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Optimization of CuInxGa1-xSe2 Solar Cells with Post Selenization

Zehra Cevher

The Graduate Center, City University of New York

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OPTIMIZATION OF CUIN$_3$GA$_{1-x}$SE$_2$ SOLAR CELLS WITH POST SELENIZATION

by ZEHRA CEVHER

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2018
Optimization of CuIn$_x$Ga$_{1-x}$Se$_2$ Solar Cells with Post Selenization

by

Zehra Cevher

This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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THE CITY UNIVERSITY OF NEW YORK
ABSTRACT

Optimization of CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} Solar Cells with Post Selenization

by

Zehra Cevher

Advisor: Dr. Yuhang Ren

The chalcopyrite semiconductor CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} is considered as the most promising material for high efficiency thin film solar cells due to its exceptional radiation stability, tunable direct bandgap, high light absorption coefficient and low cost preparation methods. In this thesis, we present the systematic investigation of the deposition conditions to optimize the CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} device performance using the two-step deposition method. Further, we utilized nonlinear optical methods to investigate the deposition parameters to optimize the bulk and interface properties of photovoltaic devices.

First, we investigated the deposition parameters to optimize the structural, electrical, optical and adhesion properties of molybdenum, Mo, and aluminum doped zinc oxide, ZnO:Al, electrode layers. Our results show that electrical and adhesion properties of Mo films can be optimized by modifying the intrinsic mechanical compressive and tensile stress. Mo films deposited under tensile stress exhibit good adhesional strength and high resistivity, whereas films deposited under compressive stress exhibit poor adhesional stress and low resistivity. In order to obtain Mo films with both good adhesion and low sheet resistance, we deposited the films in a bilayer structure. Similarly, increased Ar flux is found to improve the crystalline quality of the ZnO:Al films due to Ar-ZnO:Al collisions and heating effect which lead to increased grains size and shape, reducing intergranular voids in ZnO:Al films. Moreover, lower sputter pressure is found
to increase transmittance of light due to reduced grain boundary scattering of light. Post-annealing treatment in hydrogen atmosphere is found to enhance the conductance of the ZnO:Al film which is attributed to desorption of negatively charged species, mainly oxygen from the grain boundaries.

Second, we investigated the uniformity, morphology and homogeneity of CuInGa precursor and CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films. In order to obtain uniform chemical homogeneity, and smooth surface, we deposited the precursor in the Mo/In/CuGa/In structure. Reducing the deposition time for In resulted in a precursor film with smoother morphology, and depositing a stacked structure enabled uniform chemical homogeneity. Next, we designed our chemical vapor deposition system to fabricate uniform CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with reproducible results. In our chemical vapor deposition system, we incorporated a flow controller to control the selenium diffusion rate, hence the thickness of the Mo\textsubscript{x}Se\textsubscript{y} layer, and a pressure regulator to control the selenium vapor pressure in order to fabricate CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with the right selenium content and the stoichiometry. A sophisticated exhaust gas collection system is incorporated to trap the unreacted residual Se vapor, and prevent the CVD system from contamination and to obtain reproducible results. A graphite CuInGa precursor fixture was utilized and oriented normal to the direction of selenium flux. Our selenization results show that the CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} device performance can be optimized by tuning the Cu/In composition. An increase in Se flux facilitates In\textsubscript{2}Se\textsubscript{3} and Ga\textsubscript{2}Se\textsubscript{3} phases, resulting in CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with larger grains, and better device performances. We also show selenium cracking helps to reduce the defect density in the bulk and interface of the CuInGaSe film by filling in the copper vacancy defects.

Third, we utilized Raman spectroscopy and time-resolved photoluminescence spectroscopy to investigate the deposition parameters to optimize the crystalline quality and therefore the interval radiative quantum efficiency of MBE-grown GaAs/AlGaAs double
heterostructures. Our results reveal an improvement in lattice disorder in both the GaAs and AlGaAs layers at elevated temperatures as the As/Ga flux ratio is reduced, which is consistent with the obtained longest minority carrier lifetime. Moreover, we reveal that incorporation of a distributed Bragg reflector layer significantly reduces the defect density in the subsequent layers. Our results show that the combined analysis of Raman and TRPL spectra provide a powerful tool for understanding defect mechanism and carrier dynamics in GaAs/AlGaAs DH structures.
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# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>vii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiv</td>
</tr>
<tr>
<td>Chapter 1: Introduction and Motivation</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Significance of the Study</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Technology Review of CuIn$<em>x$Ga$</em>{1-x}$Se$_2$ Photovoltaic Devices</td>
<td>4</td>
</tr>
<tr>
<td>1.3 Classic Structure of CuIn$<em>x$Ga$</em>{1-x}$Se$_2$ Devices</td>
<td>5</td>
</tr>
<tr>
<td>1.4 CuIn$<em>x$Ga$</em>{1-x}$Se$_2$ Crystal Structure and Composition</td>
<td>6</td>
</tr>
<tr>
<td>1.5 Optical Properties of CuIn$<em>x$Ga$</em>{1-x}$Se$_2$</td>
<td>10</td>
</tr>
<tr>
<td>1.6 CuIn$<em>x$Ga$</em>{1-x}$Se$_2$ Film Fabrications</td>
<td>11</td>
</tr>
<tr>
<td>1.6.1 Coevaporation of CuIn$<em>x$Ga$</em>{1-x}$Se$_2$</td>
<td>12</td>
</tr>
<tr>
<td>1.6.2 Two-Step Process: Selenization of Metallic CuInGa Precursors</td>
<td>14</td>
</tr>
<tr>
<td>1.7 Scope of Dissertation</td>
<td>15</td>
</tr>
<tr>
<td>1.8 Outline</td>
<td>16</td>
</tr>
<tr>
<td>Chapter 2: Experimental Details</td>
<td>18</td>
</tr>
<tr>
<td>2.1 Physical sputtering deposition</td>
<td>19</td>
</tr>
<tr>
<td>2.2 Electron Beam Evaporation</td>
<td>23</td>
</tr>
<tr>
<td>2.3 Chemical Vapor Deposition</td>
<td>25</td>
</tr>
<tr>
<td>2.4 Chemical Bath Deposition</td>
<td>28</td>
</tr>
<tr>
<td>2.5 Time-Resolved Photoluminescence</td>
<td>30</td>
</tr>
</tbody>
</table>
2.6 Confocal Raman Spectroscopy ................................................................. 31
2.7 Solar Cell Characterization .................................................................... 33
2.8 Conclusion................................................................................................. 36

Chapter 3: Fabrication and Optimization of Back and Front Electrode Layers ........ 37
3.1 Optimization of Electrical and Adhesion Properties of Back Contact ............ 37
   3.1.1 Fabricating Molybdenum Films with Good Conductivity and Adhesion ....... 38
3.2 Optimization of Electrical and Optical Properties of ZnO:Al Front Contact ...... 44
   3.2.1 Effect of Chamber Back Ground Pressure on the Properties of ZnO:Al Films .... 45
   3.2.2 Effect of Argon Flux on the Properties of ZnO:Al Films ....................... 47
   3.2.3 Effect of Argon Working Pressure on Properties of ZnO:Al Films ............. 49
   3.2.4 Effect of Post-Deposition Annealing Treatment on Properties of ZnO:Al Films ...... 51
3.3 Conclusion................................................................................................. 53

Chapter 4: Optimization of CuIn\(_x\)Ga\(_{1-x}\)Se thin films by Sputtering and Selenization .... 55
4.1 Preparation of CuInGa Precursor Film with Structural and Chemical Homogeneity .... 55
4.2 Chemical Vapor Deposition System for Selenization .................................... 61
4.3 Fabrication of CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) Devices by two-step Selenization Process ............. 68
   4.3.1 The influence of Cu, In, Se stoichiometry on CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) device performance .... 70
   4.3.2 The Influence of Selenium Flux on CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) Device Performance ............ 75
   4.3.3 The Influence of Cracked Selenium on CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) device performance ............ 79
4.4 Conclusion................................................................................................. 82

Chapter 5: Optimization of the Defects and the Nonradiative Lifetime of GaAs/AlGaAs
Double Heterostructures .................................................................................. 83
5.1 Experimental Description............................................................................ 84
5.2 Effect of As/Ga Flux Ratio on the Defect Density of GaAs/AlGaAs Double Heterostructures

5.3 Effect of the Substrate Temperature on the Defect Density of GaAs/AlGaAs Double Heterostructures

5.4 Effect of the Distributed Bragg Reflector on the Defect Density of GaAs/AlGaAs Double Heterostructures

5.5 Effect of the Distributed Bragg Reflector on the Defect Density of GaAs/AlGaAs Double Heterostructures of various GaAs thicknesses

5.5 Summary

Chapter 6: Summary

Bibliography
List of Figures

Figure 1.1: Record efficiencies of CuInGaSe solar cells since 2006....................................... 4

Figure 1.2: Schematic cross-section and SEM cross section of a CuIn1-xGa1-xSe2 solar cell .... 6

Figure 1.3: Unit cell of chalcopyrite Cu(In,Ga)Se2. Each Se atom is the center of a tetrahedral 
bond with 2 Cu and 2 group II atoms. ...................................................................................... 8

Figure 1.4: Pseudobinary In2Se3-Cu2Se phase diagram........................................................... 8

Figure 1.5: Theoretical efficiency as a function of the band-gap energy .................................. 10

Figure 2.1: Sputtering chamber and sputtering process........................................................... 31

Figure 2.2: Schematic diagram of magnetron sputtering system............................................. 21

Figure 2.3: Schematic diagram of the electron beam evaporation system ............................... 24

