Solar Driven Photoelectrochemical Water Splitting For Hydrogen Generation Using Multiple Bandgap Tandem Of Cigs2 Pv Cells And Thin Film Photocatalyst

2005

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SOLAR DRIVEN PHOTOELECTROCHEMICAL WATER SPLITTING FOR HYDROGEN
GENERATION USING MULTIPLE BANDGAP TANDEM OF CIGS2 PV CELLS AND THIN
FILM PHOTOCATALYST

by

ANANT H. JAHAGIRDAR
M.S. University of Central Florida, 2002

A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
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Major Professor: Neelkanth G. Dhere
ABSTRACT

The main objective of this research was to develop efficient CuIn\(_{1-x}\)Ga\(_x\)S\(_2\) (CIGS2)/CdS thin film solar cells for photoelectrochemical (PEC) water splitting to produce very pure hydrogen and oxygen. Efficiencies obtained using CIGS2 have been lower than those achieved using CuInSe\(_2\) and CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\). The basic limitation in the efficiencies is attributed to lower open circuit voltages with respect to the bandgap of the material. Presently, the main mechanism used to increase the open circuit voltage of these copper chalcopyrites (CuInSe\(_2\) and CuInS\(_2\)) is the addition of gallium. However, addition of gallium has its own challenges. This research was intended to (i) elucidate the advantages and disadvantages of gallium addition, (ii) provide an alternative technique to the photovoltaic (PV) community to increase the open circuit voltage which is independent of gallium additions, (iii) develop highly efficient CIGS2/CdS thin film solar cells and (iv) provide an alternative material in the form of CIGS2/CdS thin film solar cells and an advanced technology in the form of a multiple bandgap tandem for PEC water splitting.

High gallium content was achieved by the incorporation of a highly excess copper composition. Attempts to achieve high gallium content produced reasonable but not the best solar cell performance. Few solar cells developed on a molybdenum back contact and an ITO/MoS\(_2\) transparent conducting back contact showed a PV conversion efficiency of 7.93% and 5.97%, respectively. The solar cells developed on the ITO/MoS\(_2\) back contact form the first generation CIGS2/CdS thin film solar cells and 5.97% is the first ever reported efficiency on an ITO/MoS\(_2\) transparent back contact. Reasons for the moderate performance of these solar cells were attributed to significant porosity and remnants of unsulfurized CuGa alloy in the bulk of CIGS2. This was the first attempt to a detailed study of materials and device characteristics of
CIGS2/CdS thin film solar cells prepared starting with a highly excess copper content CIGS2 layer.

Next, excess copper composition of 1.4 (equivalent to gallium content, $x = 0.3$) was chosen with the aim to achieve the best efficiency. The open circuit voltage was enhanced by depositing an intermediate layer of intrinsic ZnO between CdS and ZnO:Al layers. The systematic study of requirements for such a layer and further optimization of its thickness to achieve a higher open circuit voltage (which is the greatest challenge of the scientific community) forms an important scientific contribution of this research. The PV parameters for CIGS2/CdS thin film solar cell as measured officially at the National Renewable Energy Laboratory were: open circuit voltage of 830.5 mV, short circuit current density of 21.88 mA/cm$^2$, fill factor of 69.13% and photovoltaic conversion efficiency of 11.99% which sets a new world record for CIGS2 cells developed using sulfurization and the open circuit voltage of 830.5 mV has become the “$V_{oc}$ champion value”.

New PEC setups with the RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ photoanodes were developed. RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ photoanodes were more stable in the electrolyte and showed better I-V characteristics than the RuO$_2$ anode earlier used. Using two CIGS2/CdS thin film solar cells, a PEC efficiency of 8.78% was achieved with a RuS$_2$ anode and a platinum cathode. Results of this research constitute a significant advance towards achieving practical feasibility and industrially viability of the technology of PEC hydrogen generation by water splitting.
Lord Laxmi Narasimha

My Parents

My wife and My In laws

My Beloved Sister and My Niece
ACKNOWLEDGMENTS

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*Guru Brahma Guru Vishnu Guru Deva Maheshwara*

*Guru Saakshaath Para Brahma Tasmai Shree Guruve Namahaa*

Meaning of the above verse is, “Guru (Teacher) is the Brahma (creator of the world, one who plants the qualities of goodness), teacher is the Vishnu (who nurtures and fosters the qualities of goodness) and teacher is the Maheswara (who weeds out the bad quality), Teacher is the supreme Brahman itself and that is the reason I bow to him. I thank wholeheartedly my Guru Dr. Neelkanth G. Dhere for being my major advisor, giving me an opportunity to work on a very interesting project and for the constant guidance during the course of dissertation. I thank Dr. Sucharita N. Dhere for her moral support and guidance.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHAPTER ONE: INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>CHAPTER TWO: CIGS2/CdS THIN FILM SOLAR CELLS</td>
<td>9</td>
</tr>
<tr>
<td>2.1</td>
<td>2.1 Optical Properties</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>2.2 Crystal Structure</td>
<td>10</td>
</tr>
<tr>
<td>2.3</td>
<td>2.3 Deposition of CIGS2 Absorber</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1</td>
<td>2.3.1 Choice of Copper Excess Composition and Addition of gallium</td>
<td>17</td>
</tr>
<tr>
<td>2.4</td>
<td>2.4 Removal of Copper Excess</td>
<td>19</td>
</tr>
<tr>
<td>2.5</td>
<td>2.5 Heterojunction Formation</td>
<td>19</td>
</tr>
<tr>
<td>2.5.1</td>
<td>2.5.1 Buffer Layer Deposition</td>
<td>19</td>
</tr>
<tr>
<td>2.5.2</td>
<td>2.5.2 Window Layer Deposition</td>
<td>21</td>
</tr>
<tr>
<td>2.6</td>
<td>2.6 Electrical Properties</td>
<td>22</td>
</tr>
<tr>
<td>2.7</td>
<td>2.7 Challenges of Gallium Incorporation</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>CHAPTER THREE: PHOTOELECTROCHEMICAL WATER SPLITTING</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>CHAPTER FOUR: EXPERIMENTAL TECHNIQUE</td>
<td>34</td>
</tr>
<tr>
<td>4.1</td>
<td>4.1 Substrate Preparation</td>
<td>37</td>
</tr>
<tr>
<td>4.2</td>
<td>4.2 Development of CIGS2 Thin Films</td>
<td>38</td>
</tr>
<tr>
<td>4.2.1</td>
<td>4.2.1 Series 1 – CIGS2 thin film solar cells with Cu/(In+Ga) = 2.5</td>
<td>43</td>
</tr>
<tr>
<td>4.2.2</td>
<td>4.2.2 CIGS2 thin films on ITO/MoS2 back contact – Cu/(In+Ga) = 2.5</td>
<td>45</td>
</tr>
<tr>
<td>4.2.3</td>
<td>4.2.3 Series 2 CIGS2 thin films – Cu/(In+Ga) = 1.4</td>
<td>46</td>
</tr>
<tr>
<td>4.2.4</td>
<td>4.2.4 Series 3 CIGS2 thin films – Cu/(In+Ga) = 1.4 with metallic precursors annealed</td>
<td>48</td>
</tr>
<tr>
<td>4.3</td>
<td>4.3 Materials Characterization</td>
<td>48</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1: Energy Flow Diagram of United States in Quadrillion BTU [1]. ................................. 2
Figure 2: Chronological evolution of thin film solar cell efficiencies [13]. ................................. 5
Figure 3: Dependence of the absorption coefficient on the photon energy for selected semiconductors [23]. ......................................................................................................................... 10
Figure 4: Schematic diagram of the crystal structure of (a) CuInS$_2$ and (b) Zinc blend .......... 11
Figure 5: Variation of lattice constant with bandgap of copper chalcopyrite materials .......... 13
Figure 6: Ternary component diagram of Cu-In-S [48]. ............................................................... 14
Figure 7: Pseudo binary phase diagram of Cu$_2$S-In$_2$S$_3$ [48]. ................................................. 15
Figure 8: Model for the growth of polycrystalline CuInS$_2$ in the presence of a quasi-liquid surface film of Cu$_{2-x}$S on top of the CuInS$_2$ grains [49]. ......................................................... 17
Figure 9: Schematic illustration of the current density–voltage characteristics of a solar cell in the dark and under illumination. Indicated are the short-circuit current density $J_{sc}$, the open-circuit voltage $V_{oc}$, the photo-generated current density $J_{ph}$, and the maximum power point $(J_m, V_m)$. ................................................................................................................................. 22
Figure 10: Equivalent electrical circuit of a solar cell. ................................................................. 26
Figure 11: Variation of short circuit current density $J_{sc}$ with series resistance $R_s$. .............. 26
Figure 12: Variation of open circuit voltage $V_{oc}$ with shunt resistance $R_p$. ......................... 27
Figure 13: Band diagram of CIGS2/CdS thin film with the back surface field created by the movement of gallium going towards back contact. ......................................................... 28
Figure 14: Flowchart showing important steps in the formation of CIGS2/CdS thin film solar cells. ........................................................................................................................................ 36
Figure 15: Layered structure of CIGS2/CdS thin film solar cells on molybdenum back contact.

Figure 16: Large area magnetron sputtering systems for the DC magnetron sputtering of molybdenum back contact, CuGa and indium metallic precursors and RF magnetron sputtering of i-ZnO/ZnO:Al.

Figure 17: (a) Non uniform plasma and (b) uniform plasma [86].

Figure 18: Selenization/sulfurization flow diagram.

Figure 19: Stacked layering sequence for CuGa-In metallic precursor deposition.

Figure 20: Layered structure of CIGS2/CdS thin film solar cells on ITO/MoS$_2$ transparent conducting back layer.

Figure 21: CBD CdS deposition setup for 10 cm x 10 cm CIGS2 thin films.

Figure 22: Two cell PEC setup.

Figure 23: SEM images of (a) unetched (b) etched CIGS2 at x5500 (c) etched CIGS2 at x15000 and (d) etched CIGS2 at x30000.

Figure 24: XRD pattern of unetched and etched CIGS2 thin film grown in series 1 (Cu/In+Ga = 2.5).

Figure 25: AES depth profile of etched CIGS2 thin film.

Figure 26: Photocurrent spectroscopy of CIGS2 thin film showing a bandgap of 1.54 eV.

Figure 27: I-V characteristics of CIGS2/CdS thin film solar cell with Cu/(In+Ga) = 2.5.

Figure 28: Variation of transmittance with wavelength of ITO, ITO/MoS$_2$, and ITO/MoSe$_2$ thin films on glass substrate.

Figure 29: SEM micrograph of (a) unetched and (b) etched CIGS2/CdS thin film on ITO/MoS$_2$ back contact.

Figure 30: XRD pattern of CIGS2/CdS thin film on ITO/MoS$_2$ bilayer back contact.
Figure 31: IV characteristic of CIGS2/CdS solar cell on ITO/MoS2 back contact. .......................... 67

Figure 32: TEM micrograph of CIGS2/CdS thin film solar cell with copper excess composition of 2.5. ........................................................................................................................................ 69

Figure 33: Line scan of TEM image using XEDS analysis................................................................. 70

Figure 34: SEM micrographs of (a) unetched, (b) etched x5500, (c) etched x30000 and (d) cross-section of etched CIGS2 thin film with Cu/(In+Ga) = 1.4 ................................................................. 71

Figure 35: Schematic representation of dependence of coating structure on substrate temperature and argon pressure [93]........................................................................................................ 72

Figure 36: Cross-section TEM image of CIGS2 film grown with the copper excess composition of 1.4 ........................................................................................................................................ 73

Figure 37: XRD pattern of series 2 etched CIGS2 thin film............................................................... 74

Figure 38: AES depth profile of etched series 2 CIGS2 thin film....................................................... 75

Figure 39: I-V characteristics of series 2 CIGS2/CdS thin film solar cells........................................ 76

Figure 40: Cross-section SEM micrograph of (a) CIGS2 thin film prepared using sulfurization (b) CuIn1-xGaxSe2 thin film prepared by co-evaporation technique [95]........................................ 80

Figure 41: I-V characteristics of series 2 CIGS2/CdS thin film solar cell with the optimum i-ZnO thickness................................................................................................................................. 82

Figure 42: I-V measurement of CIGS/CdS thin film solar cell with copper excess composition of 1.4........................................................................................................................................ 83

Figure 43: SEM micrograph (a) at x5500 magnification and (b) cross-section of etched CIGS2 thin film with precursor annealed at 120 °C for 30 minutes......................................................... 86

Figure 44: Graph of I-V measurement of CIGS2/CdS cell with precursors annealed at 120 °C for 30 minutes........................................................................................................................................ 87
Figure 45: SEM micrographs at x1000 of (a) RuS$_2$ and (b) Ru$_{0.99}$Fe$_{0.01}$S$_2$. ................................. 89

Figure 46: XRD pattern of (a) RuS$_2$ and (b) Ru$_{0.99}$Fe$_{0.01}$S$_2$. .............................................................. 90

Figure 47: SIMS depth profile of (a) RuS$_2$ and (b) Ru$_{0.99}$Fe$_{0.01}$S$_2$. .............................................................. 90

Figure 48: I-V characterization RuO$_2$, RuS$_2$, and Ru$_{0.99}$Fe$_{0.01}$S$_2$ anodes. ................................. 91

Figure 49: I-V characteristic of two CIGS2/CdS thin film solar cells illuminated with AM1.5 illumination along with the I-V of PEC cell having RuS$_2$ anode in dark and platinum cathode. ................................................................................................................................. 92
LIST OF TABLES

Table 1: Atomic Coordinates for CuInS$_2$ ................................................................. 12

Table 5.1: Atomic concentrations of unetched CIGS$_2$ thin film analyzed by EPMA at 20kV. ... 56
Table 5.2: Atomic concentrations of etched CIGS$_2$ thin film analyzed by EPMA at 10kV. .... 56
Table 5.3: Atomic concentrations of etched CIGS$_2$ thin film analyzed by EPMA at 20kV. .... 57
Table 5.4: Solar cell parameters of series 1 CIGS$_2$/CdS thin film solar cell ......................... 63
Table 5.5: Solar cell parameters of series 1 CIGS$_2$/CdS thin film solar cell on ITO/MoS$_2$ back contact ............................................................... 67
Table 5.6: Solar cell parameters of series 2 CIGS$_2$/CdS thin film solar cell ....................... 77
Table 5.7: Solar cell parameters of series 2 CIGS$_2$/CdS thin film solar cell ....................... 77
Table 5.8: Device parameters along with the open circuit voltage values for CIGS$_2$/CdS cells with minimum i-ZnO. ....................................................... 81
Table 5.9: Device parameters along with the open circuit voltage values for CIGS$_2$/CdS cells with optimum i-ZnO. ....................................................... 81
Table 5.10: Solar cell parameters of series 2 CIGS$_2$/CdS thin film solar cell with the optimum i-ZnO thickness .............................................................. 82
Table 5.11: Device parameters of I-V measurements carried out at AM0 conditions. ........... 84
Table 5.12: Open circuit voltage values for CIGS$_2$/CdS cells with maximum i-ZnO thickness. 85
Table 5.13: Solar cell parameters of CIGS$_2$/CdS cell with precursors annealed at 120 °C for 30 minutes. ................................................................. 88
## LIST OF ACRONYMS/ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$</td>
<td>Current Density (mA/cm$^2$)</td>
</tr>
<tr>
<td>$J_0$</td>
<td>Reverse Saturation Current Density (mA/cm$^2$)</td>
</tr>
<tr>
<td>$q$</td>
<td>Electronic Charge, $1.6 \times 10^{-19}$ C</td>
</tr>
<tr>
<td>$A$</td>
<td>Diode Ideality Factor</td>
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<tr>
<td>$k$</td>
<td>Botlzmann’s Constant, $8.61 \times 10^{-5}$ eV/°C</td>
</tr>
<tr>
<td>$J_D$</td>
<td>Dark Current Density (ma/cm$^2$)</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Series Resistance (Ohm)</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Shunt or Parallel Resistance (Ohm)</td>
</tr>
<tr>
<td>$V$</td>
<td>Biased Voltage (Volts)</td>
</tr>
<tr>
<td>$J_{ph}$</td>
<td>Photo generated Current Density (mA/cm$^2$)</td>
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<td>$V_m$</td>
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<td>$V_{oc}$</td>
<td>Open Circuit Voltage (Volts)</td>
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</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency (%)</td>
</tr>
<tr>
<td>$V_{bi}$</td>
<td>Built-in Voltage (Volts)</td>
</tr>
</tbody>
</table>
CHAPTER ONE: INTRODUCTION

Modern lifestyles demand a steady, reliable supply of energy: it lies at the heart of our mobility, our prosperity and our daily comfort. However, we should not take this energy security for granted. Energy sources can be divided into three broad categories. The first derives from chemical or photophysical energy that relies on oxidizing some reduced substance, usually a hydrocarbon, or absorbing sunlight to generate either heat or electricity. The energy involved is that of a chemical bond or fractions of an electron volt (eV). The second source involves nuclear reactions that release energy either by splitting heavy nuclei or by fusing light nuclei. The energy involved in nuclear reactions is in the range of $10^6$ electron volts (MeV) per nuclear reaction. The third source is thermomechanical in the form of wind, water, or geological sources of steam or hot water. The energy involved is in the milli-electron-volt (meV) range, for example, water falling several tens of meters. The current usage of these various energy sources in the United States is depicted in Figure 1 [1]-[2].

