_2$ (CIGS)), and from 8% to 16.7% for CdTe based for small area-laboratory devices [1,2,5]. The evolution of the world-record efficiencies of laboratory cells made from a-Si, CIGS, and CdTe are shown in Fig. 1.1. Although these improvements can be expected to continue in the near future for large area modules, it will take many decades before PV modules can be substantially contributed to electricity generation. The present cost of electricity from PV installations is generally (except in remote areas) about an order of magnitude higher than the current commercial prices of electricity generated by nuclear power and fossil fuels. The reduction in PV module cost progresses with the increase of efficiency and the decrease of process cost. Thus, the PV technologies based on thin films require the use of lesser quantities of cheaper and less refined input materials.

To date, the trend of research and development in these $Cu(In,Ga)Se_2$ materials is moved to the fabrication of large area modules with conversion efficiencies above 15% and tandem structure solar cells having more than one junction with conversion efficiencies toward 20% [6].

## 1.2 Copper Indium Diselenide and Related Materials for Thin Film Solar Cells

The development of CuInSe$_2$ cells started in 1974, when the single crystal cell with an efficiency of 12% were reported by a group of Bell Laboratory [7]. Although the material has the rather low optical band gap (E$_g$ ≈ 1.04 eV), CuInSe$_2$ thin film has a direct band gap with high optical absorption coefficient (α ≈ 10$^5$ cm$^{-1}$) as shown in Fig. 1.2.
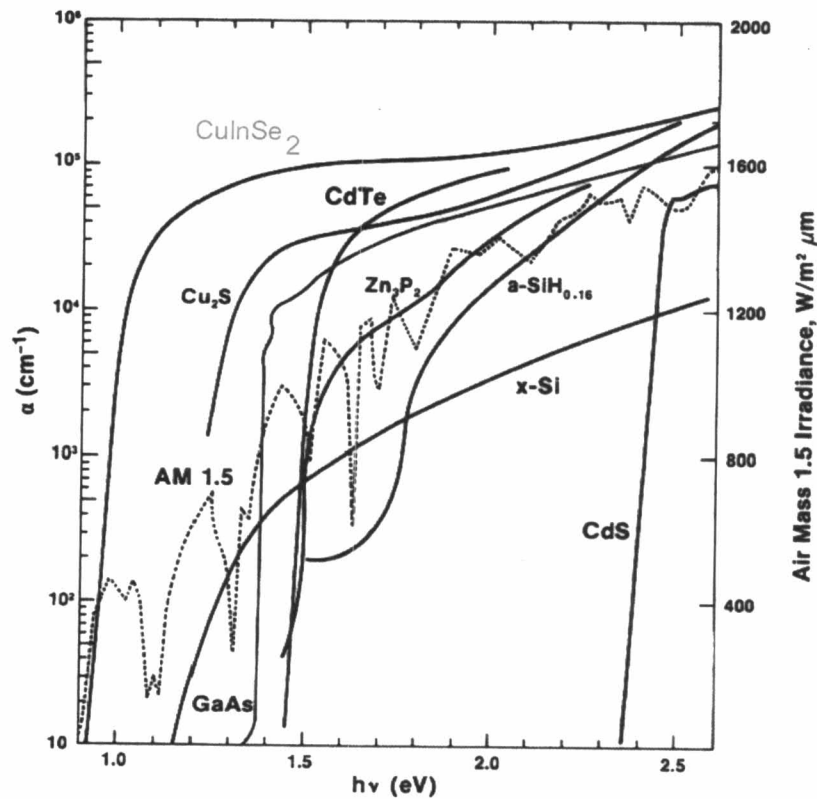


**Figure 1.2:** Absorption coefficient spectrum of CuInSe$_2$ compared with that of other photovoltaic semiconductors [8].

The thin film solar cells with 6.6% conversion efficiency were prepared by evaporating the $CuInSe_2$ compound as a source material and adding Se from a separate source by Kazmerski *et al.* [9] in 1977. It was found that the direct evaporation of the compound did not generally lead to films with stoichiometric composition. The conversion efficiency of $CuInSe_2$ thin film solar cells increased to 10.6% by 1982 with the results reported by researchers at Boeing Aerospace Corporation [10]. Their $CuInSe_2$ thin films were prepared by the co-evaporation (physical vapor deposition) of the three elemental sources. Using this technique, the films with any desired composition can be obtained. The "bi-layer" recipe, combining Cu-rich films and In-rich films (Cu-deficient films) developed by Boeing Aerospace Corporation, solved the problem of combining larger grains with suitable electronic properties [11].

The fabrication of $CuInSe_2$ thin film solar cells has been accomplished, with varying success by many different methods. The two principle methods succeeded in preparing high efficiency devices are the co-evaporation and the selenization of the deposited metals. The many other methods have been less successful in yielding high efficiency devices are electrodeposition [12], sputtering [13], spray pyrolysis [14], direct evaporation [15], and screen printing [16].

Alloying $CuInSe_2$ with $CuGaSe_2$ and $CuInS_2$ considerably increases the potential for the innovative development of solar cells. The energy gaps covered by these alloys ranging from about 1 eV to 2.4 eV. The possibility of increasing the energy gap and achieving absorber layers with graded band gaps has many advantages for the application of these materials in thin film solar cell modules [17].