Figure 2.4: Schematic diagram of the chemical vapor deposition system ............................... 26

Figure 2.5: Schematic diagram of the chemical bath deposition system .................................. 28

Figure 2.6: Schematic diagram of the time-resolved photoluminescence system ................... 31

Figure 2.7: Schematic diagram of the Raman Spectroscopy system ....................................... 32

Figure 2.8: Schematic diagram of the solar simulator system .................................................. 34

Figure 2.9: IV curve of a complete CIGS device in dark, and under illumination .................... 35

Figure 3.1: Sheet resistance as a function of Ar working pressure, and the results of the adhesion 
test ........................................................................................................................................... 41

Figure 3.2: Sheet resistance as a function of (a) sputtering power and; (b) sputtering time ...... 42

Figure 3.3: Sheet resistance as a function of the background chamber pressure before sputtering. 
.................................................................................................................................................. 46
Figure 3.4: Sheet resistance (solid sphere) and transmittance (open circles) are plotted as a function of the gas flow rate in (a) and the associated transmission spectra at different gas flow rate are displayed in (b). ................................................................. 47

Figure 3.5: XRD spectra for three AZO films sputtered at the flow rate of 10 sccm (a), 25 sccm (b), and 50 sccm (c) are displayed. ................................................................. 48

Figure 3.6: Measured values of sheet resistance and transmittance percentage of a ZnO:Al films as a function of Ar working pressure ................................................................. 50

Figure 3.7: Measured values of sheet resistance and transmittance of a ZnO:Al film. The first data point at 25 °C is for as sputtered at a gas flow rate of 30 sccm, a working pressure of 3 mTorr, and a background pressure of 1×10^{-6} Torr, and other data points are for the annealed at different temperatures. ............................................................................. 52

Figure 4.1: CuGa top and cross sectional scanning electron microscope images and the sputter yield ........................................................................................................................................ 56

Figure 4.2: In top and cross sectional scanning electron microscope images and the sputter yield. ........................................................................................................................................ 57

Figure 4.3 a) Top view and cross sectional SEM image of Mo/CuGa/In structure, b) Top view and cross sectional SEM of Mo/In/CuGa structure, c) Top view and cross sectional SEM of Mo/In/CuGa/In structure .................................................................................................................................. 60

Figure 4.4: Schematic diagram of the Chemical Vapor Deposition System. ................................. 64

Figure 4.5: Morphology and uniformity of the CuInGaSe absorber films as a function of CuInGa precursor fixture angle. The angles varied from 0 to 90 in 15 degree increments. ............... 67

Figure 4.6: Voc and Jsc of CuIn_{x}Ga_{1-x}Se films as a function of varying In and Cu content ...... 71
Figure 4.7: The surface SEM images of CIGS films selenized at a) 30 sccm, b) 50 sccm, c) 100 sccm.

Figure 4.8: \( V_{oc} \) and \( J_{sc} \) of CuInGaSe\(_2\) devices as a function a selenium flux rate.

Figure 4.9: \( V_{oc} \) and \( J_{sc} \) of CuInGaSe\(_2\) devices as a function a selenium cracking temperature.

Figure 5.1: Normalized Raman spectra of GaAs/Al\(_{0.5}\)Ga\(_{0.5}\)As DH structures grown at 595 °C with an As/Ga flux ratio of 15, 20 and 40.

Figure 5.2: Time-resolved photoluminescence (TRPL) spectra of GaAs/AlGaAs DH structures grown at 595 °C with As/Ga flux ratio 15, 20 and 40.

Figure 5.3: Normalized Raman spectra of GaAs/AlGaAs DH structures grown at 595 °C, and 550 °C.

Figure 5.4: Normalized Raman spectra of GaAs/AlGaAs DH structures grown at 595 °C with and without a Bragg reflector.

Figure 5.5: Raman scattering spectra of GaAs/AlGaAs DH structures grown with \( d=2 \) μm with and without the Bragg reflector.

Figure 5.6: TRPL spectra of GaAs/AlGaAs DH structures grown with \( d=2 \) μm with and without the Bragg reflector.

Figure 5.7: Raman scattering spectra of GaAs/AlGaAs DH structures grown with \( d=1 \) μm with and without the Bragg reflector.

Figure 5.8: TRPL spectra of GaAs/AlGaAs DH structures grown with \( d=1 \) μm with and without the Bragg reflector.

Figure 5.9: TEM images of optimized sample M1280 and non-optimized sample M1281. Selected area electron diffraction patterns of optimized sample M1280 and non-optimized sample M1281.
List of Tables

**Table 3.1**: Summary of deposition parameters, electrical properties including sheet resistance and resistivity, results of adhesion test and strain analysis of the as deposited Mo film............ 39

**Table 5.1**: Minority carrier lifetime and nonradiative recombination lifetime of GaAs/AlGaAs DH structures grown at 595°C with As/Ga flux ratios 15, 20 and 40. ................................. 89
Chapter 1: Introduction and Motivation

1.1 Significance of the Study

Since the beginning of the industrial revolution, the world population has been increasing exponentially, so is our need for energy resources. The United Nations projections predict that by 2050, the world population is expected to reach between 8.3 and 10.0 billion [1, 2]. While the global energy demand is at its peak due to fast growth of industrialization and population, fossil fuels are expected to be consumed in another 200-300 years. The impact of fossil fuel shortage was felt as early as 1970s and awareness about the energy crisis has led to research in alternative energy sources that are renewable and friendly to environment, including hydroelectric, wind, tidal, biomass and solar energy. In 2014, the world primary energy consumption was 13,699 Mtoe. Fossil fuels, including oil, coal, natural gas and biofuels made up for 91.1%, while non-conventional renewables made up only 1.4% of the world primary energy consumption. Meanwhile, photovoltaic (PV) solar energy makes up less than 1% of the worldwide electricity production. Even though solar energy makes up a very small percentage of the worldwide electricity production, it is growing with the highest rate each year. Between 2008 and 2013, average growth of electricity production from solar energy has increased 50% per year, and continues to grow. The mean incident solar power at the surface of the earth is 184 W/m², which is nearly 5000 times the global primary energy consumption, 16.9 TW. If we can utilize a fraction of the solar energy, not only can we address our energy problems, but also reduce the emission of greenhouse gasses released by fossil fuel consumption.
Currently, crystalline silicon, c-Si dominates the mainstream industry. Developed in the 1950s, crystalline silicon solar cells are often called the conventional, traditional, or first generation solar cells. The thickness of c-Si solar cells range from 160 to 200 µm and are generally the most efficient among other PV technologies. In 2013, the record laboratory efficiency was the highest for c-Si yielding 25.6%. Furthermore, commercially produced modules yield efficiencies near 23%. Conventional crystalline silicon based PV devices continue to dominate the worldwide PV production. However, because of high cost of production and fabrication complexities of c-Si, extensive efforts have been placed in thin-film photovoltaic (PV) technologies. Thin film PV devices are referred as the second generation solar cells. They are deposited on substrates and involve one or more thin layers or thin-film photovoltaic material. Thin film PV devices require less expensive raw materials and are stable and high performance devices. Three mainstream thin film PV technologies are amorphous silicon (a-Si) copper indium gallium di-selenide (CIGS) and cadmium telluride (CdTe) thin film based PV devices.

Among the thin-film technologies, CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} stands out as the one with the highest power conversion efficiency. CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} is a I-III-VI\textsubscript{2} compound semiconductor material composed of copper, indium, gallium and selenium. Unlike silicon, CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} is a direct bandgap semiconductor with bandgap varying from 1.0 eV to about 1.7 eV. CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} has an exceptionally high absorption coefficient of $10^5$/cm, so a layer of only 1-2 micrometers (µm) is enough to absorb most of the sunlight as opposed to silicon which requires thickness of 200-300 µm. The required layers in the CuInGaSe2 device are so thin that the devices are flexible when grown on thin substrates, enabling roll-to-roll deposition processes. Furthermore, CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} has proven excellent long term stability in indoor and outdoor testing, and is more tolerant to high energy radiation compared to other solar cell devices [3, 4, 5]. Hence CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} is emerging
as an excellent candidate for terrestrial and space applications. Since 2006, the record efficiency for CuIn$_x$Ga$_{1-x}$Se$_2$ modules increased from 13.5% to 18.0%, whereas, laboratory scale cell have increased from 20% to 22.6%, showing potential for improvement. Consequently, CuIn$_x$Ga$_{1-x}$Se$_2$ based devices remain to be interest in both laboratory and industrial scale.