Each energy source has some undesirable characteristics. Any process using fossil fuels produces carbon dioxide, and perhaps also other contaminants, such as nitrous oxides, sulphur oxides and ash. Nuclear plants produce radioactive fission products. Hydroelectric plants require dams and large lakes. Solar energy and wind energy require large areas and are limited geographically. Geothermal sources are limited to very few locations. Schemes using small temperature gradients in the earth or oceans have low thermal efficiencies, and hence require very large heat-exchanger areas. At present, most of the world’s energy supply comes from fossil and nuclear sources (Figure 1).
Figure 1: Energy Flow Diagram of United States in Quadrillion BTU [1].

Although mankind increasingly has to face the issues of resource limitation and environmental pollution, these sources will continue to be important in providing energy worldwide for several more years. But to meet increasing global demands for energy and to allow for the depletion of fossil fuel supplies in the coming years, alternative ‘clean’ energy sources, which do not depend on fossil fuels and which have a tolerable environmental impact, must be developed. Renewable means of producing and storing electricity are expected to become increasingly important in the future and given the recent strides in condensed-matter physics and materials technology, could compete with existing technologies [2]-[7].

Remarkable developments are taking place in the fields of fuel cells and solar cells; technologies using renewable energy sources. To use renewable sources effectively, reliable ways of storing energy are needed: exciting developments are being made in hydrogen storage, rechargeable batteries and high-temperature superconductivity. Ultimately, the energy security of future generations will not only depend on reaching acceptable scientific and technological
solutions, but will also require international cooperation on science policies to ensure continued prosperity and the safety of our environment [2]-[7].

At present, major part of the energy consumption comes from chemical energy stored in the fossil reserves. The resource accumulated over millions of years is rapidly being depleted and the combustion has led to severe pollution and disturbance of the environment. It is generally accepted that CO$_2$ (besides CH$_4$ and NO$_x$) to a great extent contributes to the greenhouse effect. Due to the dangers of climate change and the depletion of the fossil reserves, there is growing interest for development of new alternative energy sources such as solar, wind, ocean tides and sea stream energies, in addition to the thermal energy from hot water springs and volcanoes [8]-[9]. Hydrogen is a clean and sustainable form of carrier of energy that can be used in mobile and stationary applications. Hydrogen can be produced from a wide variety of domestic resources using several technologies such as (i) reforming natural gas (CH$_4$), methanol (CH$_3$OH), gasoline (C$_8$H$_{18}$), ethanol (C$_2$H$_5$OH) and (ii) water based hydrogen production by electrochemical, photoelectrochemical (PEC) and photobiological processes. At present, major problem in producing hydrogen is the cost and efficiency. Solar energy driven water splitting (photoelectrochemical, PEC) combines several attractive features for energy utilization. Both the energy source (sun) and the reactive media (water) are readily available and are renewable, and the resultant fuel (generated hydrogen) and the emission with fuel consumption (water) are each environmentally benign [10]-[11].

Over the years, solar cell designs have become specialized for terrestrial applications. Historically the great amount of commercial solar cells was made from silicon while the most expensive GaAs has become only an option for space cells. While single crystalline solar cells have proved reliable for terrestrial application, several experts predict saturation of c-Si module
production peaking in the 3-4 GW/year range with a substantial increase in the production of the thin-film solar cells within the next decade. Traditionally available crystalline silicon solar cells require material thickness of 200 – 350 µm for effective solar energy absorption and are prepared via expensive processes of high temperature, for instance, electronic grade silicon – material purification as well as mechanical treatment such as sawing of wafers and soldering of interconnection of cells and assembly of modules. The primary objective of worldwide photovoltaic (PV) solar cell research and development (R&D) is to reduce the cost of PV modules and systems to a level that will be competitive with conventional ways of generating electric power. PV technology in the marketplace today is dominated by crystalline/polycrystalline silicon. Even with greatly increased production volume and significant reduction of cost, it is doubtful whether crystalline/polycrystalline silicon will ever meet the long-term cost goals for utility scale power generation. If one accepts this rationale, it will be useful to see whether thin film technologies can realistically meet these goals. There is a reason to be very optimistic, particularly in view of progress that has been made in terms of high conversion efficiency, long-term stability, and demonstrated large scale manufacturing capabilities in several thin film technologies [12].

The main barrier impeding the expansion of thin film technology is lack of comprehensive literature in comparison to the one available for c-Si solar cells from the extensive research and development on microelectronic devices. Currently, thin film technologies based on alloys of amorphous silicon (a-Si:H), cadmium telluride (CdTe), ternary and multinary copper indium diselenide, CuInSe₂ and CuIn₁₋ₓGaₓSe₂ are the leading contenders for economic and large-scale production. Figure 2 shows the chronological evolution of small area research cell efficiencies [13].
After the disastrous experience of rapid degradation of the first generation CdS/Cu₂S thin-film solar cells, researchers were seeking a robust material system and found a near-perfect solution in CuInSe₂ [14]-[16]. It has a very stable chalcopyrite structure, can be doped p-type by growing it copper-poor over a wide range, has mostly benign grain-boundaries and an excellent n-type heterojunction partner, CdS and provided greater than 5% efficient cells easily in early attempts [15]. In 2004, the world production of CuIn_{1-x}Ga_{x}Se_{2-y}S_{y} and CuIn_{1-x}Ga_{x}Se_{2} thin-film PV modules was as follows: Shell Solar 2 MW, Global Solar 0.5 MW and Würtz Solar 1.3 MW [17]-[18]. In May 2005, Würtz Solar announced the construction of a new production site with a production capacity of 15 MW for CIGS PV modules with an investment of around 55 Million
Euros. More recently, Showa Shell Sekiyu, Japan has announced plans to build a CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\) thin-film solar cell manufacturing plant with commercial production to begin in early 2007 with the final production capacity of 20 MW per annum.

The present PV conversion efficiency of champion CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\)/CdS thin-film solar cells is 19.5% [19]. Spec-sheet efficiencies of commercial CuInSe\(_2\) modules of Würth Solar and Shell Solar are 11.0 and 9.4% respectively. Compared to this, spec-sheet efficiency ratings of commercial c-Si PV modules range from 11.1% to 16.9%, most being in the range of 12.7-13.5%. Thus efficiencies of CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\)/CdS modules are comparable to those of lower end c-Si modules and considerably improved efficiencies can be expected based on the champion cell efficiencies.

The material under study through the present research is CuIn\(_{1-x}\)Ga\(_x\)S\(_2\) (CIGS\(_2\)) belonging to the family of chalcopyrite compounds copper indium disulfide, CuInS\(_2\) and copper gallium disulfide, CuGaS\(_2\) which themselves have not been studied even as much as the family of chalcopyrite compounds CuInSe\(_2\) which include CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\) and CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\)-yS\(_y\). Polycrystalline thin film solar cells based on CuInS\(_2\) are of promising interest for photovoltaic applications due to the band gap of 1.5 eV which perfectly matches the solar spectrum for energy conversion [20]. Furthermore, the use of sulfur and its compounds is expected to be less problematic with respect to impacts on the environment and handling in commercial production [21]. However, the efficiencies obtained using CuInS\(_2\) have been less than those achieved using CuInSe\(_2\) and CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\). The basic limitation in the efficiency is attributed to lower open circuit voltages compared to the bandgap of the material. The challenge of the PV scientific community is to achieve high efficiencies along with high open circuit voltage. So far, efforts to increase the open circuit voltage and still maintain high efficiency have been only partially
successful [22]. Increasing the open circuit voltage requires major scientific contributions because it not only involves improvements in the materials properties but also needs improvements in the heterojunction properties to enhance the device performance.

Variety of process technologies available for deposition of thin films differ to a large extent in their physical or chemical principles of operation and in the commercially available type of equipment. Each process technology has been pursued or developed because of its unique advantages over others. There are also limitations to each process and in order to optimize the desired film characteristics a good understanding of restriction and advantages applicable to each technology is necessary. The important properties of CuInS₂ (optical, structural and electrical), various deposition techniques and cell completion are discussed in Chapter 2. Photoelectrochemical water splitting using PV energy for splitting water to get hydrogen and oxygen is addressed in a Chapter 3.

A typical structure of CuInS₂ device consists of CuInS₂ absorber layer deposited on the molybdenum coated substrate. The hetero-junction is then completed by chemical bath deposition of a CdS layer (typically 50 nm) and by the sputter deposition of a ZnO window layer. An important part of this study was the deposition of CuInS₂ thin films with optimum structural and electrical characteristics. The structural and electrical properties of these CuInS₂ layers are strongly dependant on the processing parameters. The experimental details involving the deposition of each constituent layer are discussed in Chapter 4. Chapter 4 also discusses the growth technique of photoanodes for efficient hydrogen and oxygen generation.

Materials and device characterization of the CuInS₂ absorber layer to ensure the desired film quality and device parameters of CuInS₂/CdS thin film solar cells are discussed in Chapter 5. Chapter 5 also discusses the materials and I-V characterization of photoanodes. Chapter 6
presents a summary of the results discussed in Chapter 5. Important conclusions and contributions to the scientific world from this study are drawn.
CHAPTER TWO: CIGS2/CdS THIN FILM SOLAR CELLS

This chapter will first give an overview of optical and structural properties of Cu–In–S compounds, as far as they are relevant for the understanding and growth of CuInS$_2$ thin films. Thereafter, different approaches for the deposition of CuInS$_2$ thin films will be discussed. Understanding these deposition techniques is not only important for the improvement of absorber properties and hence the solar cell efficiency, but also for recognizing the importance and challenges of adding gallium into CuInS$_2$ to form CIGS2 will be seen. Towards the end, electrical properties of CIGS2/CdS thin film solar cells will be discussed.

2.1 Optical Properties

One of the properties that make CIGS2 a material well suited for solar cells is its high absorption coefficient. In contrast to, for example crystalline silicon, CIGS2 has a direct band gap and therefore absorbs light much more efficiently, such that CIGS2 absorbers require much less material. The intensity of monochromatic light in an absorbing material falls exponentially with depth $d$ according to the well-known relation

$$I(h\nu,d) = I(h\nu,0)e^{-\alpha(h\nu)d} \quad \text{..............2.1}$$

The absorption coefficient, $\alpha(h\nu)$ of CuInS$_2$ is $\sim 10^5$ cm$^{-1}$ (crystalline silicon $\sim 10^3$ cm$^{-1}$) for a photon energy of $h\nu = E_g + 0.2$ eV, where $E_g$ is the bandgap energy of the respective material [23]. The wavelength dependence of the absorption coefficient (Figure 3) implies that all high-energy photons will be absorbed in CIGS2 very close to the surface, while photons with energies only slightly larger than the band gap of the absorber will penetrate more deeply into the CIGS2.
2.2 Crystal Structure

Copper indium disulfide, CuInS$_2$ belongs to the semiconducting I-III-VI$_2$ materials family that crystallizes in the tetragonal chalcopyrite. The tetragonal structure of CuInS$_2$ (Figure 4a) results from the stacking of two cubic zinc blend structures along the z-axis. The primitive cell for this structure is made up of eight tetrahedrons with shared vertices, so that the whole cell is just two stacked cubes. By convention, the short edge is labeled ‘a’ and the long edge is labeled ‘c’. This gives rise to the condition that, given perfect tetragonal symmetry, c/a = 2 [23]-[24]. For crystals containing two different atoms in the primitive cell, the structure becomes zinc blende, with ZnS as the prototype (Figure 4b). In this case, each cation has four tetrahedrally
arranged anion neighbors, and each anion has four nearest cation neighbors. Similarly, the primitive cell may contain three different atoms, two cations (A and B) and one anion (C). If these are arranged so that each C anion has two A cations and two B cations as nearest neighbors, the resulting structure is chalcopyrite. In CuInS$_2$, each group I (copper) or group III (indium) atom has four bonds to the group VI atom (S). In turn each S atom has two bonds to copper and two to indium. The tetrahedral structure becomes distorted due to differing bond strengths between I-VI and III-VI atoms, so the value of ‘c’ changes relative to ‘a’. The measure of this distortion can be described by the quantity $2 - \frac{c}{a}$. For CuInS$_2$, the lattice parameters are, $a = 5.523\ \text{Å}$ and $c = 11.141\ \text{Å}$. In this case, each cation has four tetrahedrally arranged anion neighbors, and each anion has four nearest cation neighbors. Table 1 lists its atomic coordinates [25]. The value of $u$ depends upon the differences in bonding between copper and Sulfur and indium and sulfur.

Figure 4: Schematic diagram of the crystal structure of (a) CuInS$_2$ and (b) Zinc blend
Table 1: Atomic Coordinates for CuInS$_2$

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0,0,0</td>
</tr>
<tr>
<td>In</td>
<td>0,0, ½</td>
</tr>
<tr>
<td>S</td>
<td>u, ¼, ⅛</td>
</tr>
<tr>
<td></td>
<td>½+u, ¾, ¾</td>
</tr>
</tbody>
</table>

Another semiconductor with a similar structure to CuInS$_2$ is CuGaS$_2$, which has a band gap of 2.4 eV. Gallium is in the same group of the periodic table as indium. Thus, by substituting gallium for indium in some places in the lattice, the band gap of CuIn$_{1-x}$Ga$_x$S$_2$ (CIGS$_2$) can range from 1.5 eV < $E_g$ < 2.4 eV [26]. Thus, addition of gallium can be considered as alloying between the ternary compounds CuInS$_2$ and CuGaS$_2$.

Alloying allows optimization of material properties and also changes other properties such as defect chemistry, defect levels within the bandgap, electron and hole affinities, carrier concentration, resistivity, crystal structure and lattice constants. Figure 5 shows various combinations of alloying between ternary chalcopyrite structures.
Figure 5: Variation of lattice constant with bandgap of copper chalcopyrite materials

2.3 Deposition of CIGS2 Absorber

CuInS$_2$ thin films have been prepared by spray-pyrolysis [27], electrochemical deposition [28]-[29], physical vapor deposition (PVD) techniques (sulfurization of sputtered metallic precursors (Cu-In-Ga) in H$_2$S ambient [30]-[39] and evaporation/co-evaporation [40]-[46]).

CuInS$_2$ or CIGS2 thin film absorbers are grown in either cu-rich or in cu-poor composition. Each technique has its own advantages and disadvantages. The advantages and disadvantages of each technique can be understood by the pseudobinary phase diagram of Cu$_2$S and In$_2$S$_3$. Due to the multitude of elements involved in the formation of CuIn$_{1-x}$Ga$_x$Se$_2$, CIGS2 or CuIn$_{1-x}$Ga$_x$Se$_{2-y}$S$_y$, defects and growth of the films are very complex. The phase diagrams have been extensively investigated by Godecke et al. [47]. These investigations had a special focus on temperatures and compositions relevant to preparation of thin films.
Figure 6 displays equivalent ternary component diagram, which comprises all ternary Cu-In-S compounds that have been identified at the time along the tie line of Cu$_2$S - In$_2$S$_3$ [48]. This ternary diagram can be reduced to simple pseudobinary phase diagram along the tie line between Cu$_2$S-In$_2$S$_3$ (central line in Figure 6). The bold points along this line represent the range of photovoltaic quality material. By combining these two compounds, CuInS$_2$ can be formed:

$$x \text{ (Cu}_2\text{S)} + (1-x) \text{ In}_2\text{S}_3, \ 0<x<1 \ [12].$$

Figure 7 shows the relevant portion of the phase diagram of CuInS$_2$ given in Figure 6. There are four different phases which have been found relevant in this range: $\alpha$ – phase (CuInS$_2$), $\beta$ – phase (CuIn$_3$S$_5$), the $\delta$ – phase (high temperature sphalerite phase) and Cu$_{2-x}$S phase. An interesting point is that the phases adjacent to $\alpha$ – phase have similar structure. The $\beta$ – phase is actually a defect chalcopyrite phase built by ordered arrays of defect pairs (copper vacancies $V_{cu}$ and In-Cu antisites In$_{cu}$). This defect pair is electrically neutral. This forms only at the surface. However, this phase has not been used by itself for preparation of PV cells [12].
Similarly $\text{Cu}_{2-x}\text{S}$ can be viewed as being constructed from chalcopyrite by using Cu-In antisites $\text{Cu}_{\text{In}}$ and copper interstitials $\text{Cu}_i$. The transition to the sphalerite phase arises from disordered the cation (copper, indium) sub-lattice, and leads back to the zinc blende structure. The existence range of $\alpha$ – phase in pure $\text{Cu}_2\text{S-}\text{In}_2\text{S}_3$ at room temperature extends from a copper content of 24% to 24.5% on a quasi-binary tie line [47]-[48]. Thus the existence range of single phase $\text{CuInS}_2$ is astonishingly small and does not even include the stoichiometric composition of 25% copper. The copper content of absorbers for efficient thin film solar cells typically varies between 22 and 24 at% copper. At the growth temperature of 450 °C – 550 °C this region lies within the single phase $\text{CuInS}_2$. However at room temperature it lies in the two phase $\alpha + \beta$ region of the equilibrium phase diagram [47]-[48]. Hence there is a tendency for phase separation in $\text{CuInS}_2$ after deposition. Fortunately, it turns out that partial replacement of indium
with gallium and use of sodium during the CuInS$_2$ growth considerably widens the single phase CuInS$_2$ region at room temperature [48]. As can be seen from Figure 7, if CuInS$_2$ is grown in copper excess composition the excess copper will form Cu$_{2-x}$S quasi-liquid phase at the grain boundaries and on the surface of CuInS$_2$ thin film. The growth kinetics for copper rich CuIn$_{1-x}$Ga$_x$Se$_2$ thin films was studied by Klenk et al who proposed a model for growth of Cu$_{2-x}$Se phase on near stoichiometric CuIn$_{1-x}$Ga$_x$Se$_2$ thin film [49]. The same argument can be extended to the CuInS$_2$ thin films grown in copper excess composition. The model proposed by Klenk et al is shown in Figure 8 [49]-[51]. The Cu$_{2-x}$S is a quasi-liquid phase and acts as a flux during the growth of CuInS$_2$ thin films. The formation of this copper excess phase slows the growth of CuInS$_2$, thus assisting in adequate incorporation of sulfur into CuInS$_2$ lattice. This reduces the sulfur vacancies that act as compensating donors. Several studies by Scheer et al on copper rich CIGS2 thin films have also shown the formation of Cu$_{2-x}$S phase on the surface and at the grain boundaries [41]-[46]. The model shown in Figure 8 was proposed by Klenk et al shows the formation of Cu$_{2-x}$Se on the surface of near stoichiometry CuInSe$_2$. FSEC PV Materials Lab has usually considered the possibility of the phase also being present at the grain boundaries during the growth prior to segregating on the surface.
2.3.1 Choice of Copper Excess Composition and Addition of Gallium.