Recently, the National Renewable Energy Laboratory (NREL) group has reported on a new world-record efficiency of $Cu(In,Ga)Se_2$ thin film solar cells with 18.8% by Contreras *et al.* [6] in 1999. Their $Cu(In,Ga)Se_2$ absorber layers were prepared by a "three-stage" recipe using the multi-source co-evaporation technique. In the first stage, a precursor layer compound (In, Ga and Se) was deposited onto a substrate (Mo-coated glass) with temperature ($T_{sub}$) of about $350^{\circ}C$, and subsequently Cu and Se were exposed at $T_{sub}$ above $570^{\circ}C$. At the end of the second stage, the Cu-content on the film was changed to slightly Cu-rich composition where the atomic ratios of [Cu]/([In]+[Ga]) were about 1.1 to 1.2. Finally, the additional In, Ga and Se fluxes were used to convert the Cu-content of the film to a slightly (In+Ga)-rich (or Cu-poor) composition, where the desired compositions of [Cu]/([In]+[Ga]) were about 0.8 to 0.9. However, the growth mechanism is limited for a small area of substrate because the deposition process uses the changes in the substrate temperature during growth, and requires an extremely high temperature (over the annealing point) of the glass substrate. These are the main reasons to obstruct technology transfer from laboratories to manufactories.

In terms of stability, CIS and CIGS thin film solar cells do not have a problem of light-induced degradation. Generally, they show a slight increase in open-circuit voltage and efficiency during the first hour of operation and can be remarkably stable, as proven for periods up to 8 years [18]. However, they have a problem of instability in a hot and humidity environment [19].

The impressive performance levels of CIGS thin film solar cells and mini-modules have demonstrated the highest efficiencies of 19.2% and 16.6%, respectively, the average efficiencies of modules are still less than 10%. These indicate that the technology transfer from laboratory scale to large area

manufacturing scale has been much more difficult than expected due to the complexity of the fabrication process and the unsatisfactory understanding of the functional property of CIGS absorber layers. The fundamental science and engineering basis for the materials remain a necessary need to research and development.

For the PV market, the thin film technologies based on CIS and related compounds are expected to substantially reduce the manufacturing costs due to the lowering of material expenses and the ability to deposit on large area substrates of a module size. At present, the efficiencies of CIGS modules (30x30 $cm^2$) with integrated series connection, as fabricated in pilot lines, are between 9 and 12% [20].

The main objectives of this research were to design and construct a direct formation deposition system for CIGS thin films using the co-evaporation technique and to fabricate CIGS thin films for high efficiency solar cells.

## 1.3   Outline of the Research

In this research, the work was carried out at two research centers; Semiconductor Physics Research Laboratory (SPRL), Chulalongkorn University, Thailand and Ångstrom Solar Center (ÅSC), Uppsala University, Sweden. All the CIGS films were grown by the co-evaporation based two-stage method at a constant substrate temperature. Although a study as a function of the substrate temperature is presented, the "base" recipe should run at 500°C.

The first part of research was carried out at SPRL and it was outlined as the following. The CIGS thin films grown by the two-stage process, referred to

as Cu-Rich-Off (CURO), were produced from the prototype deposition system. The CIGS thin film solar cells were also fabricated based on the recipe of SPRL. The growth of CIGS absorber layers were intended on the *in situ* monitoring signals. The substrate temperature was controlled and kept constant by regulating the output power of the temperature controller. The substrate temperature was detected by a thermocouple at the back surface of the glass substrate. The thermal radiation from the front surface of the sample was monitored by a pyrometer. The *in situ* monitoring of the signals in the growth of CIGS thin films were established as the end point detection (EPD) to detect the desired Cu-deficient composition. The crystal structure and morphology of CIGS thin films were characterized using X-ray diffraction (XRD) technique and scanning electron microscopy (SEM). The cell performances were characterized using a standard current-voltage measurement system and a quantum efficiency measurement system.

The second part of research was carried out at ÅSC and it was outlined as the following. The CIGS thin films grown by the modified two-stage process, referred to as Cu-Poor-Rich-Off (CUPRO) were produced from the similar deposition system. The cells were also fabricated based on the recipe of ÅSC. The growth of CIGS absorber layers used the output power signal as the control signal. The heating output power was used for regulating the substrate at a constant temperature. The five-growth model for the CUPRO film was proposed based on the characterization results of the X-ray diffraction technique, scanning electron microscopy, and etc. The cell performances were also characterized using the similar systems.

This thesis contains six Chapters, with a main emphasis on the fabrication of CIGS thin films for high efficiency solar cells using the

co-evaporation technique. Chapter 1 gives the overview of photovoltaic from the discovery of PV effect to the present status of CIGS thin film solar cells and the outline of the research. The overview of chalcopyrite semiconductors and their solar cells is given in Chapter 2. Chapter 3 gives the basic of the evaporation process and details of the CIGS deposition system. Chapter 4 describes the experimental procedures that involve the fabrication of CIGS thin film solar cells and the growth of CIGS thin films by the physical vapor deposition (PVD) techniques based on the calculations for two-stage and modified two-stage processes. Chapter 5 provides the results and discussions of the CIGS films and devices using the two recipes and the models for each growth process. Finally, the conclusions and suggestions are exhibited in Chapter 6 of this thesis.