The power conversion efficiencies of CuIn$_x$Ga$_{1-x}$Se$_2$ based devices still have a potential for improvement. The growth conditions, thicknesses, pre-and post-annealing of each layers of the device significantly affect the optoelectronic properties of those layers, mainly the bandgap, transparency, sheet resistance and carrier concentration. Thus, it is very important to investigate the growth conditions of the techniques used to grow the devices. While both the back-contact and the front contact need to be deposited with the lowest sheet resistance, the front contact needs to transmit as much light into the p-n junction in order to minimize their contribution to the series resistance of the cell. Furthermore, an ongoing challenge is to fabricate CuIn$_x$Ga$_{1-x}$Se$_2$ with smooth morphology and uniform homogeneity. Failure to fabricate CuIn$_x$Ga$_{1-x}$Se$_2$ with smooth surface morphology results in scattering of the incoming photons, thus reducing the absorbed light density. Moreover, CuIn$_x$Ga$_{1-x}$Se$_2$ films usually end up having two phases, an In rich phase with CuIn$_x$Se$_2$ at the top of the film, and a Ga rich phase with CuGa$_x$Se$_2$ at the bottom. Hence, the overall performance of the device is like that of CuInSe$_2$. Thus, it is crucial to investigate the deposition parameters and sequence Cu, In, Ga deposition in order to improve the CuIn$_x$Ga$_{1-x}$Se$_2$ film. Moreover, selenization setup and selenization conditions greatly affect the CuIn$_x$Ga$_{1-x}$Se$_2$ grain size, homogeneity and morphology. We demonstrate how the selenium flux angle, flux rate, and selenium temperature affects the CuIn$_x$Ga$_{1-x}$Se$_2$ grain size, homogeneity and morphology. Finally, we demonstrate how using optical techniques can reveal the effect of growing Distributed Bragg Reflectors (DBR) on the subsequent layers.
1.2 Technology Review of \( \text{CuIn}_{x}\text{Ga}_{1-x}\text{Se}_2 \) Photovoltaic Devices

The history of \( \text{CuInSe}_2 \) solar cells starts with synthesis of chalcopyrite \( \text{CuInSe}_2 \) by Hahn et al. in 1953 [6]. Following the synthesis of \( \text{CuInSe}_2 \), its structural, electronic and optical properties were investigated, and in 1973, \( \text{CuInSe}_2 \) was proposed as a photovoltaic material by Wagner et al. Bell laboratories accomplished 12% efficient CIGS solar cells by evaporating n-type CdS onto p-type monocrystalline \( \text{CuInSe}_2 \) in 1976 [7]. Furthermore, thin-film \( \text{CuInSe}_2 \) solar were fabricated with efficiencies around 5% in 1976 [8]. From then on, different companies started to fabricate CIGS solar cells and modules using different techniques. An efficiency of 11% has been achieved by Boeing Corporation using the three-source coevaporation of Cu, In, and Se in 1984 [9]. During the same time, Arco Solar reached efficiencies of 14% using the two-step process during which

![Figure 1.1: Record efficiencies of CuInGaSe solar cells since 2006](image-url)
Cu and In metallic precursors are reacted with H₂Se to form CuInSe₂ and was further doped with Na.

CuInSe₂ deposition methods demonstrated by Boeing Corporation and Arco Solar remain the most common methods to achieve the highest device and module efficiencies [10]. As a result of extensive research efforts during the past decades, many companies are pursuing the commercial development of and CuInₓGa₁₋ₓSe₂ based modules, including Shell Solar Industries, Wurth Solar, Energy Photovoltaics, In, International Solar Electric Technology, Global Solar Energy and Matsushita. An overview about the record efficiencies periodically published since 2006 is shown in Fig. 1.1. The performance of CIGS has reached a conversion efficiency of above 20.0% over an area of 0.5 cm² by the National Renewable Energy Laboratory (NREL and the Swiss Federal Laboratories for Materials Science and Technology (EMPA) [11]. An efficiency of 21.7% has been claimed by the German Zentrum fur Sonnenenergie und Wasserstoff Forschung (ZSW) which is the highest record among all thin film solar cells. Solar Frontier is the latest company to achieve a record, producing a 22.3% CIGS cell on December 8, 2015. Similarly, large area modules with efficiencies greater than 18% have been reported by Henergy and Solar Frontier.

1.3 Classic Structure of CuInₓGa₁₋ₓSe₂ Devices

While many processing technologies have been demonstrated for CuInₓGa₁₋ₓSe₂ devices, the general solar cell structure, implemented by Boeing is SLG/Mo/CuInₓGa₁₋ₓSe₂/CdS/i-ZnO/ZnO:Al/Ni/Al as shown in Fig. 1.2. Soda lime glass (SLG) is the most commonly used substrate. Molybdenum is deposited on SLG as the current collecting back contact, reflecting most of the unabsorbed light back into the Cu(In₁₋ₓGaₓ)Se₂ absorber. A 1.0-2.5 μm p-type Cu(In₁-
\( \text{Ga}_x\text{Se}_2 \) absorber layer is deposited on top of the molybdenum back contact, followed by a thin n-type cadmium sulfide (CdS) buffer layer with thickness of nearly 50 nm, forming the Cu(In\(_{1-x}\text{Ga}_x\))Se\(_2\)/CdS p-n junction. Then a high-resistance i-ZnO layer is deposited on the CdS to protect the CdS and Cu(In\(_{1-x}\text{Ga}_x\))Se\(_2\) layer from damage due to processing methods, followed by 500-600 nm aluminum doped zinc oxide, ZnO:Al, which serves to collect and move electrons out of the cell while absorbing as little light as possible. Following the ZnO:Al window layer, a current collecting grid completes the devices.

**Figure 1.2:** Schematic cross-section and SEM cross section of a typical CuIn\(_{1-x}\text{Ga}_x\)Se\(_2\) solar cell

1.4 CuIn\(_x\text{Ga}_{1-x}\)Se\(_2\) Crystal Structure and Composition

Cu(In, Ga)Se\(_2\) is a I-II-VI2 compound semiconductor with the chalcopyrite lattice structure. The chalcopyrite unit cell is face-centered tetragonal with tetragonal lattice constants
a=5.718 Å and c=11.553 Å, with ratio of lattice constants c/a≈2. In the unit cell of CuInSe$_2$, each Se atom is tetrahedrally bonded to two Cu atoms and two In atoms as shown in Fig. 1.3.

Similarly, Ga atoms replace the In atoms in the unit cell of CuGaSe$_2$, resulting in each Se atom tetrahedrally bonded to two Cu atoms and two Ga atoms. Furthermore, Ga can substitute In atoms to form the CuInGaSe$_2$ compound without altering the unit cell. The deviation from c/a≈2 is due to larger atom radius of In compared to Ga atoms and different strengths of Cu-Se, In-Se and Ga-Se bonds. The lattice constants a and c can be determined from the following relations:

\[
a = 5.783 \, \text{Å} - 0.171 \, \text{Å} \cdot x
\]

\[
c = 11.618 \, \text{Å} - 0.585 \, \text{Å} \cdot x
\]

where x is the compositional ratio Ga/(Ga+In) [12].
The ternary phase diagram shows the possible phases in the Cu-In-Se system. Polycrystalline Cu(In$_{1-x}$Ga$_x$)Se$_2$ thin films have compositions that vary between Cu$_2$Se and In$_2$Se$_3$ tie-line. In addition to the chalcopyrite Cu(In$_{1-x}$Ga$_x$)Se$_2$ phase, a number of ordered defect compound (ODC) phases also exist on this line. These ordered defect compound phases have chalcopyrite lattice structure with an ordered insertion of intrinsic defects. The pseudobinary phase

![Figure 1.4: Pseudobinary In$_2$Se$_3$-Cu$_2$Se phase diagram](image)

**Figure 1.4:** Pseudobinary In$_2$Se$_3$-Cu$_2$Se phase diagram

![Figure 1.3: Unit cell of chalcopyrite Cu(In,Ga)Se2. Each Se atom is the center of a tetrahedral bond with 2 Cu and 2 group II atoms.](image)

**Figure 1.3:** Unit cell of chalcopyrite Cu(In,Ga)Se2. Each Se atom is the center of a tetrahedral bond with 2 Cu and 2 group II atoms.
diagram in Fig. 1.4 shows the Cu$_2$Se-In$_2$Se$_3$ tie-line in more detail. $\alpha$ is the chalcopyrite CuInSe$_2$, $\delta$ is the high temperature (HT) phase of the $\alpha$-CIS and is unstable at room temperature.

The structure of $\delta$-CIS is sphalerite and its Cu and In atoms are randomly distributed on the cation sites. On the Cu-deficient side of the phase diagram, the $\beta$-CIS phase including CuIn$_2$Se$_{3.5}$, CuIn$_3$Se$_5$ and $\gamma$-CIS, CuIn$_5$Se$_8$ and indium sesquiselenide In$_2$Se$_3$ exist. The $\beta$-CIS is also called the ordered vacancy compound or ordered defect compound. At low temperatures, $\alpha$ phase, used in device quality films is relatively narrow, tolerating 24 to 25% at. Cu content. As the temperature is increased to 500 C, typical processing temperature, device quality films can be fabricated with 22 to 25% Cu content. Moreover, high performance devices can be fabricated with Cu/(In+Ga) ratios from 0.7 to 1.0. In other words, Cu content can vary from 17.5% to 25%. The chalcopyrite $\alpha$ phase can be widened by incorporation of Ga and Na. An important characteristic of CIGS is its ability to tolerate large variations in composition without appreciable differences in optoelectronic properties.
1.5 Optical Properties of CuIn$_x$Ga$_{1-x}$Se$_2$

Compared to other materials, including crystalline silicon, CuInGaSe has a very high absorption coefficient which makes it well suited for solar cell application. CuInGaSe exhibits a direct band gap, hence absorbs light more efficiently and require thinner material. When a monochromatic light penetrates the surface of an absorbing material, its intensity falls exponentially with depth, d, and is given by

\[ I(hv, d) = I(hv, 0) e^{-\alpha(hv)d} \]  

(1.3)

where \( \alpha(hv) \) is the absorption coefficient. For CuInSe$_2$, the absorption coefficient is \(2.0 \times 10^5 \text{ cm}^{-1}\) and is \(1.0 \times 10^3 \text{ cm}^{-1}\) for crystalline silicon for photon energy of \(hv = E_g + 0.2 \text{ eV}\) where \(E_g\) is

![Figure 1.5: Theoretical efficiency as a function of the band-gap energy](image-url)
the bandgap energy of the material. Most of the high-energy photons are absorbed very close to the surface of CIGS, and those that are slightly higher than the bandgap will penetrate deeper into the CIGS film.