Major difference between CuInSe$_2$ and CuInS$_2$ is that the latter cannot be prepared with an overall copper poor composition. Copper poor CuInS$_2$ displays an extremely low conductivity, making it almost unusable as photovoltaic absorber material [52]. Even at small deviations from stoichiometry on the indium rich side, segregation of the spinel phase is observed [52]. Very few groups in the world have achieved good efficiencies on CuInS$_2$ thin film solar cells with copper poor growth technique [53].

Gallium is added to the CuInS$_2$ lattice to increase the bandgap and hence the open circuit voltage, $V_{oc}$. CuInS$_2$ has a bandgap of 1.5 eV. The bandgap can be increased with the incorporation of small amounts of gallium. CuInS$_2$ and CIGS$_2$ form perfect match for the PEC
applications and for space application (air mass zero, AM0) as they provide higher open circuit voltages (> 800 mV).

In the earlier work at FSEC PV Materials Lab as well as during the recent years, [54]-[56] the copper excess composition was varied from 1.4 to 1.8 and gallium content was increased systematically from \( x = 0.3 \) to \( >0.6 \) [55],[57],[58]. The gallium incorporation into the CuInS\(_2\) lattice was carried out by using two alloy targets of CuGa (22 at% Ga) and CuGa (67 at% Ga). The crystallographic phases and variation of lattice parameters with the gallium concentration were studied systematically. CIGS\(_2\) films consisting of following phases were prepared by systematically varying the gallium content and their composition, structure and morphology were studied by electron probe microanalysis at NREL and by X-ray diffraction and scanning electron microscopy at the FSEC PV Materials Laboratory: CuIn\(_{0.5}\)Ga\(_{0.5}\)S\(_2\), CuIn\(_{0.6}\)Ga\(_{0.4}\)S\(_2\), CuIn\(_{0.5}\)Ga\(_{0.5}\)S\(_2\), and CuIn\(_{0.4}\)Ga\(_{0.6}\)S\(_2\). It may be noted that at the time no JCPDS files were available for CIGS\(_2\) thin films with various gallium content. Therefore, the lattice parameters of CuIn\(_{1-x}\)Ga\(_{x}\)S\(_2\) with varied gallium concentration \((x = 0\) to 0.6\) were matched by extrapolation of the lattice parameters of CuInS\(_2\) and CuGaS\(_2\) after verifying that the lattice parameters of CIGS phases with various Ga content followed the solid-solution rule. The crystallographic properties and morphology of thin films were found to deteriorate with the gallium content 0.6 and above the composition CuIn\(_{0.4}\)Ga\(_{0.6}\)S\(_2\) [55],[57],[58].

The results of earlier research were used to define the scope of the present research and especially to choose the copper excess compositions. From earlier work [55],[57],[58], a gallium concentration of \( x = 0.55 \) was chosen so as to incorporate the highest gallium content while still to remain within the composition to achieve satisfactory morphology. It may be noted that the excess copper segregates in the form of Cu\(_{2-x}\)S phase and while the additional gallium is
incorporated in nearly stoichiometric CIGS$_2$ lattice. Therefore to achieve gallium content, $x = 0.55$ using a CuGa (22% target, the copper excess composition of 2.5 was selected $[0.22 \times 2.5 = 0.55]$).

According to Rau et al, in the case of CuIn$_{1-x}$Ga$_x$Se$_2$, the variation of open circuit voltage is superlinear till the gallium content, $x = 0.3$ while above 0.3 it is sublinear [59]. Consequently, the highest efficiency is achieved for the gallium content of, $x = 0.3$. In an analogous manner, for CIGS$_2$ the highest efficiency is expected for Ga content $x$ of 0.3. Therefore, the copper excess composition Cu/(In+Ga) of 1.4 was chosen $[0.22 \times 1.4 = 0.308]$.

2.4 Removal of Copper Excess

As in the case of CuInSe$_2$, a copper rich preparation route implies the removal of unavoidable secondary phase (Cu$_{2-x}$S) by etching in KCN [41]-[46]. Such an etching may involve some damage to the CuInS$_2$ surface as well as introduction of non-stoichiometric surface with many dangling bonds created due to the presence of anion vacancies. However, highest cell efficiencies of $>10\%$ [60] have been achieved with KCN treatment.

2.5 Heterojunction Formation

2.5.1 Buffer Layer Deposition

Surface passivation and junction formation is most easily achieved by the CBD technique of thin CdS film from chemical solution containing CdSO$_4$ (source of Cd), Thiourea (NH$_2$CSNH$_2$, source of sulfur) and ammonium hydroxide. CdS deposited by chemical bath deposition is till date the preferred buffer layer for high-efficiency CIGS solar cells, since best
results were achieved with this n-type material. The n-type conductivity arises from excess Cd, since interstitial Cd and S vacancies are donors [61]. The n-type conductivity is usually obtained with most CdS deposition methods. However, there are a few drawbacks associated with CBD-CdS. The band gap of CdS is with 2.42 eV [62] relatively low, such that significant amounts of light is absorbed before it can reach the CuIn$_{1-x}$Ga$_x$Se$_2$, even for CdS layers as thin as 50 nm. Photons absorbed in CdS do not contribute to the photocurrent, since the small diffusion length of minority carriers (holes) in CdS leads to a high recombination rate. Furthermore, the toxicity of Cd raises environmental concerns, although the amount of Cd used for a typical buffer layer (50 nm) is very small. The third drawback of CdS buffer layers is that CBD is a wet (non vacuum) process. From a manufacturing point of view, a buffer layer that can be deposited without breaking the vacuum is desired, since energy and time are saved.

There are a number of reasons for the success of CBD-CdS over compounds deposited with dry methods, such as evaporated and sputtered CdS. Presumably one of the most important effects of the CBD, in the case of CuIn$_{1-x}$Ga$_x$Se$_2$, is the formation of a buried homo- junction between the p-type absorber bulk and a n-type surface region [63]. Solution bath consists of CdSO$_4$, Thiourea and ammonium hydroxide dissolved in DI water.

Ammonia is added in the form of NH$_4$OH. The tetra-amminecadmium ion, [Cd(NH$_3$)$_4$]$^{2+}$ is formed by the addition of NH$_3$. Adequate amount of NH$_4$OH has to be added so that Cd$^{2+}$ can form [Cd(NH$_3$)$_4$]$^{2+}$. Thick CdS film is obtained by preventing the formation of Cd(OH)$_2$. The buffer solution containing an ammonium salt is widely used to stabilize the CBD process and obtain a thicker film for CdS layers used with CdTe cells [64]-[65]. The buffer solution containing the ammonium salt slows down the reaction and prevents the formation of Cd(OH)$_2$ [64],[66].
The typical reaction is as follows

\[ [Cd(NH_3)_4]^{2+} + NH_2CSNH_2 + 2OH^- \rightarrow CdS + 4NH_3 + CH_2N_2 + 2H_2O \quad \ldots \ldots \ldots \ldots 2.2 \]

The following reaction scheme is commonly accepted [67]: S\(^{2-}\) ions are released into the solution by the hydrolysis of thiourea in basic solutions (reaction 2.3) and Cd\(^{2+}\) ions by the decomposition reaction 2.4. When the ionic product exceeds the solubility product of CdS, precipitation occurs either in the solution, leading to the formation of colloids, or on the substrate (reaction 2.5), inducing film growth.

\[ NH_2CSNH_2 + 2OH^- \rightarrow S^{2-} + CH_2N_2 + 2H_2O \quad \ldots \ldots \ldots \ldots 2.3 \]

\[ [Cd(NH_3)_4]^{2+} \rightarrow Cd^{2+} + 4NH_3 \quad \ldots \ldots \ldots \ldots 2.4 \]

\[ Cd^{2+} + S^{2-} \rightarrow CdS \quad \ldots \ldots \ldots \ldots 2.5 \]

### 2.5.2 Window Layer Deposition

The most commonly used material for the preparation of front transparent conducting window layer is zinc oxide doped with aluminum or boron. In a few cases doping with gallium or indium is claimed to be advantageous. The first large area modules produced by Arco Solar (later Shell Solar) had a ZnO:B window layer deposited by chemical vapor deposition. Later production facilities at Boeing and EUROCIS used sputtering processes. Present pilot production lines also favor sputtering [68].
2.6 Electrical Properties

The most important parameter of a solar cell is its efficiency, $\eta$. It is defined as the ratio of maximum (electrical) power density delivered by the cell to the power density irradiated by the light source. The characteristic cell parameters that are usually used in addition to describe the performance of the cell are the open-circuit voltage ($V_{oc}$), the short-circuit current density ($J_{sc}$), and the fill factor (FF). These parameters are shown in Figure 9. The current density–voltage ($J-V$) characteristics of illuminated solar cells can be described by the phenomenological diode equation [68]

$$J(V) = J_0 (e^{\frac{q(V - R_s J)}{AKT}} - 1) + \frac{V - R_s J}{R_p} - J_{ph} \quad \cdots \cdots \quad 2.6$$

Figure 9: Schematic illustration of the current density–voltage characteristics of a solar cell in the dark and under illumination. Indicated are the short-circuit current density $J_{sc}$, the open-circuit voltage $V_{oc}$, the photo-generated current density $J_{ph}$, and the maximum power point ($J_m, V_m$).
Where $J$ is the current density, $V$ is the applied bias voltage, $J_0$ is the saturation current density, $q$ is the electron charge, $R_s$ and $R_p$ are the series and shunt resistances, respectively, $A$ is the diode ideality factor, $k$ is the Boltzmann constant $T$ is the absolute temperature, and $J_{ph}$ is the photo-generated current. The diode equation 2.6 holds for bias-independent photocurrents, which is an idealization when for example minority carrier diffusion lengths are very short. In the absence of series resistance and shunt resistance, also termed parallel resistance (i.e., $R_s = 0$ and $R_p = \infty$), the diode equation simplifies to

$$J(V) = J_0 \left( e^{\frac{qV}{kT}} - 1 \right) - J_{ph} \quad \text...............2.7$$

Thus, the following expressions for the short circuit current density, $J_{sc}$ ($V = 0$) and the open-circuit voltage, $V_{oc}$ ($J = 0$) are obtained:

$$J_{sc} = -J_{ph} \quad \text...............2.8$$

$$V_{oc} = \frac{AKT}{q} \ln\left( \frac{J_{ph}}{J_0} + 1 \right) \approx \frac{AKT}{q} \ln\left( \frac{J_{ph}}{J_0} \right) \quad \text...............2.9$$

The cell efficiency is computed from the maximum power density delivered by the cell ($J_m V_m$) relative to the irradiated power density $P_s$

$$\eta = \frac{J_m V_m}{P_s} = \frac{J_{sc} V_{oc} FF}{P_s} \quad \text...............2.10$$
Where, the fill factor, FF is defined as

\[ FF = \frac{J_m V_m}{J_{sc} V_{oc}} \] \cdot 2.11

The fill factor, FF, describes how closely the area defined by the J–V curve resembles (“fills”) a rectangle. Obvious reasons for poor fill factors, FFs, can be large \( R_s \), not-large enough \( R_p \), and voltage-dependent carrier collection. Only for non-zero \( R_s \) there is a (small) influence of the diode ideality factor, \( A \) on fill factor, FF [68]. Diode ideality factor, \( A \), depends on device properties such as the dominant current transport mechanism, and is mainly a scaling factor for the voltage. An increase of the diode quality factor alone would apparently lead to a higher \( V_{oc} \). However, the saturation current density \( J_0 \) increases almost exponentially with \( A \), therefore, in real devices an increase in the diode ideality factor results in a decrease of efficiency, \( \eta \) [61]. The diode ideality factor, \( A \) and reverse saturation current density, \( J_0 \) for the world record CIGS cell were 1.3 – 1.35 and \( \sim 3 \times 10^{-8} \) mA/cm² respectively [19].

For good performance, light-generated current density \( J_{ph} \), and open circuit voltage \( V_{oc} \), should be as large as possible. Maximum value of light-generated current density \( J_{ph} \), can be obtained if all photo generated electron-hole pairs are collected as photocurrent, and light-generated current density \( J_{ph} \), can achieve 80-90% of this limit if light absorption and minority carrier collection are both highly efficient. Similarly, limiting value for open circuit voltage \( V_{oc} \), is the built-in voltage \( V_{bi} \), corresponding to complete flattening of the bands across the junction. For high open circuit voltage \( V_{oc} \), built-in voltage \( V_{bi} \), should be as high as possible (Figure 13).
This can be achieved by tailoring the bandgap of the material. For CuInS\(_2\), gallium addition is carried out to increase the bandgap in the range 1.5 – 2.4 eV (CuInS\(_2\) – CuGaS\(_2\)) [68].

Inspection of equation 2.5 shows that open circuit voltage \(V_{oc}\), increases as the saturation current density \(J_o\), decreases. In thin films, with well-passivated surfaces, saturation current density \(J_o\), can be driven down to very low values determined by the intrinsic properties such as thermally induced carrier generation rate and intrinsic carrier loss mechanisms such as Auger electron emission, and the open circuit voltage moves towards the upper limit of built-in voltage \(V_{bi}\) [68], [69]. If equivalent circuit of a solar cell is considered, the effects of series resistance \(R_s\), and shunt resistance \(R_p\), on the short circuit current density \(J_{sc}\), and open circuit voltage \(V_{oc}\), respectively can be understood. Figure 10 shows the equivalent circuit of solar cell which works as a diode and a current generator. Increase in the series resistance \(R_s\), decreases the short circuit current density \(J_{sc}\), and decrease in shunt resistance \(R_p\) decreases the open circuit voltage \(V_{oc}\). Figure 11 and Figure 12 show the variation of short circuit current density \(J_{sc}\), with series resistance \(R_s\) and open circuit voltage \(V_{oc}\), with shunt resistance \(R_p\) respectively.
Figure 10: Equivalent electrical circuit of a solar cell.

$$V = I_{RLoad} + I R_s$$

Figure 11: Variation of short circuit current density $J_{sc}$, with series resistance $R_s$. 

$$R_s = \begin{array}{c} 
0 \Omega \\
0 \Omega \\
1 \Omega \\
1 \Omega \\
5 \Omega \\
5 \Omega \\
25 \Omega \\
25 \Omega \\
\end{array}$$
2.7 Challenges of Gallium Incorporation

Another semiconductor with a similar structure to CuInS$_2$ is CuGaS$_2$, which has a band gap of 2.4 eV. Gallium is in the same group III of the periodic table as indium. Thus, by substituting gallium for indium in some places in the lattice, the band gap of CuIn$_{1-x}$Ga$_x$S$_2$ (CIGS2) can range from 1.5 eV < $E_g$ < 2.4 eV [26]. Thus, addition of gallium can be considered as alloying between the ternary compounds CuInS$_2$ and CuGaS$_2$. Gallium Addition has its own advantages and disadvantages. Advantages of adding gallium in the lattice of CuInS$_2$ are:

1. Increases the bandgap of CuInS$_2$ – A major challenge for the scientific community of copper chalcopyrite (CuIn$_{1-x}$Ga$_x$Se$_2$ or CIGS2) thin film solar cells is to increase the open circuit voltage. One of the solutions to increase open circuit voltage is by the incorporation of
gallium in CuInSe$_2$ or CuInS$_2$. Increase in the bandgap increases the built in voltage ($V_{bi}$) and thereby the open circuit voltage.

2. However, during the sulfurization, most of the gallium moves toward the back contact. It helps in good adhesion with the molybdenum back contact. This advantage can be obtained for sulfurization technique and not for co-evaporation, as in co-evaporation, gallium is added in required proportion continuously or at some stages of CIGS$_2$.

3. Since most of the gallium goes towards the back contact, where the CuGaS$_2$ phase or CIGS$_2$ with a Ga content and consequently with a higher bandgap approaching 2.4 eV may form. Therefore, it creates back surface field (BSF) or an “electron mirror” which repels the electrons towards the heterojunction (Figure 13) thus improving the minority carrier collection efficiency of the CIGS$_2$/CdS heterojunction.

![Band diagram of CIGS$_2$/CdS thin film with the back surface field created by the movement of gallium going towards back contact.](image)

Figure 13: Band diagram of CIGS$_2$/CdS thin film with the back surface field created by the movement of gallium going towards back contact.
The challenges of gallium addition evolve from the disadvantages that arise from its addition. Following are the disadvantages of adding gallium into the structure of CuInS$_2$.

1. CuGaS$_2$ and even CIGS$_2$ with a very high (>0.6) Ga content formed at the back towards molybdenum back contact have poor morphology.

2. The grain sizes obtained from CuGaS$_2$ are very small leading many grain boundaries which act as recombination centers.

These disadvantages are strictly confined to sulfurization process. PV industries usually prefer sputtering over co-evaporation technique for large-scale economic manufacturing (except Würth Solar which uses co-evaporation). Industries such as Shell Solar and Showa Shell that manufactures CIGS, CuIn$_{1-x}$Ga$_x$Se$_{2-y}$S$_y$ (CIGSS) use the selenization/sulfurization or only selenization process.

Similarly, SULFURCELL (5 MW$_p$ plant in Germany) works with the ternary compound of CuInS$_2$. Alloying with gallium is necessary to achieve higher open circuit voltages and eventually higher efficiencies. The contribution from this research work could open up an interesting technology to achieve higher efficiencies along with higher open circuit voltages to CuInS$_2$ manufacturing industries such as SULFURCELL.
CHAPTER THREE: PHOTOLECTROCHEMICAL WATER SPLITTING

In the photoelectrochemical process, the light absorbed in a semiconductor is used to decompose water molecules in molecular hydrogen and oxygen (equation 3.1). Light absorbed by the semiconductor generates electron-hole pairs that in turn help the Oxidation-Reduction reactions, at the photoanode and the photocathode, to produce oxygen and hydrogen respectively [74]. The net photochemical reaction can be summarized as

\[ H_2O + \text{Light} \rightarrow \frac{1}{2}O_2 + H_2 \]  \hspace{1cm} 3.1

The recent awakening, towards pollution free environment, amidst increasing population and escalating energy demand, has rekindled interest in developing alternative, nonpolluting and renewable energy sources. In this respect, hydrogen has established its potential as carrier of energy and can work as effective and possibly the best substitute for oil and coal (the two most commercial forms of energy, namely, fuel and electricity, being used at present). It can be used directly as a fuel, for instance, transportation when used as fuel in internal combustion engine or for electricity when used in fuel cell, without producing pollutants or green house gases upon combustion. The novel feature with hydrogen is that it can be produced from water by providing energy and burns back to water while producing energy. However, in order to make the hydrogen as a commercial carrier of energy, for example, as a new fuel, it must be produced and made available at low cost without creating any imbalance in global ecology. Out of various possible routes, production of hydrogen using solar energy seems to be the most attractive proposal. Photoelectrochemical (PEC) solar cells for the production of hydrogen have been widely studied and have been the subject matter of several reviews during last two decades. This
demands certain conditions on electrode and electrolytes chosen for the purpose. Even though some progress has been made, enormous difficulties are encountered and further studies are essential for enhancing the understanding the fundamental science that can form the basis for optimizing the oxidative and reductive half-cell reactions in these systems.

PEC solar-to-hydrogen conversion stands at a point where in the efficient PEC cells are highly expensive and cheaper cells are not as efficient [75]-[79]. Research is being carried out in increasing the PEC solar-to-hydrogen efficiencies using a-Si:H by careful design considerations in developing integrated multijunction photoelectrode, comprising low-cost semiconductor, catalytic, and protective thin films deposited, on low-cost substrates [75],[76]. In an attempt to meet the cost and performance goals, efforts are also being concentrated on development of a “Hybrid Photoelectrode” (HPE), which incorporates low-cost metal-oxide (such as Fe2O3 and WO3) and photovoltaic-grade semiconductor thin films (such as CIGS and a:Si) [75]-[79]. Along with the a:Si hybrid photoelectrode, III-V semiconductors for efficient PEC water splitting are also being studied. For the GaAs/GaInP2 system, the solar-to-hydrogen conversion efficiency of over 16% has already been achieved [79]. GaAs-based cells utilize an expensive, fragile, bulk single-crystalline substrate and they are suitable for concentrator type application where high efficiency is of paramount importance. The research presented in this thesis is based on development of CIGS2 polycrystalline-thin film solar cells for use in PEC water splitting. CIGS2 thin film solar cells have following advantages over III-V based and a-Si:H solar cells.

1) Cost considerably less because they utilize cheaper and more robust soda-lime glass substrate and 100-200 times thinner semiconductor as compared to the (GaIn)P/GaAs and GaAs/AlGaAs III-V cells.
2) Large area depositions and integral interconnects can be achieved more easily in the thin-film cells.

3) The polycrystalline-thin film cells do not suffer from intrinsic degradation mechanisms such as the Staebler-Wronski effect in a-Si:H cells whilst attainable efficiencies are 50-80% higher than that for a-Si:H triple junction cells.

Licht et al. studied the concept of multiple bandgap tandem for the PEC water splitting [80]. Solar-To-Hydrogen generation using illuminated AlGaAs/Si, RuO$_2$/Pt$_{black}$ PEC setup a record efficiency of 18.3% was achieved [81]. The conditions under which an oxygen photocatalyst can improve multiple band gap (semiconductor) solar energy water splitting were probed. A new photoanode RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ were introduced which had better anode characteristics than RuO$_2$ [82]. Bandgap of RuS$_2$ is 1.3 eV and addition of 1% of iron into RuS$_2$ (Ru$_{0.99}$Fe$_{0.01}$S$_2$), reduced the bandgap to 1.1 eV [82].

FSEC PV Materials Lab has been carrying out research on PEC water splitting since last six years. Earlier several experiments were carried out using CIGS$_2$/CdS thin film solar cells as cathode and platinum anode to achieve the PEC water splitting [57]. Platinum is not a very good oxygen electro catalyst. Therefore, RuO$_2$ was used as an anode instead of platinum in conjunction with CIGS$_2$/CdS thin film solar cells as a cathode and a PEC efficiency of 1.99% was achieved for generation of hydrogen and oxygen by splitting water [58]. Later a new PEC setup was developed to accommodate two thin-film solar cells in series, platinum cathode for hydrogen generation and RuO$_2$ or RuS$_2$ or Ru$_{0.99}$Fe$_{0.01}$S$_2$ photoanode for oxygen generation. Using two illuminated CIGS$_2$/CdS thin film solar cells, RuO$_2$ anode for oxygen generation and platinum cathode for hydrogen generation, PEC efficiency of 4.29% was
achieved [83]. The above research at the FSEC PV Materials Lab together with the published literature formed the basis for the present research.
CHAPTER FOUR: EXPERIMENTAL TECHNIQUE

The main objective in this research was to prepare efficient CIGS2/CdS thin film solar cells for photoelectrochemical water splitting application and to characterize them. A two step process was employed to develop CIGS2 thin films. Step one consisted of the deposition of stacked elemental layers of copper, gallium, and indium metallic precursors on molybdenum coated glass substrates using DC magnetron sputtering. Melting point of gallium is 29 °C. Therefore, an alloy target of CuGa (22 at% gallium) was used to deposit the CuGa precursor layers. The step two consisted of sulfurization of the as deposited precursors at elevated temperatures in the presence of H$_2$S gas diluted in nitrogen (8% H$_2$S). Material properties of CIGS2 thin films were studied for optimizing process parameters. Surface morphology of the CIGS2 thin film was studied using scanning electron microscopy (SEM). X-ray diffraction (XRD) was used to identify the crystalline phases and to measure lattice parameters. Chemical composition was analyzed by employing electron probe microanalysis (EPMA) and variation of elemental composition with depth was studied using Auger electron spectroscopy (AES) in conjunction with ion etching. Few samples were analyzed using photocurrent spectroscopy for bandgap measurements.

CIGS2/CdS thin film solar cells were completed by the deposition of n-type CdS layer by chemical bath deposition (CBD) followed by transparent conducting bilayer window of intrinsic ZnO (i-ZnO) and doped ZnO:Al by RF magnetron sputtering and Ni/Al or Cr/Ag front contact fingers through metal masks by e-beam or thermal evaporation technique. The device parameters of the CIGS2/CdS thin film solar cells were analyzed by current-voltage (I-V) measurements. Flowchart showing major steps in the formation of CIGS2/CdS thin film solar
cells is shown in Figure 14. Figure 15 shows the layered structure of CIGS2/CdS thin film solar cell on molybdenum coated glass substrate prepared using the steps shown in Figure 14.
10 cm x 15 cm molybdenum coated glass substrate cleaned thoroughly and mounted into deposition chamber, kept for overnight in vacuum

DC magnetron sputtering of stacked metallic precursor layer of 70% CuGa (22%), 100% In and 30% CuGa (22%) metallic precursors

Sulfurization of metallic precursors in N₂:H₂S (8% H₂S) ambient in selenization/sulfurization furnace

Etching of Cu₂-xS phase segregated on the surface after sulfurization

Materials Characterization of CIGS₂ thin film by SEM, XRD, EPMA, AES etc.

CdS deposition using chemical bath deposition technique

Bilayer window deposition of i-ZnO/ZnO:Al using RF magnetron sputtering

Ni/Al or Cr/Ag front contact finger deposition using e-beam or thermal evaporation technique

Device characterization – I-V and QE measurements

Figure 14: Flowchart showing important steps in the formation of CIGS₂/CdS thin film solar cells.
4.1 Substrate Preparation

10 cm x 15 cm size molybdenum coated glass substrates were washed with tap water. Cotton swabs were used to clean the surface with soap solution. Then the surface was thoroughly rinsed with tap water and finally washed with deionized (DI) water. The substrate was finally blow-dried using compressed jet of nitrogen gas. Then the substrate was mounted into the DC magnetron sputtering chamber (Figure 16) and maintained overnight in high vacuum of ~3 x 10^{-6} Torr before the deposition of metallic precursors.
4.2 Development of CIGS2 Thin Films

For the last 15 years FSEC PV Materials Lab has been carrying out research and development of CIGS2/CdS and CIGS/CdS thin film solar cells. Earlier, the substrate size was limited to 2.5 cm x 2.5 cm and CIGS2/CdS thin film solar cells were prepared on glass and stainless steel substrates. Several master’s thesis were completed on the development and analysis of CIGS2/CdS and/or CIGS/CdS thin film solar cells [54]-[58] and the results have been published in several scientific journals [14],[16],[18],[39],[64],[83]. This research has enhanced the understanding of the relationship between the preparation, material properties and device characteristics. This knowledge base at the FSEC PV Materials Lab was used fruitfully to set the record efficiency of 10.4% for AM 1.5 and 8.84% for AM 0 for CIGS2/CdS thin film solar cells grown on stainless steel substrate [84].

Over the last six years, excellent facilities have been developed at FSEC PV Materials Lab for the development of CIGS2 thin films on large, 10 cm x 15 cm substrates from 2.5 cm x 2.5 cm [84]-[86]. The enhanced facilities designed and developed at FSEC PV Materials, the Lab knowledge gained through scaling up, and improved processing techniques would be very useful for scale up for economic large-scale production. Two large area magnetron sputtering systems were designed and installed for DC magnetron sputtering of molybdenum back contact, CuGa and indium metallic precursors and RF magnetron sputtering of intrinsic ZnO (i-ZnO) and doped ZnO:Al layers respectively (Figure 16) [58], [87]-[89].

Initially three sputtering sources each accommodating 10 cm x 30 cm targets were procured. Series of experiments were carried out to improve thickness uniformity over a large area of 10 cm x 15 cm by empirically modifying the magnetron configuration. Those sputtering
sources were found to produce non uniform plasma (Figure 17a) distribution within the racetrack because of the loss of electrons leading to a glow having varying plasma intensity. This was attributed to the varying magnetic field along the 10 cm x 30 cm target area. The magnetic field was measured parallel to the target surface along the race track at several locations using a gauss meter. The map of the magnetic field was supplied to the manufacturer. At this stage they agreed to modify the layout design of the magnetron configuration in their newer sputtering sources.

Figure 16: Large area magnetron sputtering systems for the DC magnetron sputtering of molybdenum back contact, CuGa and indium metallic precursors and RF magnetron sputtering of i-ZnO/ZnO:Al.

Two new sputtering sources with the modified magnetron configuration were procured from the same company. After verifying that the new magnetron sputtering sources did not suffer
from the problems encountered earlier, the magnetic arrays in the three older magnetron sputtering sources were modified at the FSEC PV Materials Lab to obtain the uniform plasma (Figure 17b). For this purpose, the copper body holding the magnetic assembly was machined to accommodate the modified assembly [86]. Afterwards necessary modifications were carried out in the arrangement of magnets. This led to considerable improvement in the uniformity of the magnetic field distribution and the plasma and consequently the uniformity of the thin films, With the modifications in the magnetic array the following thickness uniformities were achieved over central lengths: molybdenum, CuGa and In: ±2.24% over 10cm, ±2.40% over 12.7cm, ±2.95% over 15.2cm and zinc oxide: ±2.46% over 10cm, ±3.84% over 12.7cm, and ±5.60% over 15.2 cm. These results paved the way for preparation of large area (15cm x 10cm) thin film solar cells [86].

Figure 17: (a) Non uniform plasma and (b) uniform plasma [86].
Along with the design and development of large area magnetron sputtering systems, a selenization/sulfurization furnace unit donated by Shell Solar Industries which can accommodate 100 samples of 10 cm x 10 cm substrates was repaired, upgraded and installed. The volume of the quartz furnace tube was 15.3 liter. The furnace works on the principle of batch process. The schematic layout of the selenization/sulfurization furnace is as shown in Figure 18. After all the connections were made the furnace was tested for leak using cryopump and residual gas analyzer (RGA). The pneumatic control, temperature control (proportional integral and derivative, PID controllers) and the pressure controls were tested systematically for their satisfactory operation. The PID controllers were tuned carefully to achieve the required ramp and set point stability. Moreover, a wet scrubber for \( \text{H}_2\text{Se} \) and \( \text{H}_2\text{S} \) gas consisting of two packed bed columns was designed from first principles developed and installed [90].
Figure 18: Selenization/sulfurization flow diagram.
4.2.1 Series 1 – CIGS2 thin film solar cells with Cu/(In+Ga) = 2.5

In series 1, the copper excess composition was fixed to 2.5. Since alloy target of Cu-Ga was used to incorporate gallium, high value of copper excess composition was selected to increase the gallium content. This is because only the excess copper is etched away while the additional gallium gets incorporated in the film to replace a fraction of indium. Advantages of addition of gallium have been discussed in Introduction. The copper excess composition of 2.5 was chosen to add more gallium to increase the bandgap of CIGS2 thin film solar cell and consequently to increase the open circuit voltage, $V_{oc}$. Precursor layer of CuGa and In were deposited on cleaned 10 cm x 15 cm molybdenum coated glass substrates using 10 cm x 30 cm size CuGa and In targets. Series of experiments were carried out to optimize the deposition parameters (argon pressure, DC power and time of deposition) to achieve the requisite thickness and copper-excess composition. Pressure and power during magnetron sputtering were varied systematically to achieve the desired deposition rates for CuGa and In targets. Linear substrate motion mechanism was designed and developed. This was coupled to a stepper motor to achieve slow linear motion and LabView program was developed to control the substrate movement [91].

Based on the earlier research, indium was sandwiched between two layers of Cu-Ga so as to minimize loss of indium by sublimation during sulfurization [54]. The stacked layering sequence with deposition of 70% of Cu-Ga (22 at% gallium), followed by 100% of the requisite thickness of indium, and deposition of 30% of Cu-Ga (22 at% gallium) is shown in Figure 19. The stacked precursors were sulfurized in dilute H$_2$S (8% H$_2$S) ambient. Series of experiments were carried out to optimize the maximum temperature of sulfurization, the ramp rate and the dwell time at maximum temperature for the selenization/sulfurization furnace. The maximum
temperature of sulfurization was varied from 450 - 500 °C, ramp rate was varied from 6 – 20 °C/minute and dwell time at maximum temperature was varied from 10 – 60 minutes. Maximum ramp that could be achieved in the selenization/sulfurization furnace is 20 °C/minute.

The ramp rate chosen for the sulfurization process was 6 °C/minute. The excess copper form the quasi-liquid Cu$_{2-x}$S phase. It assists in slowing down the kinetics of formation of CIGS2 phase and thus enhances an incorporation of sulfur into the CIGS2 structure consequently eliminating the sulfur vacancies that act as donor impurity. Moreover it promotes the coalescence of grains and thus helps in the formation of highly crystalline CIGS2. Finally the Cu$_{2-x}$S phase segregated on top of a stoichiometric CIGS2 layer was removed by etching in 10% KCN for 3 minutes. The Sheet resistance of CIGS2 films was used as an indicator to find whether the films were Cu-rich or Cu-poor. Earlier research has shown that the sheet resistance values below 100 Ω/ indicate Cu-rich CIGS2 films. On the other hand, high values above 10 kΩ/ indicate Cu-poor CIGS2 films. Two end 10 cm x 2.5 cm pieces were cut from 10 cm x 15 cm CIGS2 thin films and were used for materials characterization while the central 10 cm x 10 cm piece was used for completion of the cells. Out of the two end pieces, a few pieces were analyzed without etching and the remaining were etched prior to the study of their material properties.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>30% of Cu-Ga (22%)</td>
<td></td>
</tr>
<tr>
<td>100% of In (100%)</td>
<td></td>
</tr>
<tr>
<td>70% of Cu-Ga (22%)</td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td></td>
</tr>
</tbody>
</table>

Figure 19: Stacked layering sequence for CuGa-In metallic precursor deposition.
4.2.2 CIGS2 thin films on ITO/MoS2 back contact – Cu/(In+Ga) = 2.5

Several experiments were carried out on the development of CIGS2/CdS thin film solar cells on indium tin oxide (ITO)/MoS2 bilayer transparent conducting back contact. These are the first ever experiments being carried out on CIGS2/CdS thin film solar cells on ITO/MoS2 back contact.