The maximum efficiency for single-junction solar cells are obtained with bandgap energies between 1.1 and 1.5 eV as shown in figure #. Another advantage of CuInGaSe is that its bandgap can be engineered by tuning the Ga/In concentration ratio and also the Cu content. The bandgap of CuInSe2 is approximately 1.01 eV whereas the bandgap of CuGaSe is approximately 1.65 eV. The bandgap can be varied between 1.01 to 1.65 eV by alloying CuInSe2 and CuGaSe2 through the relations

\[ E_{g,CIGS}(x) = (1 - x)E_{g,CIS} + xE_{g,CGS} - bx(1 - x) \]  

(1.4)

and

\[ E_{g,CIGS}[\text{in eV}] \approx 1.01(1 - x) + 1.65x - 0.15x(1 - x) \]  

(1.5)

where \( x = \text{Ga/In+Ga} \) and \( b = 0.15-0.24 \text{eV} \) is the bowing parameter which describes the deviation from the linear relationship.

## 1.6 CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) Film Fabrications

Numerous thin film deposition methods have been investigated for fabricating Cu(In,Ga)Se2 thin films with high deposition rates, compositional uniformity, low cost while maintaining reproducibility. In all the deposition methods, the Cu(In,Ga)Se2 thin films exhibit a thickness of at least 1 \( \mu \text{m} \) with Cu, In, Ga, Se elemental composition similar to that of device
quality ratio. These deposition methods are usually listed under three broad approaches, each of which has advantages and disadvantages. The first approach is vacuum coevaporation, in which Cu, In, Ga and Se elements are simultaneously or consecutively evaporated onto a substrate and reacted at elevated temperatures. In the second approach, also called the two-step process, the Cu, In, Ga metallic precursors are deposited in a vacuum system, followed by the selenization process in which the metallic precursor is reacted in a Se atmosphere at elevated temperatures. The third approach, also called the non-vacuum approach involves preparation of Cu, In, Ga precursor film in atmospheric pressure, followed by the selenization process similar to that of the two-step process.

1.6.1 Coevaporation of CuIn$_x$Ga$_{1-x}$Se$_2$

Coevaporation of Cu(In,Ga)Se$_2$ absorber layer is considered as the most successful method for fabricating high efficiency devices, reaching up to 22.7% conversion efficiency. Coevaporation method involves simultaneous or sequential evaporation of Cu, In, Ga Se elements in a high vacuum chamber. During the deposition process, while the substrate is heated 450 to 550 C, the Cu, In, Ga, Se source temperatures vary for each element: 1300 to 1400 C for Cu, 950 to 1050 C for In, 1150 to 1250 C for Ga and 250 to 300 C for Se. The film composition, growth rate, and thickness are determined by Cu, In, Ga, Se flux rate and substrate temperature. The bandgap of the film is determined by the relative In and Ga content. Furthermore, the final composition of the film stands between (InGa)$_2$Se$_3$ and Cu$_2$Se pseudobinary tie-line. The most commonly performed coevaporation techniques are the one-stage process, Boeing process, and the three-stage process. Each method is distinguished by the evaporation sequence, evaporation rates and substrate temperatures.
Among the coevaporation deposition methods, the simplest approach for Cu(In,Ga)Se absorber is the one-stage process. The one-stage process, proposed by Shafarman et al. involves deposition of Cu, In, Ga and Se elements simultaneously at constant evaporation rates and constant substrate temperature [13]. Cu, In, Ga and Se evaporation rates are adjusted to yield a Cu-poor film with Cu/(In+Ga)≈0.85 and Ga content with Ga/(In+Ga) ≈0.35. The one-stage process, first proposed by Shafarman et al. has yielded conversion efficiencies up to 15%.

The Boeing process, also called the two-stage process was first proposed by Mickelsen and Chen [14]. The deposition is similar to that of a single-step process, all the Cu, In, Ga, Se rates and substrate temperature are varied during the deposition process. The deposition involves two-stages. In the first stage, Cu, In, Ga Se are evaporated at substrate temperatures of 400 to 450 C to yield a Cu-rich film, Cu/(In+Ga)>1. In the second stage, In and Ga deposition rates are increased and the substrate temperature is elevated to 500 to 550 C to yield an overall Cu-poor final absorber layer with Cu/(In+Ga) ≈0.85. The advantage of the first-stage is, Cu-rich films yield much larger grain size compared to that of the one-stage process film.

Developed by the National Renewable Energy Laboratory (NREL) the three stage process has yielded the most efficient CIGS solar cells, exceeding 21% [15] [16] [17]. It consists of three stages. In the first stage, a Cu-poor (In,Ga)2Se3 precursor is deposited during which In, Ga, Se are simultaneously evaporated at low substrate temperature of 250 to 400 C. During the second stage, the substrate temperature is elevated to 500 to 550 C and Cu and Se are coevaporated, reaching Cu-rich phase with Cu/(In+Ga)>1. During the third stage, the substrate is kept at the same temperature and In, Ga and Se are evaporated in order to reach a final Cu-poor composition of Cu/(In+Ga) ≈0.85. The three-stage process provides comparatively smooth surface, reducing the number of defects at the junction.
1.6.2 Two-Step Process: Selenization of Metallic CuInGa Precursors

The two-step process, first demonstrated by Grindle et al. involves deposition of Cu, In, Ga metallic precursor film on a substrate, followed by the selenization process in which the metallic precursor is reacted in a Se atmosphere at elevated temperatures [18]. The metallic precursor is deposited with a low cost, high deposition rate and good uniformity system. Numerous deposition processes have been demonstrated including sputtering, electron beam evaporation, screen printing, thermal evaporation and electrodeposition. CuInGa precursor films may or may not include Se, and can be stacked in various sequences or combinations. Deposition parameters and Cu/In/Ga/Se stoichiometry are often controlled to determine the spatial uniformity and the final composition of CuInGaSe absorber film. The deposited precursor film is then reacted in Se or H₂Se vapor at elevated temperatures of 400 to 600 °C for a duration time of 30 to 60 minutes. While reacting the precursor film with H₂Se vapor has yielded better performance devices compared to Se vapor, it is highly toxic and requires precautions. An alternative approach is, depositing Se on top of the precursor, followed by an annealing step using rapid thermal processing (RTP) system.

CuInSe₂ formation from elemental Cu, In, Se has been investigated by x-ray diffraction of time-progressive reactions, and by in situ differential scanning calorimetry. Formation of CuInSe₂ begins with Cu₁₁In₉ and In liquid with small concentration of dissolved Cu. These then react with Se and follow a sequence of reactions:

\[ 2InSe + Cu₂Se + Se \rightarrow 2CuInSe₂. \] (1.6)
The reaction chemistry is the same for the reaction of Cu/In layers in both Se vapor and H\textsubscript{2}Se vapor. While the reaction duration is temperature dependent, at 400 C, the reaction will complete in nearly 15 minutes. Regardless of the deposition method, incorporating Ga into CuInSe\textsubscript{2} film will result in accumulation of Ga near the Mo back contact. The resulting absorber layer is Mo/CuGaSe\textsubscript{2}/CuInSe\textsubscript{2} and resembles the behavior of CuInSe\textsubscript{2}.

### 1.7 Scope of Dissertation

Fabricating high quality CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} solar cell modules requires a CuInGa precursor with smooth surface morphology, and uniform chemical homogeneity. Since the surface energies of indium, copper, gallium and molybdenum are different, it is difficult to fabricate CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with smooth surface morphology and chemical homogeneity using post selenization process. The deposition conditions and of copper, indium and gallium sputtering sequence metallic must be carefully studied to yield the best chemical homogeneity, surface morphology of the CuInGa film, as well as the CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films during the chalcogenization process.

The primary issue involving the selenization process in chemical vapor deposition system is, fabricating uniform CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with reproducible results. The selenium pressure and selenium diffusion rate must be precisely controlled to ensure sufficient Se vapor pressure in the reactor chamber to produce CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with the correct stoichiometry. Furthermore, the selenium vapor flow must be regulated to control the Se diffusion rate into the CuInGa precursor as well as the thickness of the MoSe\textsubscript{x} film at the Mo/ CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} interface.

Another issue involving the selenization process is, the Ga-related binary selenides are buried by fast growth of In-related binary selenides. This is due to reaction activation energy of In-Se is much lower than that of Ga-Se activation energy at low temperatures. As a result, the In-
rich CuIn$_x$Ga$_{1-x}$Se$_2$ grains cover the top of the film, while the Ga-rich grains aggregate near the backside. This leads to phase separation of in the CuIn$_x$Ga$_{1-x}$Se$_2$ films. Consequently, the film behaves like CuInSe$_2$, inducing a low open circuit voltage and efficiency of the device. Furthermore, during the selenization process, the selenium source affects the resulting CuIn$_x$Ga$_{1-x}$Se$_2$ properties drastically. Elemental vapor selenium can be incorporated into the CuInGa precursor at reaction temperatures above 500 °C. This can be improved with the use of H$_2$Se. H$_2$Se is commonly used because it easily reacts with the CuInGa precursor to form stale ternary selenides due to its high chemical and diffusive activity. However, H$_2$Se is expensive, highly toxic and explosive, hence must be replaced with a more efficient selenium source.

### 1.8 Outline

Chapter 1 provides introduction and motivation for investigating CuIn$_x$Ga$_{1-x}$Se$_2$ based photovoltaic devices and introduces the currently existing problems in improving the performance of CuIn$_x$Ga$_{1-x}$Se$_2$ based photovoltaic devices. This is followed by the technology review and classic structure of CuIn$_x$Ga$_{1-x}$Se photovoltaic devices, as well as the crystal structure and optoelectronic properties of CuIn$_x$Ga$_{1-x}$Se absorber layer. Finally, the chapter discusses CuIn$_x$Ga$_{1-x}$Se absorber film deposition methods.