ITO layer of 450 nm thick was deposited on 10 cm x 15 cm glass substrate using RF magnetron sputtering. Initially the argon pressure, RF power and time of deposition were optimized for the deposition of 450 nm ITO film with optimum conductivity and transparency. Finer tuning of transparency was carried by the addition of small amount of oxygen during the sputter deposition of ITO layer. After the deposition of ITO layer on glass substrate, the substrate was moved to the DC magnetron sputtering unit for the deposition of thin layer of molybdenum (10 nm) and CuGa-In metallic precursors. Precursor layer deposition was carried out to achieve a copper excess composition of 2.5. The stacked precursors were sulfurized in dilute H2S (8% H2S) ambient. During sulfurization of stacked precursor layers, thin layer of molybdenum gets converted to MoS2. The bilayer of ITO/MoS2 was found to give highly conducting and ohmic contact to the CIGS2 thin films. Figure 20 gives the layered structure of CIGS2/CdS thin film solar cell on transparent and conducting back contact. Two end 10 cm x 2.5 cm pieces were cut from 10 cm x 15 cm CIGS2 thin films and used for materials characterization and central 10 cm x 10 cm piece was used for further completion of the cell. Out of two end pieces few pieces were kept without etching and few were etched. Both the unetched and etched samples were used for the material characterization.
4.2.3 Series 2 CIGS2 thin films – Cu/(In+Ga) = 1.4

In series 2, the copper excess composition was reduced to 1.4. Precursor layers of CuGa and In were deposited as explained in section 2.2.1 on 10 cm x 15 cm molybdenum coated glass substrates. Series of experiments were carried out to optimize the deposition parameters to achieve the required thickness and copper excess composition. The stacked precursors were sulfurized in dilute H₂S (8% H₂S) ambient. Advantages of higher ramp rates have been explained in Introduction. However, the maximum ramp rate that could be achieved using
selenization/sulfurization furnace was 20 °C/minute. Further sulfurizations were carried out using small Lindberg™ furnace where the ramp rate of 50 °C/minute could be achieved.

The ramp rate chosen for the sulfurization process was 50 °C/minute. The 10 cm x 15 cm CuGa-In precursor deposited on molybdenum coated glass substrates were cut into six pieces of 10 cm x 2.5 cm and each piece was sulfurized with 8% dilute H₂S ambient for optimum time at optimized temperature. Maximum temperature of sulfurization and the dwell time were optimized for the small furnace. The excess copper segregated in the form of Cu₂₋ₓS phase was removed by etching the samples in 10% KCN.
4.2.4 Series 3 CIGS2 thin films – Cu/(In+Ga) = 1.4 with metallic precursors annealed

In series 3, the copper excess composition was kept at 1.4; however the CuGa-In metallic precursors were annealed prior to the sulfurization. Precursor layers of CuGa and In metallic precursors were deposited on molybdenum coated glass substrate as explained in section 2.2.3. The stacked precursor layers were annealed in nitrogen ambient at 120 °C (<156.6 °C, melting point of indium) for 30 minutes before sulfurization. The 10 cm x 15 cm CuGa-In deposited molybdenum coated glass substrates were cut into six pieces of 10 cm x 2.5 cm and each piece was sulfurized in 8% dilute H$_2$S ambient for optimum time at optimized temperature. The ramp rate chosen for the sulfurization process was 25 °C/minute from 25 - 120 °C so as to avoid very fast shooting up of the temperature to over 120 °C and 50 °C/minute from 120 °C – optimum temperature. The excess copper segregated in the form of Cu$_{2-x}$S phase was removed by etching in 10% KCN.

4.3 Materials Characterization

Material properties of series 1, 2 and 3 CIGS2 thin films on molybdenum back contacts and on ITO/MoS$_2$ back contact were studied for optimizing process parameters. Surface morphology of the CIGS2 thin film was studied using SEM. The surface morphology analysis of CIGS2 thin films was carried out at Advanced Materials Processing and Analysis Center’s (AMPAC’s) Materials Characterization Facility (MCF) using JEOL 6400F field emission scanning electron microscope. X-ray diffraction (XRD) was used to identify the crystallographic phases and to measure lattice parameters. XRD was carried out at MCF using Rigaku DMAX B X-ray diffractometer, Philips X'Pert MRD diffractometer at Major Analytical Instrumentation
Center (MAIC), University of Florida and few samples were sent to NREL for XRD analysis. Atomic concentrations were analyzed by employing electron probe microanalysis (EPMA) at NREL and variation of elemental compositions with depth was studied using Auger electron spectroscopy (AES) in conjunction with ion etching at MAIC using Perkin-Elmer PHI 660 scanning Auger multiprobe. Few CIGS2 thin films were characterized by photocurrent spectroscopy for the bandgap measurements. The bandgap measurements were carried out at NREL.

4.4 CdS Deposition

Buffer layer of CdS was deposited using chemical bath deposition (CBD) technique. Advantages of using CBD have been described in Introduction. Earlier a new chemical bath deposition setup was designed and developed for 10 cm x 10 cm glass and stainless steel substrates [90]. The chemical bath consisted of 0.015M CdSO$_4$, 1.5M (NH$_2$)$_2$CS, and ammonium hydroxide (NH$_4$OH). The chemical bath was placed inside a beaker consisting of hot water. Figure 21 shows a photograph of CBD experimental setup. The temperature of water in the outside bath must be controlled properly to achieve the maximum temperature of CdS deposition in the chemical bath. The CIGS2 thin films with Cu$_{2-x}$S layer were etched and immersed in the chemical bath. The chemical bath was then placed inside a beaker consisting of hot water (outside beaker). Because of the temperature difference in the chemical bath and outside beaker, temperature in the chemical bath starts increasing and reaches the maximum required temperature. The ramp rate to achieve maximum temperature depends on the volume of solution in the chemical bath.
Series 1 CIGS2 thin films were prepared in the large selenization/sulfurization furnace. The setup designed for 10 cm x 10 cm was used for the CdS deposition. The temperature and time of deposition were optimized to achieve conformal growth of ~ 50 nm thick CdS layer on CIGS2 thin film. CdS deposition was carried out at 60 °C for 90 seconds which confirmed the growth of ~ 50 nm CdS layer on etched CIGS2 thin film. However since the volume of solution was very high, the achieved ramp rate was slow. The process took ~ 11 minutes to reach 60 °C from room temperature.

For series 2 and 3 CIGS2 thin films, since the size of CIGS2 thin films was reduced to 10 cm x 2.5 cm the CdS bath was accordingly modified. The volume of the chemical bath was systematically reduced so as to be able to achieve higher ramp rates. The process took ~ 5 minutes to reach 60 °C from room temperature and the dwell time at 60 °C was varied systematically to achieve ~ 50 nm CdS layer deposition on CIGS2 thin films.
4.5 Deposition of i-ZnO/ZnO:Al bilayer windows

Bilayer of i-ZnO/ZnO:Al was deposited using RF magnetron sputtering. The CIGS2/CdS cells were mounted into the RF magnetron sputtering chamber and kept overnight in vacuum (~3 x 10^{-6} Torr). Linear substrate motion mechanism was used to move the substrates at the requisite speed to achieve desired thickness. Earlier series of experiments carried out to optimize the process parameters for deposition of highly transparent and conducting i-ZnO/ZnO:Al bilayer served as a base for this research [92]. A thin layer of ~ 50 nm i-ZnO layer was deposited at RF power of 200 W and argon pressure of 1.5 mTorr and ~ 500 nm thick ZnO:Al was deposited at RF power of 300 W and argon pressure of 1.5 mTorr. The RF power for the ZnO:Al was varied between 300 – 425 W to achieve the required conductivity corresponding to the sheet resistance of the ZnO:Al films of 40 – 60 Ω/□.

4.6 Current – Voltage measurements

FSEC PV Materials Lab has developed a highly reliable, very accurate and robust current – voltage (I-V) measurement setup. The setup consists of a wooden box where the solar cells were illuminated with AM 1.5 illumination (100 mW/cm²). High-accuracy power supply and multi-meters were procured from Kepco and Agilent technologies respectively to forward and reverse bias the solar cell and to measure current readings. A LabView program was developed to measure and plot the I-V characteristics [91].

I-V measurements were carried out both in the dark and with light. Dark I-V analysis was carried out to obtain values of the fundamental parameters of the solar cell as a p-n junction or the diode. These are the reverse saturation current density \( J_0 \) and diode factor, etc. Analysis of
light I-V characteristics of CIGS2/CdS thin film solar cells was carried out to obtain the relevant photovoltaic parameters using the open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$), series resistance ($R_s$), shunt resistance ($R_p$) and fill factor.

The final and official I-V measurements of CIGS2/CdS thin film solar cells were carried out at NREL for authentication. The cells that gave >10% efficiency in the lab were sent to NREL for I-V measurements. Antireflection coating of MgF$_2$ was deposited at NREL prior to the I-V measurements.

4.7 Development of RuS$_2$ and Ru$_{1-x}$Fe$_x$S$_2$ photoanodes

RuS$_2$ and Ru$_{1-x}$Fe$_x$S$_2$ photoanodes were prepared for the efficient oxygen generation. For this purpose, a titanium (120 µm) foil was mechanically etched (sand blasted), then chemically etched with 20% HCl for 2min, and washed in water. 0.1M RuCl$_3$ (Ruthenium chloride) solution was prepared in 20% aqueous HCl and evaporated. Paste of 0.1M RuCl$_3$ was prepared by dissolving in a minimum volume of 2-propanol. Titanium foil was then coated with RuCl$_3$ - 2-propanol paste using a brush and was sintered in diluted H$_2$S ambient for 15 minutes at 350 °C. This procedure of applying paste and annealing was repeated five times and final annealing was carried out for 60 minute at 350 °C. ~ 2 – 2.5 µm thick RuS$_2$ layer was obtained on the titanium foil with this process.

Ru$_{1-x}$Fe$_x$S$_2$ photoanodes were prepared in the same way as that of RuS$_2$, except that 1 % of FeCl$_3$ was added to RuCl$_3$ and paste was prepared in minimum volume of 2- propanol. The electrodes were characterized with SEM for morphology, XRD for crystallographic structure and secondary ion mass spectroscopy (SIMS) for depth profile. SIMS analysis was carried out AMPAC’s MCF.
4.8 Development of a PEC setup

Earlier a PEC setup consisting of CIGS2/CdS thin film solar cell as cathode, RuO$_2$ as anode was designed and developed [58]. In this setup and as well as in other PEC setups developed elsewhere [76],[80]; the solar cells are in contact with the electrolyte leading to the corrosion and instability problems.

A new PEC setup was designed and developed to accommodate two CIGS2/CdS thin film solar cells, a RuS$_2$ or Ru$_{1-x}$Fe$_x$S$_2$ photoanode for oxygen generation and platinum for hydrogen generation (Figure 22). In the new setup the solar cells are not in contact with the electrolyte. Therefore, the problem of corrosion is minimized.
Figure 22: Two cell PEC setup.
CHAPTER FIVE: RESULTS AND DISCUSSION

5.1 Series 1 CIGS2/CdS thin film solar cells – Cu/(In+Ga) = 2.5

Series 1 CIGS2/CdS thin film solar cells were prepared with the experimental procedure explained in chapter 4. The substrate size was 10 cm x 15 cm. The CIGS2 thin films were grown with a copper excess composition Cu/(In+Ga), of 2.5. Sulfurization was carried out in selenization/sulfurization furnace in the dilute H2S ambient (8% H2S) at 475 °C with a dwell time of 20 minutes. The ramp rate used from 25°C to 475 °C was 6 °C/min. The excess copper that segregated on the surface as Cu2−xS phase was etched in 10% KCN solution. The 2.5 cm x 10 cm pieces at the edge of as deposited and etched CIGS2 thin films were analyzed routinely using EPMA, and in the case of selected samples using Auger electron spectroscopy and secondary ion mass spectrometry for atomic concentrations, SEM for morphology and XRD for crystallographic structure and central 10 cm x 10 cm piece from each batch of deposition was used for cell completion.

EPMA analyses were carried out at NREL at 10 kV (depth of penetration ~ 0.3 µm) and at 20 kV (depth penetration of couple of microns) on a 2.5 cm x 2.5 cm unetched and etched CIGS2 thin films. As can be seen from Table 5.1, the unetched EPMA carried out at 20 kV, shows very high concentration of copper (55.04 at% ~ copper excess composition of 2.4) showing the formation of Cu2−xS phase.
Table 5.1: Atomic concentrations of unetched CIGS2 thin film analyzed by EPMA at 20kV.

<table>
<thead>
<tr>
<th>No</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>S</th>
<th>Total</th>
</tr>
</thead>
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<td>1</td>
<td>56.40</td>
<td>7.03</td>
<td>1.34</td>
<td>35.23</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>56.08</td>
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<td>1.43</td>
<td>35.21</td>
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<td>3</td>
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<td>4</td>
<td>53.98</td>
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<td>1.59</td>
<td>37.67</td>
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</tr>
<tr>
<td>5</td>
<td>54.68</td>
<td>6.86</td>
<td>1.48</td>
<td>36.98</td>
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</tr>
<tr>
<td>6</td>
<td>54.83</td>
<td>7.09</td>
<td>1.62</td>
<td>36.46</td>
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<tr>
<td>7</td>
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<td>7.18</td>
<td>1.58</td>
<td>36.66</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>54.53</td>
<td>7.06</td>
<td>1.43</td>
<td>36.98</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>53.92</td>
<td>6.94</td>
<td>3.76</td>
<td>35.37</td>
<td>100</td>
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<tr>
<td>10</td>
<td>55.73</td>
<td>7.07</td>
<td>1.58</td>
<td>35.62</td>
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</tr>
<tr>
<td>Average</td>
<td>55.04</td>
<td>7.00</td>
<td>1.73</td>
<td>36.23</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5.2 and Table 5.3 show the atomic concentrations of etched CIGS2 thin films obtained at 10 and 20 kV respectively. The copper excess Cu$_{2-x}$S was etched away in the 10% KCN solution.

Table 5.2: Atomic concentrations of etched CIGS2 thin film analyzed by EPMA at 10kV.

<table>
<thead>
<tr>
<th>No</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>S</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.72</td>
<td>25.94</td>
<td>2.45</td>
<td>47.89</td>
<td>100</td>
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<td>2</td>
<td>23.58</td>
<td>25.67</td>
<td>2.49</td>
<td>48.26</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>24.07</td>
<td>25.38</td>
<td>2.77</td>
<td>47.78</td>
<td>100</td>
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<td>4</td>
<td>23.78</td>
<td>25.97</td>
<td>2.74</td>
<td>47.51</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>24.50</td>
<td>25.21</td>
<td>2.70</td>
<td>47.60</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>23.86</td>
<td>25.54</td>
<td>2.46</td>
<td>48.15</td>
<td>100</td>
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<td>7</td>
<td>24.17</td>
<td>25.96</td>
<td>2.53</td>
<td>47.35</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>24.40</td>
<td>25.60</td>
<td>2.50</td>
<td>47.50</td>
<td>100</td>
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<td>9</td>
<td>23.67</td>
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<td>10</td>
<td>24.16</td>
<td>26.08</td>
<td>2.38</td>
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<tr>
<td>Average</td>
<td>23.99</td>
<td>25.71</td>
<td>2.57</td>
<td>47.74</td>
<td>100</td>
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</tbody>
</table>
Table 5.3: Atomic concentrations of etched CIGS2 thin film analyzed by EPMA at 20kV.

<table>
<thead>
<tr>
<th>No</th>
<th>Cu</th>
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<th>Ga</th>
<th>S</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.05</td>
<td>23.47</td>
<td>4.59</td>
<td>48.88</td>
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<td>2</td>
<td>23.11</td>
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<td>4.59</td>
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</tr>
<tr>
<td>3</td>
<td>23.26</td>
<td>23.55</td>
<td>4.59</td>
<td>48.60</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>23.37</td>
<td>23.23</td>
<td>4.55</td>
<td>48.85</td>
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<td>4.59</td>
<td>48.58</td>
<td>100</td>
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<td>6</td>
<td>22.92</td>
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<td>4.82</td>
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<td>7</td>
<td>23.09</td>
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<td>48.93</td>
<td>100</td>
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<td>8</td>
<td>23.51</td>
<td>23.34</td>
<td>4.46</td>
<td>48.69</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>22.90</td>
<td>23.59</td>
<td>4.47</td>
<td>49.05</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>22.93</td>
<td>23.55</td>
<td>4.50</td>
<td>49.03</td>
<td>100</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>23.16</strong></td>
<td><strong>23.46</strong></td>
<td><strong>4.57</strong></td>
<td><strong>48.81</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

Both 10 kV and 20 kV EPMA analysis show near stoichiometric, copper poor CIGS2 thin film. Interestingly, in Table 5.2 and Table 5.3 show the atomic concentrations of etched CIGS2 thin films obtained at 10 and 20 kV respectively. The copper excess Cu$_{2-x}$S was etched away in the 10% KCN solution. Table 5.2 and Table 5.3 gallium concentration obtained at 10 kV is less than that obtained at 20 kV and there is a systematic decrease in the indium concentration. This shows that gallium diffuses towards back contact and also replaces indium in the lattice of CIGS2. Diffusion of gallium towards back contact is attributed to the compressive stresses in the film, the smaller size of gallium atoms and the lower formation energy of In$_2$S$_3$ than that of Ga$_2$S$_3$.

Figure 23a, b, c and d show the SEM micrographs of unetched, etched CIGS2 thin film at x5500, etched CIGS2 thin film at x15000 and etched CIGS2 thin film at x30000 magnification respectively. Unetched film shows larger grains of Cu$_{2-x}$S and etched film shows compactly packed CIGS2 grains of size 1 – 2 µm with no porosity.
Figure 23: SEM images of (a) unetched (b) etched CIGS2 at x5500 (c) etched CIGS2 at x15000 and (d) etched CIGS2 at x30000.

Figure 24 shows the XRD pattern of etched and unetched CIGS2 thin film. Small differences are detected between the unetched and etched XRD patterns. The Cu$_{2-x}$S is a cubic phase and has d-spacing very close to that of CuInS$_2$. In most cases the peak positions of Cu$_{2-x}$S overlap with the major [112], [220/204] and [312] peak positions of the ternary alloy CuInS$_2$. This overlap of peak positions typically leads to a shoulder or asymmetric broadening of the chalcopyrite peaks. This often leads to difficulty in detecting the secondary peaks with XRD, requiring a much higher resolution using grazing incidence XRD. The XRD pattern of etched, near stoichiometric, slightly copper rich CIGS2 thin film showed very sharp, well-defined (101), (112), (103), (200), (220/204), (312), (400), (316) and (424) reflections of the chalcopyrite CuIn$_{0.85}$Ga$_{0.15}$S$_2$ phase. The strongest reflection was from (112) plane at $2\theta = 28.04^\circ$. The lattice
parameters calculated were $a = 5.51 \, \text{Å}$ and $c = 11.01 \, \text{Å}$. Molybdenum reflection was observed at $2\theta = 40.6^\circ$. In the case of random orientation, the intensity ratio of (112) with respect to (220)/(204) peaks, should be 1.5. The intensity ratio of $I_{112}/I_{(220/204)}$, for these films was 3.37, which is significantly higher, thus showing a preferred $\{112\}$ orientation.

CIGS2 thin films were characterized with AES for composition-depth profiling. Figure 25 shows the AES profile of etched CIGS2 thin film. Copper and sulfur signals are constant in the CIGS2 thickness. Gallium concentration is increasing towards the back contact while indium is decreasing (replaced by gallium). The surface of the sample was not cleaned by sputter etch prior to the analysis; hence the concentration of oxygen was high at the surface. However, the oxygen concentration throughout the depth of CIGS2 is very low.

![Figure 24: XRD pattern of unetched and etched CIGS2 thin film grown in series 1 (Cu/In+Ga = 2.5).](image)

Figure 24: XRD pattern of unetched and etched CIGS2 thin film grown in series 1 (Cu/In+Ga = 2.5).
The bandgap of CuInS$_2$ is around 1.5 eV. Gallium incorporation increases the bandgap thus increasing the open circuit voltage ($V_{oc}$). However gallium has a tendency to diffuse towards the back contact because of the compressive stresses in the film and smaller size of gallium atoms (Figure 25). Therefore, the effective bandgap towards the p-n junction will be same as that of CuInS$_2$. Bandgap measurements were carried out at NREL using photocurrent spectroscopy. Figure 26 shows the bandgap measurement plot of CIGS2 thin film. The measured bandgap was 1.54 eV (measuring ~5% gallium towards the junction). Diffusion of gallium towards the back contact helps in improving adhesion of the film to the molybdenum back contact and also provides a back surface field (BSF) or “electron mirror”, which repels minority charge carriers towards the p-n junction and thus prevents electrons being lost due to recombination.

![AES CIGS2 - S531E, Depth Profile](image_url)

Figure 25: AES depth profile of etched CIGS2 thin film.
CIGS2/CdS thin film solar cells were completed by the deposition of ~50 nm thick CdS layer using chemical bath deposition technique, intrinsic ZnO (i-ZnO)/ZnO:Al (~550 nm) bilayer window using RF magnetron sputtering and Ni/Al (~ 50 nm/500 nm) contact fingers using e-beam evaporation technique. The CIGS2/CdS thin film solar cells were characterized using current – voltage (I-V) measurements. Several CIGS2/CdS thin film solar cells with copper excess composition were prepared and characterized using the I-V measurements. Only a few chosen cells were sent to NREL for official I-V measurements under air mass 1.5 (AM 1.5) conditions. FSEC PV Materials Lab has developed a robust I-V measurement setup. The major differences between the I-V setup at FSEC PV Materials Lab and NREL are the cooling of solar cells during measurements and the simulator of solar irradiance. At FSEC the simulator is less elaborate. However, the intensity is measured with a LiCor pyranometer, thus providing the correct intensity without spectral correction. At NREL the solar cells are maintained at 25 °C.
Such a cooling facility is not available at FSEC. Figure 27 gives the graph of I-V measurements carried out at NREL. Table 5.4 gives the device parameters calculated from the I-V measurements. Shunt resistance, $R_p$ was calculated using nine point differential of change in voltage to change in current towards short circuit current density $J_{sc}$ and series resistance, $R_s$ was calculated in the similar manner towards the open circuit voltage, $V_{oc}$.

![Figure 27: I-V characteristics of CIGS2/CdS thin film solar cell with Cu/(In+Ga) = 2.5.](image-url)
Table 5.4: Solar cell parameters of series 1 CIGS2/CdS thin film solar cell.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunt Resistance, $R_p$</td>
<td>644.1 Ω</td>
</tr>
<tr>
<td>Series Resistance, $R_s$</td>
<td>20.6 Ω</td>
</tr>
<tr>
<td>Area</td>
<td>0.449 cm²</td>
</tr>
<tr>
<td>Short Circuit Current Density, $J_{sc}$</td>
<td>21.08 mA/cm²</td>
</tr>
<tr>
<td>Open Circuit Voltage, $V_{oc}$</td>
<td>722.2 mV</td>
</tr>
<tr>
<td>Peak current, $I_p$</td>
<td>7.22 mA</td>
</tr>
<tr>
<td>Peak Voltage, $V_p$</td>
<td>493.1 mV</td>
</tr>
<tr>
<td>Fill Factor, $FF$</td>
<td>52.08%</td>
</tr>
<tr>
<td>Efficiency, $\eta$</td>
<td>7.93%</td>
</tr>
</tbody>
</table>
5.1.1 Transparent conducting back layer preparation and characterization

CIGS2/CdS thin film solar cells were prepared on transparent and conducting back layer of ITO/MoS2. Bilayer of ITO/MoS2 forms a highly conducting and transparent back contact for the CIGS2/CdS thin film solar cells. ITO films (~ 450 nm) were deposited on glass substrates. A thin layer of molybdenum (~10 nm) was deposited on ITO thin film and annealed in diluted H2S atmosphere at 475 °C for 20 minutes. During annealing thin molybdenum layer got converted to MoS2. A few experiments were carried out to selenize the thin molybdenum layer deposited on ITO. Figure 28 shows the transmittance data of ITO, ITO/MoS2 and ITO/MoSe2 thin films deposited on glass. As can be seen, the transmittance of bilayer of ITO/MoS2 was high (~ 50%) compared to bilayer of ITO/MoSe2.

![Figure 28: Variation of transmittance with wavelength of ITO, ITO/MoS2, and ITO/MoSe2 thin films on glass substrate.](image)
So far, development of thin film solar cells on transparent conducting back contacts has been studied with respect to CuIn$_{1-x}$Ga$_x$Se$_2$/CdS thin film solar cell on ITO/MoSe$_2$ bilayer back contacts. The result obtained in Figure 28 is very promising as this is the first successful experiment to achieve higher bandgap CIGS2 thin film solar cells on transparent and conducting back contacts of ITO/MoS$_2$. Any improvements in the cell efficiency and the transparency through this would have a considerable impact on the PV community. Since CIGS2 is a wide bandgap chalcopyrite, compared to its selenide partner CuIn$_{1-x}$Ga$_x$Se$_2$, it can be used in the PEC water splitting setup to transmit the unabsorbed infrared (IR) photons to activate the photoanode for efficient hydrogen generation and also as the top cell in the tandem solar cell structure.

Precursor layers of CuGa-In were deposited on bilayer of ITO/Mo using the techniques described in chapter 4. The Cu/(In+Ga) ratio was maintained at 2.5. During sulfurization of precursors in the presence of dilute H$_2$S ambient, thin layer of molybdenum gets converted to MoS$_2$. This MoS$_2$ formation during precursor sulfurization prevents an extra step to be added to sulfurize molybdenum.

Unetched and etched CIGS2 thin films were analyzed using SEM for morphology and XRD for crystallographic structure. SEM was carried out at AMPAC’s MCF, Orlando, FL and XRD was carried out at MAIC, Gainesville, FL. Figure 29 shows the SEM micrographs of unetched and etched CIGS2 thin films on ITO/MoS$_2$ back contact. The SEM micrograph of unetched film shows large grains of Cu$_{2-x}$S phase and that of etched CIGS2 thin film shows compactly packed grains with no porosity.

XRD pattern for etched, near stoichiometric, copper poor CIGS2 thin film shows (101), (112), (103), (200), (220), (312), (400) and (316) reflections of highly crystalline chalcopyrite CIGS2 phase and also peaks from ITO back contact (Figure 30).
Figure 29: SEM micrograph of (a) unetched and (b) etched CIGS2/CdS thin film on ITO/MoS$_2$ back contact.

Figure 30: XRD pattern of CIGS2/CdS thin film on ITO/MoS$_2$ bilayer back contact.

Thin film solar cells were completed by the deposition of CdS using CBD, ZnO/ZnO:Al bilayer window using RF magnetron sputtering and Ni/Al contact fingers through metal masks.
Figure 31 shows the I-V measurements carried out at NREL. Table 5.5 summarizes the diode parameters from I-V measurements.

![IV characteristic of CIGS2/CdS solar cell on ITO/MoS\textsubscript{2} back contact.](image)

Table 5.5: Solar cell parameters of series 1 CIGS2/CdS thin film solar cell on ITO/MoS\textsubscript{2} back contact.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunt Resistance, $R_p$</td>
<td>448.34 Ω</td>
</tr>
<tr>
<td>Series Resistance, $R_s$</td>
<td>29.71 Ω</td>
</tr>
<tr>
<td>Area</td>
<td>0.431 cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Short Circuit Current Density, $J_{sc}$</td>
<td>18.02 mA/cm\textsuperscript{2}</td>
</tr>
<tr>
<td>Open Circuit Voltage, $V_{oc}$</td>
<td>702 mV</td>
</tr>
<tr>
<td>Peak current, $I_p$</td>
<td>5.57 mA</td>
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<td>Peak Voltage, $V_p$</td>
<td>461.8 mV</td>
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<td>Fill Factor, $FF$</td>
<td>47.14%</td>
</tr>
<tr>
<td>Efficiency, $\eta$</td>
<td>5.97%</td>
</tr>
</tbody>
</table>

67
Compared to the earlier efforts at FSEC PV Materials Lab on the development of CIGS2/CdS thin film solar cells on 2.5 cm x 2.5 cm stainless steel substrates, which had resulted in a world record efficiency of 10.4% (under AM 1.5 conditions) and 8.84(9\%)% (under AM 0 conditions), the efficiencies obtained on CIGS2/CdS thin film solar cells with the copper excess composition 2.5 were low. PV conversion efficiency of ~ 6\% obtained using CIGS2/CdS thin film solar cells on ITO/MoS\textsubscript{2} back contact is the first ever reported efficiency on ITO/MoS\textsubscript{2} back contact. However, the analysis of I-V characteristics of CIGS2/CdS thin films solar cells using copper excess composition of 2.5, grown on molybdenum and ITO/MoS\textsubscript{2}, shows low shunt resistance (~ 450-650 Ω), low fill factor (47 – 52\%) and low efficiencies (6 – 8\%). The effects of shunt resistance and series resistance on the open circuit voltage and short circuit current density respectively and eventually on the efficiency of the solar cell were discussed in detail in Chapter 2.6.

In order to study the reasons behind having low values of shunt resistance and efficiency, transmission electron microscopy (TEM) was carried out, where in the cross-section of the cell can be studied carefully and the reasons behind low shunt resistance, fill factors and efficiency would be found. TEM of CIGS2/CdS thin film solar cells were carried out at AMPAC’s MCF. Figure 32 shows the TEM micrograph of CIGS2/CdS thin film solar cell with Cu/(In+Ga) = 2.5. Cross-section TEM image shows fairly large grains of CuInS\textsubscript{2} near the surface and small grains of CuGaS\textsubscript{2} towards the molybdenum back contact. The grains of CuGaS\textsubscript{2} are small and they lead to the formation of many grain boundaries towards the molybdenum back contact. If the copper excess composition is too high, then excess copper segregates in the form of Cu\textsubscript{2-x}S at the surface, at the grain boundaries and may be towards the molybdenum back contact. Etching of excess copper can lead to the voids or porosity. As can be seen from Figure 32, many voids
(porosity) have been formed. Such heavy porosity leads to shunt paths which result in loss of charge carriers due to recombination. Further, at few locations near the molybdenum back contact, binary phase of CuGa remained unsulfurized (phase shown in circle in Figure 32). Figure 33 shows the line scan using energy dispersive x-ray spectroscopy (XEDS). At the location circled in Figure 33, the copper and gallium counts increase showing the presence of CuGa alloy which was not sulfurized properly. The high porosity and remnants of CuGa phase in the chalcopyrite structure had contributed to the low values of shunt resistance and photovoltaic conversion efficiency.

![TEM micrograph of CIGS2/CdS thin film solar cell with copper excess composition of 2.5.](image)

The greatest challenge in the PV community is to achieve high open circuit voltages. In the case of copper chalcopyrites (CuInSe₂, CuInS₂) addition of gallium has been the common practice followed to increase the bandgap of the chalcopyrite and consequently to increase the open circuit voltages. Therefore, during this research a copper excess composition of 2.5 was
chosen to incorporate gallium concentration, $x = 0.55$ into CuInS$_2$ (explained in detail in Chapter 2.3.1). However, employing very high copper excess composition lead to voids and thus to the poor performance of the solar cell. Moreover, additional gallium tends to diffuse towards molybdenum back contact. This could have been circumvented by annealing in inert gas which restores gallium towards the junction. However due to the problems of very high porosity at very high CuGa-excess, the copper excess composition was reduced to 1.4 for further experimentation.

Figure 33: Line scan of TEM image using XEDS analysis.
5.2 Series 2 CIGS2/CdS thin film solar cells with Cu/(In+Ga) = 1.4

Series of experiments were carried out to obtain CIGS2 thin films with stoichiometry of 40% more copper as explained in chapter 2. The thin films were analyzed with SEM for morphology, XRD for crystallographic structure and AES analysis for the concentration across the thickness of CIGS2 thin film. SEM micrographs are shown in Figure 34a (unetched), b (etched, x5500), c (etched, x30000) and d (cross-section SEM).

![SEM micrographs of (a) unetched, (b) etched x5500, (c) etched x30000 and (d) cross-section of etched CIGS2 thin film with Cu/(In+Ga) = 1.4](image)

Cross-section SEM was carried out by cleaving the sample from glass side. This showed that there is no porosity. Figure 36 shows the cross-section TEM image of CIGS2/CdS thin film solar cell with copper excess composition 1.4. Figure 34d shows no porosity and Figure 36
shows reduced porosity compared to copper excess composition of 2.5. Therefore by reducing the copper excess composition to 1.4 the problem of porosity has been eliminated. The small porosity shown by TEM may be an artifact of focused ion beam (FIB) sample preparation. Large grains are observed towards the heterojunction layer while smaller grains of CuGaS$_2$ (gallium diffusing towards back contact) were observed towards the molybdenum back contact. This grain growth technique shows the Zone 3 type of growth which is characterized by compactly packed equiaxed, columnar grains without any distinct, dense intercrystalline boundaries [93]. Figure 35 shows the schematic representation of influence of substrate temperature and argon working pressure on the structure of metal coatings [93]. Such a growth is known to result from bulk diffusion processes such as recrystallization.

![Figure 35: Schematic representation of dependence of coating structure on substrate temperature and argon pressure [93].](image)

In this growth technique, the grains with the preferred orientation grow larger at the cost of not so favorably oriented grains and finally coalescing with similar grains leaving indistinct, dense intercrystalline boundaries. Therefore large coalescent grains exist near the heterojunction
and small grains towards the molybdenum back contact. However, the smaller grains do not take part in the photocurrent flow, the photocurrent flows through the bulk of larger grains while flowing to the back contact. These small grains towards the molybdenum back contact may fall off during FIB, though the SEM cross-section shows no porosity.