Chapter 2 consists of a brief review of fundamental concepts and a detailed discussion of all the fabrication and characterization techniques. In particular, we discuss magnetron sputtering deposition, chemical vapor deposition, electron beam evaporation deposition, chemical bath deposition, Raman spectroscopy and time-resolved photoluminescence spectroscopy techniques.

Chapter 3 discusses investigation of deposition parameters to optimize the structural, electrical, optical and adhesion properties of molybdenum, Mo, back contact and aluminum-doped
zinc oxide, ZnO:Al, front contact of CuIn$_x$Ga$_{1-x}$Se$_2$ photovoltaic devices. Both films are deposited using magnetron sputtering, and their electrical resistivity, morphological, structural, optical and adhesive properties have been examined with respect to the deposition parameters and post-deposition annealing treatment.

Chapter 4 presents investigation of deposition parameters to optimize the uniformity, morphology and homogeneity of CuInGa precursor and CuIn$_x$Ga$_{1-x}$Se$_2$ thin films. CuInGa film was deposited using magnetron sputtering, and selenization process was performed by two step chemical vapor deposition method. Next, we introduce the design and assembly of chemical vapor deposition system in order to perform uniform films with reproducible results. Next, we show the effect of Cu/In ratio tuning, Se flux and thermal cracking of Se on the CuIn$_x$Ga$_{1-x}$Se$_2$ device performance.

Chapter 5 presents our complementary use of Raman spectroscopy and time-resolved photoluminescence (TRPL) measurements to optimize the growth parameters for improving crystalline defect density, heterojunction interface quality, and minority carrier dynamics in GaAs DH structures.

Finally, the last chapter summarizes the key findings.
Chapter 2: Experimental Details

In this chapter, we discuss the different experimental methods and setups used to fabricate and characterize our CuIn$_x$Ga$_{1-x}$Se$_2$ and GaAs/AlGaAs devices. The fabrication methods, including magnetron sputtering, low pressure chemical vapor deposition (LPCVD), electron beam evaporation deposition (EBPVD) and chemical bath deposition are discussed in sections 3.1 to 3.4. The optoelectronic characterization tools, including IV curve measurements, Raman spectroscopy, time-resolved photoluminescence, are discussed in sections 3.5 to 3.7.
2.1 Physical sputtering deposition

Physical sputter deposition is a widely practiced thin film deposition technique for large scale commercial production to fabricate uniform films on large substrates, with high deposition rates. This section describes the sputtering process and focuses on the fabrication parameters relevant for this thesis work. The CuInGa, ZnO, ZnO:Al, Mo films described in this thesis have been fabricated in a commercial magnetron sputtering system. Physical sputtering is a thin film deposition technique, where high energy particles strike the surface of source materials, called targets, and release the surface atoms of the targets. Physical sputtering relies on the transfer of physical momentum and kinetic energy from the incident particle to the surface atoms. Sputtering species can be atoms, ions, electrons, photons, neutrons as well as molecules and molecular ions. The most commonly used sputtering species include ions such as $\text{Ar}^+$ and $\text{Kr}^+$, or small molecular ions such as $\text{N}_2^+$, and $\text{O}_2^+$. The released surface target atoms are accumulated onto a nearby substrate on which the thin film grows. Sputter deposition takes place in a tightly sealed high vacuum chamber. Both the source material, target, and the substrate are held at a close range, facing each other.

The sputter yield is the average number of atoms ejected from the target per incident sputtering species.

\[
\text{Sputter yield, } Y = \frac{\text{average number of emitted particles}}{\text{incident sputtering species}}
\]  

(2.1)

Two modes of diode sputtering, DC and RF are used in almost all sputtering systems. Sputtering metals usually takes place in DC sputtering, whereas sputtering insulators usually takes
place in RF sputtering. During DC sputtering, inside the sputtering processing chamber, a power supplier is connected to the target, which serves as the cathode (negative potential), and the substrate holder as well as the walls of the processing chamber serve as the anode (positive potential). This generates a uniform electric field, and potential difference between the cathode and the anode. Under vacuum conditions, adequate voltage across the electrodes is generated. An inert gas is introduced into the chamber with a desired pressure. The electric field ionizes the inert gas atoms, resulting in a plasma discharge. The electrons will accelerate present toward the anode, and ions will accelerate toward the cathode and strike the surface of the target. This collision will create collision cascades between atoms within the target surface region. Surface atoms, as well as secondary electron, ions, photons and clusters are thus ejected from the target, referred to as physical sputtering. These atoms then traverse the chamber to condense onto the substrate and form a thin film of the target material. During RF sputtering, the cathode and the anode are electrically reversed. The standard frequency used in the RF sputtering source is 13.56 MHz. This eliminates charge buildup on an insulating surface. The plasma density during RF sputtering is also higher than that of DC sputtering. As a result, RF sputtering exhibits high deposition rates at low voltages and low sputter pressures. Sputtering systems also use a static magnetic field confined at the cathode location. The magnetic field is located parallel to the cathode surface and perpendicular to the electric field lines. Secondary electrons which are emitted from the cathode due to ion bombardment are constrained in this region, increasing the plasma density. The magnetic field causes the secondary electrons to remain in path in the ExB direction, trapping the electrons near the cathode surface. This magnetic field results in enhanced ion bombardment and
higher DC and RF sputtering rates.

The sputter system used in our work is a Denton Vacuum magnetron sputtering system as shown in Fig. 2.1. Metallic films were deposited by direct current (DC) magnetron sputtering, and oxide films were grown by radio-frequency (RF) sputtering. The processing chamber is a cylindrical stainless steel with dimensions of 30” ID x 18”. The chamber door as well as the top plate of the chamber can be opened to access the targets and the substrates. Three equally spaced cathodes are mounted to the center of the top plate. Two cathodes are used for DC sputtering and one cathode is used for RF sputtering. All three cathodes have static magnets situated parallel to the surface of the cathodes. The targets are mounted to the planar cathodes and are held at a close range from the rotating substrate holder which serves as the anode surface. Both the substrate holder and the walls of the sputtering chamber are grounded. For DC sputtering ENI DC plasma generator power supply is used; for RF sputtering Cesar RF power generator and matching network

![Schematic diagram of magnetron sputtering system](image)

**Figure 2.1: Schematic diagram of magnetron sputtering system**
is used. Disk shaped targets are manufactured by Angstron Sciences and Kurt Lesker Co. with 3” diameter and 2.5” thickness. Samples are introduced into the processing chamber through the loadlock. Both the loadlock and the processing chamber are pumped down with a rotary pump reaching less than 1.0e-2 Torr. The processing chamber is then pumped down with the aid of Varian Turbo-V 300HT turbo pump with 50k rpm, reaching a base pressure of 10e-7 Torr, which is detected by an Inficon manometer vacuum gauge. An MKS instruments flow meter is used to regulate the gas flux into the chamber. The experimental parameters, such as the gas flux, power and pressure can be viewed and adjusted on the color touch panel of the system.

In this research, the Mo, CuInGa, ZnO, ZnO:Al films are deposited using the magnetron sputtering system. Each film is deposited in high vacuum level in order to prevent contamination. Prior to deposition, the substrates are pretreated in a vacuum oven at 100 °C for 10 min to eliminate moisture on the substrate surface. After the heat treatment, the substrates are immediately loaded into the sputtering system through the load lock and transferred to the processing chamber. After the samples are transferred to the processing chamber, the deposition parameters are adjusted on the control panel. First the sputtering power, P=IV, which determines the cathode-anode potential difference, V, is adjusted. Next, the Ar flow rate in cm³ is adjusted to control the Ar⁺ plasma in the chamber. Next, the turbo-pump valve position is tuned in order to adjust the Ar⁺ plasma pressure in the processing chamber. The pre-sputter and sputter duration time are also adjusted. First, the pre-sputtering takes place in order to etch the surface of the target which may be contaminated. During pre-sputtering, which takes about 5-10 min, both the target shutter and the substrate shutter are closed, hence no deposition takes place. After pre-sputtering, both the target shutter and the substrate shutter turn on, and the deposition takes place. To ensure uniform deposition, the
substrate holder rotates. The sputter time is between 10-20 minutes depending on the deposited film.

2.2 Electron Beam Evaporation

Electron beam physical vapor deposition is a deposition technique in which a target material is bombarded with an electron beam under high vacuum. The electron beam causes the atoms in the target material to transform from solid to vapor phase. These atoms then precipitate into solid form, coating the substrate with a thin layer of the target material. An electron gun assembly produces the beam of electrons. The tungsten filament is heated in the electron gun, releasing electrons by thermionic emission. The electrons are deflected toward the target material with the aid of focusing and deflecting magnets. Once the electron beams contact the target material, the material is heated up to a boiling point. Once the boiling point is reached, the solid molecules turn into liquid, then vapor, and the deposition takes place. The deposition takes place under high vacuum to allow target material atoms to move freely in the chamber.
The schematic experimental setup of the e-beam evaporator used in our research is shown in Fig. 2.2. Sharon Vacuum electron-beam evaporation system was used with deposition chamber of dimensions 24” x 24” x 18”. The deposition chamber was pumped down with rotary pump and CT-8 cryo pump. The power supply with 9 kV electron beam gun and the deflection and focusing apparatus is by TT6-Telemark. Sycon deposition controller was used and the chamber pressure was controlled with Granville-Phillips Vacuum Gauge Controller.

![Figure 2.2: Schematic diagram of the electron beam evaporation system](image)

In this research, the Ni and Al contact films have been deposited using the electron beam evaporation deposition system. In an experiment, an aperture mask is placed on top of the solar cell device, and the metal contact is deposited in the shape of a grid to allow as much light as possible into the device. During the metal contact deposition process, 50 nm of Ni is deposited in order to avoid the formation of high resistance oxide layer, followed by 5.0 µm of Al using the
electron beam evaporator. In the target holder, crucibles 2 and 4 are filled with Al and Ni pellets respectively. After loading the sample and the pellets, the chamber door is closed. Both the chamber and the cryopump are pumped with a rotary pump to reach 500 mTorr. After the cryopump pressure reaches 500 mTorr, helium recycler is turned on and purged into the cryopump cavity to lower its temperature and pressure. After about two hours, the temperature of the cryopump cavity reaches 15 K. Following this, the high vacuum valve in the chamber is turned on, and the chamber pressure reaches $1 \times 10^{-7}$ Torr. On the power supplier, the accelerating voltage is adjusted to 7 kV while the current is tuned from 0 mA to 1 A, until the electron beam strikes the target region. Next, the sweeping amplitude and frequency of the magnets are adjusted to uniformly heat up the pellets in the crucibles. After the crucible is heated and deposition starts taking place, the sample shutter is removed and the deposition takes place. The thickness of the film is monitored from the Sycon deposition controller. After the deposition, the acceleration voltage and current are turned off, the high vacuum valve is closed and nitrogen is purged in to vent the chamber.

2.3 Chemical Vapor Deposition

Chemical vapor deposition (CVD) is used to produce high quality, high performance solid materials. Chemical vapor deposition is a process in which the chemical constituents evaporate and then decomposes on the substrate surface and reacts to produce the desired deposit. The deposition species are atoms or molecules or a combination of these. A typical CVD setup involves a gas supply system, a reactor system, exhaust system and a control system. Inside the LPCVD reactor is the reaction chamber. The reaction chamber consists of a source zone where the Se powder is evaporated, and a sample zone where the CuInGa precursor is reacted with Se vapor.
The control system regulates the reaction time, temperature and the gas supply system. While the gas supply system provides the carrier gasses to carry the Se source vapor into the sample zone in the reaction chamber, the exhaust system serves to remove the waste gases through rotary pump and reduces the reaction chamber pressure required for the process.

The schematic diagram of our CVD system is shown in Fig. 2.3. The CVD reactor consists of a dual zone MTI OTF-1200X-II-UL steel furnace with dimensions 590 mm(L) x 380 mm (W) x 520 mm (H). The reactor has a dual zone which include a sample zone and a source zone. Each zone has a length of 20 mm whose temperature can be adjusted from room temperature to 1200 °C through Joule heating. The control module on the furnace is used to program the reaction time as well as the heating and cooling rates. Inside the reactor, the reaction chamber, which consists of an 800 mL quartz tube is installed. The reaction chamber is sealed with vacuum flanges. In the gas supply system, MFC-A digital mass flow controller as well as NIST traceable
anti-corrosive digital vacuum gauge and controller are installed in order to control both the gas flow and pressure in the reactor chamber. Immediately exiting the CVD reactor, the exhaust gas collection system was installed in order to trap the residual Se gas. The exhaust gas collection system consists of 30 cm long ¼” thick stainless steel pipe which was partially bent. The bent portion of the pipe was placed in ice bath during the selenization process to condense the unreacted Se vapor. A 240 L/m heavy duty double stage rotary vane vacuum pump with exhaust filter is installed to remove the waste gases and to reduce the reaction chamber pressure required for the process. Each component in the CVD system is connected through ¼” thick stainless steel pipes, while a series of needle valves are installed to manually control the carrier gas flow and the pressure within the CVD system.

In this research, the selenization process, where incorporation of Se into the CuInGa precursor film and chalcogenization process takes place through chemical vapor deposition. A typical experiment involves placing SLG/Mo/CuInGa precursor into the sample zone, and a chemically pure selenium powder (99.9999%) into the source zone. To fabricate a uniform CuInGaSe film, the SLG/Mo/CuInGa precursor was placed on a custom designed graphite holder, and the Se powder was placed in a graphite boat. Nitrogen (99.99%) was used as a carrier gas. The vacuum flanges are tightened to maintain a vacuum level. The rotary pump is then turned on until the reaction chamber reaches its base pressure. Once the reaction chamber reaches its minimum pressure, the N2 gas is turned on and the chamber is flushed with N2 three times. Next, the temperature profile of the source and sample zone is adjusted in the control module. In order to control the Se vapor flow and pressure during the selenization process, the MFC-A digital mass flow controller is adjusted and the needle valves are tuned until the desired pressure in the chamber is reached and monitored by the NIST digital vacuum gauge and controller. The selenization
process takes place for 90 min. After the selenization process is over, when the sample zone temperature gets lower than 300 °C, open the furnace lid is opened for faster cooling. After the sample zone temperature indicates 40 °C, MFC-A digital mass flow controller, NIST digital vacuum gauge, the N2 gas as well as all the valves are turned off along with the rotary pump. The samples are then unloaded.

2.4 Chemical Bath Deposition

Chemical bath deposition (CBD) also referred to as the chemical solution deposition is a thin film deposition technique in liquid phase. Among thin film deposition techniques, CBD stands out for being simple, low temperature, large area and cost effective deposition technique which yields stable, adherent, uniform films with good reproducibility. CBD has been extensively used

Figure 2.4: Schematic diagram of the chemical bath deposition system

out for being simple, low temperature, large area and cost effective deposition technique which yields stable, adherent, uniform films with good reproducibility. CBD has been extensively used
in growing group II-VI semiconductors, such as CdS [18, 20-47], CdSe [48-54], CdO [55-58],
HgS [59- 61], HgSe [54, 62, 63], ZnS [64-75], ZnSe [76-83], and ZnO [84-94].

The CBD film deposition takes place by immersing the substrate in to a chemical bath
containing the solution which comprises the precursors, materials to be deposited, and a
complexing agent. The deposition takes place by a chemical reaction of the dissolved precursors
with the help of the complexing agent. The deposition rate is controlled by the bath temperature,
pH of the solution and concentration of the chemicals. The growth of the thin films occur by
nucleation and particle growth to form a stable, adherent, uniform solid phase films. The cadmium
sulfate film, CdS, described in this thesis have been fabricated by chemical bath deposition.
Deposition of CdS is made in a chemical bath with constituents including the cadmium salt CdSO₄,
the complexing agent ammonia NH₃, and the sulfur precursor thiourea, SC(NH₂)₂.

The apparatus for CBD is shown in Fig. 2.4. It consists of a hot plate and magnetic stirrer
to maintain uniform temperature in the chemical bath. On top of the hot plate, a glass container
with water is placed and heated up to a desired temperature while the temperature is monitored
with a thermometer. In the glass container, a beaker is placed holding the solution with cadmium
salt CdSO₄ the complexing agent ammonia NH₃, and the sulfur precursor thiourea, SC(NH₂)₂. The
CuInGaSe film is then immersed in the beaker and the film deposition takes place for 15 minutes
at 75 °C. The reaction follows the formula:

\[
\text{Cd}(NH₃)₄^{2+} + \text{SC}(NH₂)₂ + 2OH^- \rightarrow \text{CdS} + H₂NCN + 4NH₃ + 2H₂O
\]  

(2.2)

The resulting CdS lattice structure is a combination of cubic and hexagonal structure, with
a grain size of the order of few nanometers. In this research, the CdS films were deposited by
chemical bath deposition on SLG/Mo/CIGS substrates. The chemical bath deposition apparatus consists of a hotplate with a magnetic spin control. In an experiment, a 1000 mL beaker is filled halfway with water and placed on the hotplate. While the temperature of the hotplate is adjusted to 225 °C, a thermometer is immersed into the beaker to monitor its temperature. Simultaneously, the chemical bath for CdS deposition is prepared in a 250 mL beaker. Inside the chemical bath beaker, 0.065 g cadmium sulfate, 1.14 g thiourea, 25 mL ammonium hydroxide is placed, and the beaker is filled with deionized water upto 200 mL. All the chemical constituents are mixed for 10 min. At the same time, the SLG/Mo/CIGS structures are mounted on a holder using a double-sided scotch tape, and immersed in the chemical bath. Once the temperature of the 1000 mL beaker reaches 78 °C the chemical bath is immersed in it, and the deposition takes place for 15 min. After the deposition, the samples are taken out, rinsed with de-ionized water, blow dried with compressed nitrogen, and placed in a vacuum oven at 100 °C for 10 minutes so the CdS layer can diffuse into the CIGS layer.

2.5 Time-Resolved Photoluminescence

Time-resolved photoluminescence (TRPL) is a contactless technique used to investigate the charge carrier dynamics in semiconductors. TRPL is carried out by exciting samples with a pulsed laser source, and then measuring the subsequent luminescence decay as a function of time. During the experiments, the short laser pulses generates electron-hole pairs that decay to lower energy levels of the sample. These electron hole pairs can subsequently recombine and emit light. The emitted light is composed of a set of wavelengths corresponding to transition energies of the
sample and as a result, the measurement of the optical spectrum as a function of time provides a means to measure the transition energies and their lifetimes. The experimental setup for taking TRPL measurements is shown in Fig. 2.5 Samples were excited using a 250-kHz repetition rate, ultrafast 632-nm laser (~1.5-mm beam diameter) that was derived from frequency doubling the output of a regenerative amplifier-pumped optical parametric amplifier. Photoluminescence was detected through a 700-nm long-pass filter, to minimize the laser scattering signal, with a fast 300-m diameter Si photodiode. Data were acquired on a PCI averager card. The system response was measured to be ~2 ns.