Figure 36: Cross-section TEM image of CIGS2 film grown with the copper excess composition of 1.4

XRD pattern of etched CIGS2 thin film shows (101), (112), (103), (200), (220), (312), (400), (316) and (424) reflections of highly crystalline chalcopyrite CIGS2 and also reflections from molybdenum (Figure 37). The strongest reflection was from (112) plane at 2θ = 27.92°. The lattice parameters calculated were a = 5.52 Å and c = 11.04 Å. Molybdenum reflection was observed at 2θ = 40.4°. The intensity ratio of I_{112}/I_{(220/204)} for these films, measured was 2.74, showing a preferred {112} orientation.
Figure 37: XRD pattern of series 2 etched CIGS2 thin film.

Figure 38 shows the AES profile of etched CIGS2 thin film. Copper and sulfur signals are constant in the CIGS2 thickness. Gallium is increasing towards the back contact while indium is decreasing (replaced by gallium).
Figure 38: AES depth profile of etched series 2 CIGS2 thin film.

CIGS2 thin film solar cells were completed by the deposition of CdS by CBD, ZnO/ZnO:Al using RF magnetron sputtering and Cr/Ag front contact finger deposition by thermal evaporation. I-V measurement was carried out to understand the diode characteristics. Figure 39 shows the I-V measurement in dark and light carried out at FSEC PV Materials Lab. Solar cell is a diode and under illumination it is the current generator. Therefore, by usual diode convention where the forward current is positive, the recombination current in the solar cell is positive while the photo generated current is negative. The typical I-V curve of a solar cell is plotted in the fourth quadrant. However the I-V measurement data obtained from NREL the current converted to positive and so is plotted it in the first quadrant (Figure 27 and Figure 31). This is just a different way of presenting the data; however the photo generated current by standard diode convention is always negative. Table 5.6 gives the diode parameters measured
from I-V characteristics and Table 5.7 gives the device parameters for few cells which were prepared using the copper excess composition of 1.4. Shunt resistance, \( R_p \) was calculated using nine point differential of change in voltage to change in current at near-zero short circuit current density \( J_{sc} \) values and series resistance was calculated in the similar manner at near-zero values of open circuit voltage, \( V_{oc} \).

The shunt resistance and fill factor can be seen to have improved as compared to those for CIGS2/CdS thin film solar cells with copper excess composition of 2.5; however the open circuit voltage, \( V_{oc} \) and efficiency did not show improvement.

Reduction in the copper excess composition had reduced the gallium content in the film and eventually reduced the bandgap and open circuit voltage. Since increasing the gallium content in the CuInS\(_2\) using an alloy target of CuGa (22 at% gallium) was not feasible it became essential to improve the open circuit voltage using technique other than that of gallium addition.

![Figure 39: I-V characteristics of series 2 CIGS2/CdS thin film solar cells.](image-url)
Table 5.6: Solar cell parameters of series 2 CIGS2/CdS thin film solar cell

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunt Resistance, $R_p$</td>
<td>711.67 Ω</td>
</tr>
<tr>
<td>Series Resistance, $R_s$</td>
<td>25.57 Ω</td>
</tr>
<tr>
<td>Area</td>
<td>0.44 cm²</td>
</tr>
<tr>
<td>Short Circuit Current Density, $J_{sc}$</td>
<td>17.16 mA/cm²</td>
</tr>
<tr>
<td>Open Circuit Voltage, $V_{oc}$</td>
<td>670 mV</td>
</tr>
<tr>
<td>Peak current, $I_p$</td>
<td>5.86 mA</td>
</tr>
<tr>
<td>Peak Voltage, $V_p$</td>
<td>460 mV</td>
</tr>
<tr>
<td>Fill Factor, $FF$</td>
<td>53.29%</td>
</tr>
<tr>
<td>Efficiency, $\eta$</td>
<td>6.12%</td>
</tr>
</tbody>
</table>

Table 5.7: Solar cell parameters of series 2 CIGS2/CdS thin film solar cell

<table>
<thead>
<tr>
<th>Sample ID.</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (AM 1.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS926-1</td>
<td>650</td>
<td>15.93</td>
<td>54.98</td>
<td>5.69</td>
</tr>
<tr>
<td>SS926-2</td>
<td>660</td>
<td>17.25</td>
<td>53.69</td>
<td>6.11</td>
</tr>
<tr>
<td>SS926-3</td>
<td>660</td>
<td>16.21</td>
<td>55.2</td>
<td>5.9</td>
</tr>
<tr>
<td>SS926-4</td>
<td>650</td>
<td>16.78</td>
<td>55.17</td>
<td>6.02</td>
</tr>
<tr>
<td>SS926-5</td>
<td>650</td>
<td>17.15</td>
<td>54.69</td>
<td>6.09</td>
</tr>
<tr>
<td>SS926-6</td>
<td>640</td>
<td>14.32</td>
<td>55.47</td>
<td>5.08</td>
</tr>
<tr>
<td>SS926-7</td>
<td>640</td>
<td>17.22</td>
<td>51.97</td>
<td>5.73</td>
</tr>
<tr>
<td>SS926-8</td>
<td>620</td>
<td>16.73</td>
<td>50.95</td>
<td>5.28</td>
</tr>
<tr>
<td>SS926-11</td>
<td>680</td>
<td>15.36</td>
<td>55.21</td>
<td>5.76</td>
</tr>
<tr>
<td>SS926-12</td>
<td>670</td>
<td>15.68</td>
<td>54.64</td>
<td>5.74</td>
</tr>
<tr>
<td>SS926-13</td>
<td>670</td>
<td>17.15</td>
<td>53.29</td>
<td>6.12</td>
</tr>
<tr>
<td>SS926-14</td>
<td>660</td>
<td>14.59</td>
<td>55.04</td>
<td>5.29</td>
</tr>
<tr>
<td>SS926-15</td>
<td>660</td>
<td>16.19</td>
<td>53.79</td>
<td>5.75</td>
</tr>
<tr>
<td>SS926-16</td>
<td>660</td>
<td>16.39</td>
<td>53.54</td>
<td>5.79</td>
</tr>
<tr>
<td>SS926-17</td>
<td>660</td>
<td>15.52</td>
<td>53.66</td>
<td>5.49</td>
</tr>
<tr>
<td>SS926-18</td>
<td>660</td>
<td>16.55</td>
<td>53.2</td>
<td>5.81</td>
</tr>
</tbody>
</table>
5.2.2 Voc improvements by varying intrinsic ZnO thickness variation

Theoretical value of open circuit voltage that can be achieved by CuInS$_2$/CdS thin film solar cells is around 950 to 1000 mV. From the earlier discussions on the electrical properties of the solar cells, we have understood that one of the parameters that directly affect the open circuit voltage $V_{occ}$ is shunt resistance $R_p$. As shunt resistance increases the open circuit voltage also increases. Therefore, the key factor to be targeted was the shunt resistance. The surface of CIGS$_2$ thin films grown using the sulfurization technique (sulfurization of sputtered metallic precursors) is considerably rougher as compared to co-evaporated surface. The cross-section SEM of the sulfurized CIGS$_2$ thin film and a co-evaporated CuIn$_{1-x}$Ga$_x$Se$_2$ thin film solar cell [95] is shown in Figure 40a and b respectively. The advantage of having smooth absorber surface is significant during the growth of CdS layer. If the surface of the absorber is smooth, then CdS deposition is conformal with a uniform thickness CdS deposited all over the surface of the absorber layer. However, if the surface of absorber is not smooth (which is the case in this research), then CdS growth cannot be expected to be conformal with a uniform thickness over the entire surface of the absorber. In such cases, at few isolated regions where CdS layer does not cover CIGS$_2$ surface, the deposition of ZnO:Al, which is followed by the deposition of CdS layer, can lead to direct contact between ZnO:Al and CIGS$_2$ resulting in a high bandgap discontinuity and consequently in the loss of open circuit voltage. To circumvent this eventuality, a transparent and highly resistive layer of intrinsic ZnO (i-ZnO) is required between the ZnO:Al and CdS layer so that the defective regions do not suppress the open circuit voltage. Such highly resistive layer of intrinsic ZnO (i-ZnO) is deposited between CdS and ZnO:Al. Thus far all the CIGS groups all over the world employ the deposition of the i-ZnO as a matter of routine independent of the
process used for absorber growth and without consideration of the smoother surface of their absorber. However, thickness of i-ZnO plays a major role in the improvement of open circuit voltages only when the CIGS layer is relatively rougher. In that case, too low thicknesses (including no i-ZnO) will have regions of high bandgap discontinuity leading to overall low open circuit voltage. On the other hand, too high i-ZnO thicknesses will weaken the built in field by spreading the space charge region over the thickness of i-ZnO thus reducing the efficiency. Therefore, it is essential to first to decide whether an intrinsic layer is needed at all and if so to determine its optimum thickness so as to achieve the highest photovoltaic conversion efficiency.

The basic contributions of this research was to

1. provide to the photovoltaic scientific world an alternative technique, other than gallium addition, to increase the open circuit voltage of the CIGS2/CdS thin film solar cells,

2. improve the understanding of the necessity for having or not having a highly resistive layer i-ZnO layer between CdS and ZnO:Al, and

3. to emphasize the need to optimize the thickness of i-ZnO layer to achieve the highest PV conversion efficiency as and when needed.
Based on this criterion, it was decided that an intrinsic i-ZnO thickness was essential for the present research and therefore, the thickness of i-ZnO layer was varied systematically. For the systematic variation of i-ZnO layer from the minimum i-ZnO thickness to the optimum value there was a corresponding variation from 710 to 830 mV in the open circuit voltage of the CIGS2/CdS thin film solar cells. Further increase in i-ZnO thickness decreased the open circuit voltage from 830 mV to around 450 mV. Table 5.8 and Table 5.9 give the device parameters along with the open circuit voltage, $V_{oc}$ values for CIGS2/CdS thin film solar cells with minimum and optimum i-ZnO thickness.
Table 5.8: Device parameters along with the open circuit voltage values for CIGS2/CdS cells with minimum i-ZnO.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS10111-1</td>
<td>730</td>
<td>17.65</td>
<td>63.48</td>
<td>8.18</td>
</tr>
<tr>
<td>SS10111-2</td>
<td>730</td>
<td>18.18</td>
<td>63.69</td>
<td>8.45</td>
</tr>
<tr>
<td>SS10111-3</td>
<td>730</td>
<td>17.8</td>
<td>63.71</td>
<td>8.28</td>
</tr>
<tr>
<td>SS10111-4</td>
<td>730</td>
<td>18.15</td>
<td>63.87</td>
<td>8.46</td>
</tr>
<tr>
<td>SS10111-5</td>
<td>730</td>
<td>17.74</td>
<td>63.3</td>
<td>8.2</td>
</tr>
<tr>
<td>SS10111-6</td>
<td>740</td>
<td>20.12</td>
<td>61.87</td>
<td>9.21</td>
</tr>
<tr>
<td>SS10111-7</td>
<td>730</td>
<td>17.92</td>
<td>62.95</td>
<td>8.24</td>
</tr>
<tr>
<td>SS10111-8</td>
<td>710</td>
<td>19.49</td>
<td>61.36</td>
<td>8.49</td>
</tr>
</tbody>
</table>

Table 5.9: Device parameters along with the open circuit voltage values for CIGS2/CdS cells with optimum i-ZnO.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (AM 1.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS1020-1</td>
<td>810</td>
<td>18.69</td>
<td>63.77</td>
<td>9.65</td>
</tr>
<tr>
<td>SS1020-2</td>
<td>810</td>
<td>18.23</td>
<td>63.81</td>
<td>9.42</td>
</tr>
<tr>
<td>SS1020-3</td>
<td>810</td>
<td>18.79</td>
<td>64.49</td>
<td>9.81</td>
</tr>
<tr>
<td>SS1020-4</td>
<td>810</td>
<td>18.55</td>
<td>64.86</td>
<td>9.75</td>
</tr>
<tr>
<td>SS1020-5</td>
<td>810</td>
<td>19.64</td>
<td>63.07</td>
<td>10.03</td>
</tr>
<tr>
<td>SS1020-6</td>
<td>820</td>
<td>19.09</td>
<td>60.89</td>
<td>9.53</td>
</tr>
<tr>
<td>SS1020-7</td>
<td>810</td>
<td>19.36</td>
<td>63.55</td>
<td>9.96</td>
</tr>
<tr>
<td>SS1020-8</td>
<td>800</td>
<td>18.46</td>
<td>63.53</td>
<td>9.38</td>
</tr>
<tr>
<td>SS1020-9</td>
<td>800</td>
<td>19.29</td>
<td>62.42</td>
<td>9.63</td>
</tr>
</tbody>
</table>

Figure 41 shows the I-V characteristics of series 2 CIGS2/CdS thin film solar cell with optimum thickness of i-ZnO. Table 5.10 shows the solar cell properties calculated from I-V curve.
Figure 41: I-V characteristics of series 2 CIGS2/CdS thin film solar cell with the optimum i-ZnO thickness.

Table 5.10: Solar cell parameters of series 2 CIGS2/CdS thin film solar cell with the optimum i-ZnO thickness

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunt Resistance, $R_s$</td>
<td>961.7 Ω</td>
</tr>
<tr>
<td>Series Resistance, $R_s$</td>
<td>19.07 Ω</td>
</tr>
<tr>
<td>Area</td>
<td>0.44 cm²</td>
</tr>
<tr>
<td>Short Circuit Current Density, $J_{sc}$</td>
<td>19.64 mA/cm²</td>
</tr>
<tr>
<td>Open Circuit Voltage, $V_{oc}$</td>
<td>810 mV</td>
</tr>
<tr>
<td>Peak current, $I_p$</td>
<td>6.99 mA</td>
</tr>
<tr>
<td>Peak Voltage, $V_p$</td>
<td>620 mV</td>
</tr>
<tr>
<td>Fill Factor, $FF$</td>
<td>63.04%</td>
</tr>
<tr>
<td>Efficiency, $\eta$</td>
<td>10.03%</td>
</tr>
</tbody>
</table>
Figure 42: I-V measurement of CIGS/CdS thin film solar cell with copper excess composition of 1.4.
The cell which measured 10.03% at FSEC PV Materials Lab was sent to NREL for the deposition of MgF$_2$ antireflection coating and I-V measurement in AM 1.5 conditions (1000 W/m$^2$ illumination). Figure 42 shows the I-V characteristic of the same cell shown in Figure 41. The photovoltaic conversion efficiency obtained was 11.99% with an open circuit voltage of 830 mV.

This is a world record efficiency to date on a selenide free CIGS$_2$/CdS thin film solar cells, developed using sulfurization technique. The highest efficiency so far on CIGS$_2$/CdS thin film solar cells is 12.3% developed using two stage co-evaporation techniques [94]. The open circuit voltage reported through this research (830.5 mV) is the highest ever obtained on CIGS$_2$/CdS thin film solar cells. The open circuit voltage of 830.5 mV has become the “$V_{oc}$ champion value”. The same cell was sent to NASA Glenn Research Center (NASA GRC) for the I-V measurements in AM0 conditions. Table 5.11 shows the device parameters obtained from I-V measurements in AM0 conditions at NASA GRC.

Table 5.11: Device parameters of I-V measurements carried out at AM0 conditions.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (AM0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS1020-1</td>
<td>827.08</td>
<td>24.13</td>
<td>68</td>
<td>9.93</td>
</tr>
<tr>
<td>SS1020-2</td>
<td>824.14</td>
<td>23.76</td>
<td>68</td>
<td>9.75</td>
</tr>
<tr>
<td>SS1020-3</td>
<td>825.13</td>
<td>24.40</td>
<td>68.6</td>
<td>10.01</td>
</tr>
<tr>
<td>SS1020-4</td>
<td>825.69</td>
<td>24.00</td>
<td>69.1</td>
<td>10.01</td>
</tr>
<tr>
<td>SS1020-5</td>
<td>827.52</td>
<td>25.00</td>
<td>67.7</td>
<td>10.25</td>
</tr>
<tr>
<td>SS1020-6</td>
<td>825.37</td>
<td>24.56</td>
<td>63.5</td>
<td>9.41</td>
</tr>
<tr>
<td>SS1020-7</td>
<td>822.37</td>
<td>24.57</td>
<td>67.1</td>
<td>9.92</td>
</tr>
<tr>
<td>SS1020-8</td>
<td>819.96</td>
<td>24.31</td>
<td>67.5</td>
<td>9.84</td>
</tr>
<tr>
<td>SS1020-9</td>
<td>814.83</td>
<td>25.23</td>
<td>64.7</td>
<td>9.73</td>
</tr>
</tbody>
</table>

As can be seen from above tables, the solar cell parameters, over a large area of 2.5 cm x 10 cm, especially the photovoltaic conversion efficiencies are highly uniform.
Since, the results obtained were through a process which can be easily upgraded to an industrially profitable scale; this research will have a great impact on the PV community, especially on many thin film solar cell manufacturers. A scientifically refined process was developed to improve the open circuit voltage and efficiency of CIGS2/CdS thin film solar cells, which are less toxic, have optimum bandgap (~1.5 eV) for the space application and can have much higher open circuit voltages compared to highly studied and industrially applied CuIn$_{1-x}$Ga$_x$Se$_2$/CdS thin film solar cells.

Further, intrinsic ZnO thickness was increased to a maximum value. However the V$_{oc}$ decreased to an average value of 460-530 mV. The decrease in open circuit voltage was attributed to spreading of the space-charge region into i-ZnO thickness, thus weakening the built-in field and consequently degradation in solar cell performances. Table 5.12 gives the V$_{oc}$ values of CIGS2/CdS thin film solar cells grown in series 2 composition with maximum thick i-ZnO.