### 2.6 Confocal Raman Spectroscopy

Confocal Raman spectroscopy is a contactless spectroscopic technique used to observe vibrational, rotational and other low-frequency modes in materials. The laser light interacts with molecular vibrations, phonons, or other excitations in the system, resulting in the energy of the
laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system. Incident laser light is directed onto the material and the scattered signal is composed of Elastic scattered radiation, Rayleigh scattering, which is filtered out while the rest of the inelastic light, called Raman scattering, is collected with a lens and sent through a monochromator. Raman scattering only occurs if the laser-induced collective vibrations alter the molecular polarizability of the probed material. The resulting Raman intensity peak positions depend on mechanical parameters such as bond length, bond strength, atomic masses, and molecular symmetry while the Raman intensities depend on electronic parameters such as band structure, and charge defect concentrations.

![Figure 2.6: Schematic diagram of the Raman Spectroscopy system](image)

The experimental setup for taking Raman scattering measurements is shown in Fig. 2.6. Raman scattering measurements of MBE-grown GaAs/AlGaAs DH structures were obtained at
room temperature using a 5145 Å line of Ar-ion laser at normal incidence for excitation. The laser beam was focused to a diameter of 2.0 µm on the samples with 10.0 mW of power, and the scattered signal was analyzed using MonoVista confocal Raman microscope with SP 2750 series spectrograph in the backscattering geometry. Data were acquired using thermoelectrically-cooled PIXIS: 400 CCD detector. Spectrum acquisition time was held at 60 s to eliminate the sample heating effects.

2.7 Solar Cell Characterization

Solar simulator is a controllable indoor test facility that provides illumination approximating natural light for the testing of solar cells, materials and devices. The solar simulator provides continuous illumination in time with intensity of 1000 W/m2, which is the full sunlight intensity on a bright clear day on earth. The solar simulator is utilized to measure the I/V curve, along with the conversion efficiency, maximum power output, fill factor, series resistance, resistivity and shunt resistance of solar cells and other materials and devices. Conventional solar simulators include a power supplier for the xenon lamp, which serves as the light source, a source meter which measures the device current and voltage while applying bias voltage during the measurement. The obtained data is then processed in a simulation software. The experimental setup for the solar simulator is shown in Fig. 2.7. The solar simulator consists of Newport 94021A Class ABB source, which uses xenon lamp supplying 1 sun output power. Keithley 2400 sourcemeter was used to measure the I/V curve while applying bias voltage during the experiments. The data was obtained and processed using LabVIEW software.
After the solar cell device is complete the devices are prepared for I-V curve measurement on the solar simulator station. Each device is sliced into 16 smaller sections and the Mo back contact is exposed in one corner by removing the layers on top of the Mo through mechanical scribing. Then, metal wires are soldered on top and bottom contacts. The clips of the I-V measurement station are then connected to the top and bottom contacts of the device. Next, the power of the solar lap is turned on, followed by the lamp shutter. Simultaneously, the multimeter is turned on. On the computer, on LabVIEW program, I-V measurement file is opened. When ready, the program is run. While the voltage is swept from -4 V to 4 V, the corresponding current is collected from the device in dark and upon illumination. After the I-V curve is measured, the data is automatically saved. The saved data is then transferred into OriginPro software for analysis.

Figure 2.7: Schematic diagram of the solar simulator system

![Schematic diagram of the solar simulator system](image)
From the IV curve, the device performance parameters can be derived. In the absence of light illumination, the PV cell has the same electrical characteristics as a diode with the current-voltage, I-V characteristics curve as shown in Fig. 2.8. As the intensity of the light increases, the IV curve shifts equal to the amount of the light generated current. The short circuit current, \( I_{SC} \), is the light generated current, and is the maximum current, occurring at the beginning of the forward bias sweep, when the voltage is zero.

\[
I_{SC} = I(V = 0) = I_{MAX} = I_L
\]  \hspace{1cm} (2.2)

The open circuit voltage, \( V_{OC} \), is the maximum voltage difference across the device for a forward-bias sweep and occurs when there is no current passing through the device:

\[
V_{OC} = V(I = 0) = V_{MAX}
\]  \hspace{1cm} (2.3)
The electrical power generated by the device can be calculated along the IV curve with the equation $P=IV$. The maximum power will be between the two limits $V_{OC}$ and $I_{SC}$ at which the power equals to zero. The voltage and current at the maximum power, $P_{MAX}$, are indicated as $V_{MP}$ and $I_{MP}$ respectively. Fill factor, FF, is a measure of the quality of the PV device. It is defined as the ratio of the maximum power, $P_{MAX}$, to the theoretical power, $P_T$, which is calculated using the open circuit voltage, $V_{OC}$, and short circuit current, $I_{SC}$.

$$FF = \frac{P_{MAX}}{P_T} = \frac{I_{MP}V_{MP}}{I_{SC}V_{OC}}$$

(2.4)

Fill factors typically vary from 0.5 to 0.82. Efficiency, $\eta$, is the ratio of the electrical power output, $P_{OUT}$, compared to the solar power input, $P_{IN}$, into the PV cell. Maximum efficiency is taken to be the ratio of $P_{MAX}$ to $P_{IN}$:

$$\eta = \frac{P_{OUT}}{P_{IN}} \rightarrow \eta_{MAX} = \frac{P_{MAX}}{P_{IN}}$$

(2.5)

### 2.8 Conclusion

In summary, this chapter discusses the experimental techniques and setups used to fabricate and characterize our CuIn$_x$Ga$_{1-x}$Se$_2$ and GaAs/AlGaAs devices. The fabrication methods, including magnetron sputtering, low pressure chemical vapor deposition (LPCVD), electron beam evaporation deposition (EBPVD) and chemical bath deposition are discussed in sections 3.1 to 3.4. The optoelectronic characterization tools, including IV curve measurements, Raman spectroscopy, time-resolved photoluminescence, are discussed in sections 3.5 to 3.7.
Chapter 3: Fabrication and Optimization of Back and Front Electrode Layers

This chapter presents investigation of deposition parameters to optimize the structural, electrical, optical and adhesion properties of molybdenum, Mo, back contact and aluminum-doped zinc oxide, ZnO:Al, front contact of CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} photovoltaic devices. Both films were deposited using magnetron sputtering, and their electrical resistivity, morphological, structural, optical and adhesive properties have been examined with respect to the deposition parameters and post-deposition annealing treatment. Section 4.1.1 discusses optimization of Mo film with bi-layer structure where the lower layer is deposited with high pressure, and upper layer is deposited with low pressure and high sputtering power. Section 4.2.1 discusses the importance of having a minimal chamber background pressure to deposit high quality ZnO:Al films. Section 4.2.2 shows that increased Ar flux improves the crystallization, increases the grain shape and size, and reduces intergranular voids of the ZnO:Al film. Section 4.2.3 discusses that lower sputter pressure increases transmittance of light due to reduced grain boundary scattering of light. Section 4.2.4 shows that post-deposition annealing treatment in hydrogen atmosphere enhances the conductance and transmittance of the film. Section 4.2.5 summarizes the results presented in this chapter.

3.1 Optimization of Electrical and Adhesion Properties of Back Contact
3.1.1 Fabricating Molybdenum Films with Good Conductivity and Adhesion

Mo has emerged as the dominant choice for the back-contact layer because of its high conductivity, good chemical stability, high melting point and possibility for forming Ohmic contact [19] [20] [21]. Mo film sheet resistance and adhesion properties are drastically influenced by sputtering power and working gas pressure. Mo films deposited at high pressures exhibited good adhesion property, but suffered from high sheet resistance. In contrast, Mo films deposited at low pressures exhibited poor adhesion property, but had low sheet resistance. A delicate balance between sheet resistance and good adhesion property must be attained in order to obtain Mo film with optimized conditions. In this section, we present optimization of residual stress, adhesion and resistivity of the Mo films as a function of different argon working pressures and sputtering powers. The Mo films were deposited with a bilayer structure where the lower layer was optimized by the argon working pressure, and upper layer was optimized by the sputtering power.

We first investigated the adhesion property of Mo films as a function of argon working pressure. A series of six Mo films were prepared under identical conditions at room temperature except for variation in the Ar pressure during sputtering. For each Mo film, the sputtering power, P was held at 150 W, while the sputtering voltage, V and the current, I, were automatically adjusted by the power supplier to maintain constant power during the deposition. Based on calibration runs, the sputter time for each condition was chosen to yield a Mo film having a nominal thickness of 400 nm. The Ar working pressure was varied from low-pressure 0.2 mTorr to high-pressure 10
mTorr by adjusting the gate-valve to change the chamber pressure to a value of $p$ mTorr. The deposition parameters are summarized in Table 3.1.