Table 5.12: Open circuit voltage values for CIGS2/CdS cells with maximum i-ZnO thickness.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Voc (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S9192_6</td>
<td>530</td>
</tr>
<tr>
<td>S9192_7</td>
<td>490</td>
</tr>
<tr>
<td>S9192_8</td>
<td>480</td>
</tr>
<tr>
<td>S9192_9</td>
<td>490</td>
</tr>
<tr>
<td>IS9181_4</td>
<td>440</td>
</tr>
<tr>
<td>IS9181_5</td>
<td>450</td>
</tr>
<tr>
<td>IS9181_6</td>
<td>460</td>
</tr>
<tr>
<td>IS9181_8</td>
<td>420</td>
</tr>
</tbody>
</table>
5.3 Series 3 CIGS2/CdS thin film solar cells – Cu/(In+Ga) = 1.4

Several studies indicate the importance of formation of binary alloys of Cu-In before sulfurizing the precursor. This precursor (Cu-In-Ga) alloy formation helps prevent the formation of In$_2$S$_3$ binary alloy and eventual loss of indium. Series 3 CIGS2/CdS thin film solar cells were prepared using Cu/(In+Ga) ratio 1.4 and introducing a dwell of 30 minutes at 120 °C during sulfurization. Temperature of dwell was chosen to be below melting point of indium (156.6 °C) and the dwell time chosen was sufficient to form a precursor binary alloys. The annealed precursors were sulfurized in diluted H$_2$S (8% H$_2$S) ambient. The CIGS2 thin films were studied for morphology using SEM. Figure 43 shows the SEM micrograph of CIGS2 thin film with metallic precursors annealed at 120 °C for 30 minutes. As can be seen from Figure 43b the grains grow fairly large with very little porosity extending towards the back contact. This large grains are the result of precursor annealing, which helped in the formation of large precursor alloy grains (Figure 43b)).

![Figure 43: SEM micrograph (a) at x5500 magnification and (b) cross-section of etched CIGS2 thin film with precursor annealed at 120 °C for 30 minutes.](image-url)
CIGS2/CdS thin film solar cells were completed by the deposition of CdS layer by CBD, i-ZnO/ZnO:Al using RF magnetron sputtering and Cr/Ag front contact fingers using thermal evaporation through metal masks. Figure 44 shows the graph of I-V measurements carried out at FSEC PV Materials Lab and Table 5.13 gives the device parameters. As can be seen the efficiency of the cells obtained was similar to the series 2 CIGS2/CdS cells with precursors not annealed before sulfurization. There is still a scope for improvements in the cell performance with respect to the dwell temperature and dwell time.

Figure 44: Graph of I-V measurement of CIGS2/CdS cell with precursors annealed at 120 °C for 30 minutes.
Table 5.13: Solar cell parameters of CIGS2/CdS cell with precursors annealed at 120 °C for 30 minutes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shunt Resistance, $R_p$</td>
<td>1084.44 Ω</td>
</tr>
<tr>
<td>Series Resistance, $R_s$</td>
<td>18.88 Ω</td>
</tr>
<tr>
<td>Area</td>
<td>0.441 cm$^2$</td>
</tr>
<tr>
<td>Short Circuit Current Density, $J_{sc}$</td>
<td>21.2 mA/cm$^2$</td>
</tr>
<tr>
<td>Open Circuit Voltage, $V_{oc}$</td>
<td>790 mV</td>
</tr>
<tr>
<td>Peak current, $I_p$</td>
<td>7.54 mA</td>
</tr>
<tr>
<td>Peak Voltage, $V_p$</td>
<td>590 mV</td>
</tr>
<tr>
<td>Fill Factor, $FF$</td>
<td>60.33%</td>
</tr>
<tr>
<td>Efficiency, $\eta$</td>
<td>10.08%</td>
</tr>
</tbody>
</table>
5.4 RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ photoanode characterization

RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ anodes were prepared as explained in chapter 4. The anodes were analyzed with SEM for the morphology, XRD for crystal structure and SIMS for the depth composition. Figure 45a and b show the SEM micrographs, Figure 46a and b the XRD patterns and Figure 47a and b the SIMS depth profiles of RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ respectively. XEDS measurements showed Ru:S $\equiv$ 29.34:70.66 and Ru:Fe:S $\equiv$ 27.05:2.08:70.87 for RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ respectively.

![SEM micrographs](image)

Figure 45: SEM micrographs at x1000 of (a) RuS$_2$ and (b) Ru$_{0.99}$Fe$_{0.01}$S$_2$. 

89
Figure 46: XRD pattern of (a) RuS$_2$ and (b) Ru$_{0.99}$Fe$_{0.01}$S$_2$.

Figure 47: SIMS depth profile of (a) RuS$_2$ and (b) Ru$_{0.99}$Fe$_{0.01}$S$_2$.

RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ anodes were characterized by the I-V measurements in pH10 electrolyte with normal concentration and 5x concentration. The concentration of the solution was increased to reduce the series resistance. Electrolyte pH 10 with normal concentration was prepared by adding 50ml of 0.025M borax into 18.3ml of 0.1M NaOH and pH with 5x concentration was prepared by systematically increasing the concentration of each reactants by
five times (50 ml of 0.125M borax + 18.3 ml of 0.5M NaOH). Figure 48 shows the I-V characteristic of RuO$_2$, RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ anodes in pH 10 electrolyte with normal and 5x concentration. RuS$_2$ and Ru$_{0.99}$Fe$_{0.01}$S$_2$ anodes show similar trends in dark, however under the illumination of light Ru$_{0.99}$Fe$_{0.01}$S$_2$ shows better PEC characteristics than RuS$_2$.

![Graph showing I-V characteristic of RuO$_2$, RuS$_2$, and Ru$_{0.99}$Fe$_{0.01}$S$_2$ anodes.]

**Figure 48: I-V characterization RuO$_2$, RuS$_2$, and Ru$_{0.99}$Fe$_{0.01}$S$_2$ anodes.**

The better performance of Ru$_{0.99}$Fe$_{0.01}$S$_2$ under illumination is attributed to its bandgap. Bandgap of RuS$_2$ is 1.3 eV and addition of 1% (Ru$_{0.99}$Fe$_{0.01}$S$_2$) reduces the bandgap to 1.1 eV. This result gives an opportunity to use Ru$_{0.99}$Fe$_{0.01}$S$_2$ as photoanode and use the unabsorbed infrared (IR) photons from the CIGS2 solar cell to be incident on Ru$_{0.99}$Fe$_{0.01}$S$_2$ and reduce the overvoltage required for oxygen generation and further increase the PEC efficiency. As a part of this thesis, performance of RuS$_2$ in dark was used to calculate the PEC efficiency.
5.5 PEC efficiency calculations

Two CIGS2/CdS thin film solar cells were used in series with the RuS$_2$ anode for oxygen generation and platinum for hydrogen generation. Figure 49 shows the I-V characteristic of two series 2 CIGS2 thin film solar cells connected in series, illuminated with AM1.5 illumination (1000 W/m$^2$). It also shows the variation of current with voltage of PEC cell having RuS$_2$ anode in dark for oxygen generation and platinum cathode for hydrogen generation.

![I-V characteristic of two CIGS2/CdS thin film solar cells](image)

Figure 49: I-V characteristic of two CIGS2/CdS thin film solar cells illuminated with AM1.5 illumination along with the I-V of PEC cell having RuS$_2$ anode in dark and platinum cathode.

Maximum power from the PEC setup consisting of two illuminated CIGS2/CdS thin film solar cells connected in series, RuS$_2$ anode in dark for oxygen generation, and platinum for hydrogen generation is obtained at the crossover point of I-V curve of solar cells and I-V curve of anode.
From Figure 49,

Crossover point = 6.3 mA @ 1.343 V

Power input = $100 \frac{mW}{cm^2}$

\[ \text{:. Power output} = 6.3 \times 1.343 = 8.46 \ mW \]

Area of the two cells = 0.882 cm$^2$

\[ E_{H_2O}^0 = 1.23 \ V \]

PEC Efficiency = \[ \frac{P_{out}}{P_{in}} \times \frac{E_{H_2O}^0}{V} \times 100 \]

\[ = \frac{8.46}{(100 \times 0.882)} \times \frac{1.23}{1.343} \times 100 = 8.78\% \]

This is a very significant result. Presently, photoelectrochemical water splitting stands at a point where the efficient PEC cells cost fortune and cheaper PEC cells are not efficient. Hence, the results obtained through the present research become significant because of the fact that an optimum trade off can be drawn between efficient and economic generation of hydrogen. The thin film solar cells have the projection of going to as low as less than $1/W_p$ by the year 2010 [estimation of DOE] and with the increasing demand and decreasing oil production, it is imminent that we need an alternative energy source independent of fossil fuels. With the science and technology presented through this research, an alternative energy source (hydrogen) can be generated using another alternative energy (solar cells) which has the potential of becoming economical in the coming years.
CHAPTER SIX: SUMMARY AND CONCLUSIONS

Summary:

This research was intended to (i) elucidate the advantages and disadvantages related to gallium addition, (ii) provide an alternate technique to the PV community to increase the open circuit voltage, which is independent of gallium addition, (iii) develop highly efficient CIGS2/CdS thin film solar cells and (iv) provide an alternate material in the form of CIGS2/CdS thin film solar cells and a technology in the form of multiple bandgap tandem of solar cells and RuS$_2$ anode, for PEC water splitting.

The greatest challenge in the PV community is to achieve high open circuit voltages. In the case of copper chalcopyrites (CuInSe$_2$, CuInS$_2$) the addition of gallium has been the common practice followed to increase the bandgap of the chalcopyrite and consequently increase the open circuit voltages. However, the addition of gallium has its own challenges. There is an optimum value of gallium that can be added to the ternary copper chalcopyrites within which the morphology and crystallographic properties do not deteriorate and also the open circuit voltage varies in a super-linear fashion ($x = 0.6$ for CIGS2 and 0.3 for CuIn$_{1-x}$Ga$_x$Se$_2$) [58]-[59]. Therefore, any increase in the open circuit voltage is limited by the optimum value of gallium addition.

Thin films of CIGS2 were prepared and characterized using SEM, XRD, TEM, EPMA, and AES. The CIGS2 thin films were grown in excess copper composition with Cu/(In+Ga) ratios of 2.5 and 1.4. Excess copper composition of 2.5 chosen with the aim to achieve high open circuit voltage was found to be too high and thus detrimental to the performance of solar cells. Diode parameters obtained from I-V measurements were, open circuit voltage of 722.8
mV, short circuit current density of 21.07 mA/cm\(^2\), fill factor 52.08% and efficiency 7.93%. The lower efficiency was attributed to low shunt resistance and low fill factor. TEM analysis of a FIB cut from a CIGS2/CdS thin film solar cell showed voids (porosity) near the molybdenum back contact. This was attributed to a very high copper excess composition. High porosity contributed to the low resistant shunt paths which acted as recombination centers.

In series 2, CIGS2/CdS thin film solar cells, excess copper composition was optimized to 1.4 with view to achieve the highest efficiency. TEM analysis showed considerably reduced porosity. The thickness of i-ZnO between CdS and ZnO:Al was optimized to achieve high open circuit voltages. The cell parameters for CIGS2/CdS thin film solar cell with copper excess composition of 1.4 were, open circuit voltage of 830.5 mV, short circuit current density of 21.88 mA/cm\(^2\), fill factor of 69.13% and photo-conversion efficiency of 11.99%. These are official measurements carried out at the National Renewable Energy Laboratory. The photovoltaic conversion efficiency of 11.99% sets a new world record for CIGS2 cells developed using sulfurization and the open circuit voltage of 830.5 mV has been officially declared as “\(V_{oc}\) champion”.

Series 3 CIGS2/CdS thin film solar cells were prepared by sulfurizing the annealed Cu-In(Ga) metallic precursors. The solar cell parameters obtained were, open circuit voltage 790 mV, short circuit current density 21.2 mA/cm\(^2\), fill factor 60.33% and cell efficiency 10.08%.

New PEC setups with RuS\(_2\) and Ru\(_{0.99}\)Fe\(_{0.01}\)S\(_2\) photoanodes were developed. RuS\(_2\) and Ru\(_{0.99}\)Fe\(_{0.01}\)S\(_2\) photoanodes were more stable in the electrolyte and showed better I-V characteristics than RuO\(_2\) anode used earlier. Using two CIGS2/CdS thin film solar cells, a RuS\(_2\) anode and a platinum cathode a PEC efficiency of 8.78% was determined. The results of this
research constitute a significant advance towards achieving practical feasibility and industrially viability of the technology of PEC hydrogen generation by water splitting.

**Conclusions:**

Following are the contributions of this research to the PV community.

1. An alternative process to develop highly efficient CIGS2/CdS thin film solar cells was introduced. Since the process used for the development of CIGS2/CdS thin film solar cells can be easily upgraded to an economic, large-scale production.

2. A new scientifically refined process, independent of gallium addition, was introduced to improve the open circuit voltage and the efficiency of CIGS2/CdS thin film solar cells that use less toxic processing, have optimum bandgap (~1.55 eV) for PEC and the space application and can have much higher open circuit voltages compared to more extensively studied and industrially applied CuIn\textsubscript{1-x}Ga\textsubscript{x}Se\textsubscript{2}/CdS thin film solar cells. The alternative process was to deposit a highly resistive and transparent layer of intrinsic ZnO (i-ZnO) between CdS and the heavily doped ZnO:Al layers which would improve the open circuit voltages of CIGS2/CdS thin film solar cells. This research also improved the understanding of the basic necessity of whether or not to include an i-ZnO layer with optimum thickness.

3. The PEC efficiency of ~ 9% sets an important milestone for many research groups in the entire world. From the results obtained through this research, the technology of PEC hydrogen generation by water splitting becomes significantly more interesting, practically more feasible and industrially more viable.
**Broader Debate on the Enhancement of Photovoltaic Efficiencies**

One of the basic tenets of the Indian philosophical thought is “*vaade vaade jaayate tatvabodhah*” i.e. the basic principle is born through debate. The thought process itself crystallizes through contemplation. Here are some thoughts being presented as my contribution to the debate in the quest of knowledge to further the science of photovoltaics.

Grain boundaries limit the PV conversion efficiency of polycrystalline thin film solar cells. The extent of enhancement in the efficiencies in comparison to those obtained from monocrystalline materials is a gauge of the influence of grain boundaries that has to be overcome. If the unsatisfied dangling bonds at the surfaces and grain boundaries formed to the discontinuity of the periodic lattice structure are not passivated, they act as centers of recombination, causing loss of minority charge carriers [Panel Discussion on Grain Boundary Effect by the NREL R&D Group]. Single crystal and multicrystalline silicon and single crystal, multijunction III-V compound solar cells, have achieved impressive efficiencies [13]. Of course, there are no grain boundaries in silicon and III-V compound single crystal materials. The grain size in multicrystalline silicon is approximately 1 cm. Thus the total surface and interface area including that of the grain-boundaries in a 250 µm thick multicrystalline silicon wafer approximately equals the geometric surface area [69]. Even then the techniques such as hydrogen passivation are employed to improve the quality of multicrystalline silicon wafers [96]. It is interesting to note that attempts to dope amorphous silicon layers in which there is no long-range order, were successful only after the passivation technique of hydrogenation was adopted. Hydrogenation has permitted the preparation of triple p-i-n junction cells with efficiencies exceeding 13% [97]. The grain boundaries in polycrystalline silicon and III-V compound thin films are very difficult to passivate.
Therefore, the efficiencies of polycrystalline silicon and III-V compound thin film solar cells are very low as compared to those of their single crystal counterparts [98]-[99]. On the other hand reasonably high efficiencies have been achieved with CuIn_{1-x}Ga_{x}Se_{2} and CdTe polycrystalline thin film solar cells [19],[98]. It is interesting to note that these efficiencies are higher that those achieved with single crystal CuIn_{1-x}Ga_{x}Se_{2} and CdTe materials [98]. Thus, the grain boundaries in CuIn_{1-x}Ga_{x}Se_{2} and CdTe polycrystalline thin film are reasonably benign. However, still higher efficiencies would be achieved if the grain boundaries are fully passivated [59]. One method to passivate grain boundaries in CuIn_{1-x}Ga_{x}Se_{2} is to create a field to repel the minority charge carriers (electrons) by growing slightly copper-poor grains with a still lower Cu/(In+Ga) proportion near the grain boundaries. This has been achieved by carefully controlling the proportion of Cu/(In+Ga) in the range of 0.88-0.92 for CuIn_{1-x}Ga_{x}Se_{2} films so that the growth conditions allow the formation of slightly copper-poor grains with a much lower Cu/(In+Ga) proportion near the grain boundaries. This may be one of the reasons behind the high conversion efficiency of 19.5% [19]. Such an option is not available in the case of CIGS2 thin films prepared by beginning with a Cu-excess composition. A near stoichiometric, slightly copper-poor chalcopyrite film is obtained by etching away the excess Cu_{2-x}S and therefore the Cu/(In+Ga) proportion at the grain boundary cannot be lowered still further. This seems to be the reason why much higher conversion efficiencies have not been achieved. All these aspects point towards the necessity of grain boundary passivation by other means. One such alteration in the process could be to deposit a thin layer of indium after etching away excess Cu_{2-x}S and then to carry out a second sulfurization so that the overall Cu/(In+Ga) ratio is in the 0.88-0.92 range. This hypothesis should be considered in the future research at the FSEC PV Materials Lab.
LIST OF REFERENCES