<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>Electrical properties</th>
<th>Adhesion</th>
<th>Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$ (W)</td>
<td>$p$ (mTorr)</td>
<td>$R_{sh}$ (Ω/Sq)</td>
<td>$\rho$ ($\mu\Omega$cm)</td>
</tr>
<tr>
<td>150</td>
<td>0.10</td>
<td>0.09</td>
<td>9.20</td>
</tr>
<tr>
<td>150</td>
<td>0.20</td>
<td>0.10</td>
<td>10.9</td>
</tr>
<tr>
<td>150</td>
<td>0.50</td>
<td>0.22</td>
<td>13.4</td>
</tr>
<tr>
<td>150</td>
<td>1.0</td>
<td>0.34</td>
<td>18.9</td>
</tr>
<tr>
<td>150</td>
<td>2.0</td>
<td>0.69</td>
<td>26.8</td>
</tr>
<tr>
<td>150</td>
<td>5.0</td>
<td>1.35</td>
<td>35.9</td>
</tr>
<tr>
<td>150</td>
<td>10.0</td>
<td>1.69</td>
<td>68.0</td>
</tr>
</tbody>
</table>

**Table 3.1:** Summary of deposition parameters, electrical properties including sheet resistance and resistivity, results of adhesion test and strain analysis of the as deposited Mo film

First, the adhesion property of the sputtered Mo films as a function of sputter pressure was investigated with scotch tape adhesion test by sticking the tape on the surface of the film and removing the tape by applying manual force. The result of the scotch tape adhesion test is given in Table 4.1. The films which were sputtered at low pressures exhibited low resistivity but failed the tape test. After applying the scotch tape test, the surfaces of the films were covered with pinholes, indicating the tape partially peeled the Mo films from the substrate. This indicates the quality of the Mo film is not sufficient to hold the subsequent layers intact. In contrast, the films which were sputtered at high pressures exhibited high sheet resistance, but passed the tape test. After removing the scotch tape, the Mo films were intact and did not exhibit any signs of peeling from the substrate. Current research correlates the adhesion property to the level of intrinsic mechanical stress present in polycrystalline thin films which results from the intergranular spacing between the grains [22] [23]. Polycrystalline thin films with large intergranular spacing exhibit...
tensile stress, which is inversely proportional to the intergranular spacing. Each grain is attracted to its nearest neighbor, tending to pull it. The large sheet resistance of Mo films sputtered at high pressure is a direct consequence of tensile stress due to intergranular spacing generated by the films high porosity. As the sputtering pressure decreases, the intergranular spacing between the Mo grains decrease, leading to better conductivity. However, as the intergranular spacing decreases, the film gradually undergoes compressive stress where each Mo grain starts to compress the surrounding grains in all directions. As the sputtering pressure further decreases, the film then drastically undergoes compressive stress, resulting from compression of each Mo grain by the adjacent ones. As the compressive stress dominates the tensile stress, the films easily crack and peel since each Mo grain in the film is compressed by the adjacent ones. We can conclude that Mo films deposited at 5.0 mTorr and 10.0 mTorr exhibit tensile stress due to the presence of intergranular voids, high resistivity, but most importantly by its ability to pass the scotch tape test. In contrast, the films sputtered at 0.1, 0.2 and 0.5 mTorr exhibit compressive stress due to the absence of intergranular voids, low resistivity, and by its failure to pass the scotch tape test. Moreover, we can conclude between p = 5 mTorr and p = 2 mTorr, the film undergoes the maximum tensile stress, following conversion from tensile to compressive stress as the film starts to peel for pressures equal to and lower than p = 2 mTorr. In order to fabricate Mo films with good adhesion property, we deposited the film at 150 W with working pressure of 10 mTorr.

The dependency of the electrical sheet resistance, and resistivity as a function of argon working pressure is shown in Fig. 4.1. The Mo film deposited with the lowest Ar sputter pressure of 0.1 mTorr yielded the lowest sheet resistance and resistivity of 0.10 Ω/sq and 10.9 µΩcm, respectively. The obtained resistivity is approximately twice the reported room-temperature bulk value of ρ=5.4 µΩcm. During low sputtering pressures, between 1 mTorr to 2 mTorr, both the
sheet resistance and sheet resistivity increased almost linearly with the sputtering pressure. The sheet resistance and resistivity followed a logarithmic increase as a function of higher sputtering pressures.

\[ \text{Figure 3.1: Sheet resistance as a function of Ar working pressure, and the results of the adhesion test.} \]

The obtained relation between the sputter pressure and sheet resistance is in conjugation with the results of Kashyout et al. [24]. As the sputtering pressure is increased in the processing chamber, the pressure induced collisions between the Ar plasma and sputtered Mo grains reduce the mean free path of the sputtered Mo atoms as they approach the substrate. Reduced mean free path deflect the direction of the sputtered Mo atoms, increasing the angle at which they reach the surface of the substrate, resulting in formation of Mo film with scattered atoms. Moreover, pressure induced collisions lower the kinetic energy of the sputtered Mo atoms, reducing the energy needed to bond with the nearest Mo atoms, hence generating smaller Mo grains in the film.
During higher sputtering pressures, the sheet resistance followed a logarithmic increase as a function of increasing sputtering pressure. As the chamber pressure increases, the processing chamber may start to become saturated with Ar plasma, hence, the number of Ar plasma and Mo target atom collisions could be reaching a plateau, resulting in constant sputter yield.

Mo films sputtered at a single pressure do not exhibit low resistivity and good adhesion property simultaneously. One conventional method to solve this problem is to fabricate Mo bilayer films which consist of a high pressure deposited bottom layer to obtain good adhesion and a low pressure deposited top layer to maintain low electrical resistivity [25]. After depositing the lower layer at 10 mTorr, with a thickness at 400 nm, we investigated the deposition parameters to reduce the sheet resistance of the upper Mo layer. We first investigated the effect of sputtering power on the sheet resistance of the Mo films, by increasing the sputtering power from 150 W to 350 W while holding the sputter pressure constant at 1.0 mTorr. The dependence of the electrical resistance, and resistivity on sputtering power is shown in Fig 4.2a. Mo film that was deposited at

**Figure 3.2:** Sheet resistance as a function of (a) sputtering power and; (b) sputtering time

layer at 10 mTorr, with a thickness at 400 nm, we investigated the deposition parameters to reduce the sheet resistance of the upper Mo layer. We first investigated the effect of sputtering power on the sheet resistance of the Mo films, by increasing the sputtering power from 150 W to 350 W while holding the sputter pressure constant at 1.0 mTorr. The dependence of the electrical resistance, and resistivity on sputtering power is shown in Fig 4.2a. Mo film that was deposited at
150 W has a sheet resistance of 1.6 Ohm/sq. As the power is increased from 150 to 350 W in 50 W intervals, the sheet resistance exponentially decreased from 1.6 Ohm/sq to a lowest value of 0.4 Ohm/sq. Increased sputtering power reduced both the sheet resistance and resistivity of the Mo film. The sheet resistance is inversely proportional to the product of the carrier concentration and the mobility. Therefore, the decrease in sheet resistance as a function of increasing sputter power is attributed to the increase in carrier concentration or mobility. It is important to note the film growth rate increases as a function of increasing sputtering power, hence the average grain size of Mo size is larger, which reduces the grain-boundary scattering, increasing the mobility and carrier. Furthermore, reduction of sheet resistance as a function of increasing sputter power is attributed to increased grain size and shape, reduced intergranular voids and higher degree of crystallinity. Chen et al., reported Mo films sputtered at low powers exhibited small pyramidal shapes with intergranular voids. As the sputter power is increased, the grains turned to mackerel shape with larger grain size [26]. Increased grain size is attributed to Mo atoms exhibiting a longer free path way and higher kinetic energy during the deposition [27]. The atomic energy of ion bombardment of molybdenum deposited on the substrate increases, which reaches the bonding energy of Mo atoms, hence generating higher degree of crystallinity. Islam et al., reported the films sputtered at low power exhibited scattered and disoriented Mo grains. As the sputter power was increased, the films exhibited higher degree of crystallinity and larger crystallite size. We finally investigated the effect of sputtering time on the sheet resistance of Mo films. While holding the sputtering power constant at 350 W, and the Ar working pressure at 1.0 mTorr, we gradually increased the sputtering time from 500 s to 1200 s. Fig. 4.2b shows the dependency of Mo sheet resistance on the sputtering time. As the sputtering time increases, the Mo film resistance monotonically decreases. The decreases in film resistance is attributed to increase in Mo thickness. As the Mo film thickness
increases, so does the cross-sectional area of the film. While the average speed of charge carriers will not be affected by film thickness, the increased cross-sectional area will allow more charge carriers to flow per unit time [28]. While holding the potential across the film constant, increased current I through the film will result in lowered resistance. By increasing the film thickness, we reduced the film resistance from 0.47 Ohm/sq to 0.1 Ohm/sq.

In conclusion, we have systematically investigated the effect of sputtering pressure and power on the electrical and adhesion properties of Mo back contact. The films deposited at high pressure exhibited tensile stress which lead to good adhesion, but suffered from high sheet resistance due to grain boundary scattering of small Mo grains size and grain density. In contrast, the Mo films deposited at low pressure exhibited compressive stress which lead to poor adhesion, but low sheet resistance due to large Mo grain size and grain density. Moreover, increase in sputter power resulted in lower sheet resistance due to increased grain size and shape, lower intergranular voids, reduced grain-boundary scattering, increased mobility and carrier concentration. Finally, increase in sputter time controlled the film thickness, hence the cross-sectional area of the film. The increased cross-sectional area allowing more charge carrier to flow per unit time whereby reducing the sheet resistance. In order to achieve optimized Mo back contact, we fabricated the film in a bilayer structure. The lower layer was deposited at 150 W and 10 mTorr and the upper layer was deposited at 350 W at 0.1 mTorr with a total film thickness of 700 nm.

3.2 Optimization of Electrical and Optical Properties of ZnO:Al Front Contact
3.2.1 Effect of Chamber Background Pressure on the Properties of ZnO:Al Films

ZnO:Al has been widely used as a transparent conducting layer, especially in the application of solar cell front contacts [29] [30] [31]. It is commonly used in thin film CIGS solar cells with the structure of Glass/Mo/CIGS/CdS/ZnO/ZnO:Al, where the undoped ZnO serves as the protection layer and the ZnO:Al layer acts as the top transparent contact [32] [33]. In comparison with other transparent conducting oxides such as indium tin oxide (ITO), ZnO:Al has the advantages on cost, on abundance in nature, and on toxicity. The performance of this oxide layer is evaluated by its conductivity and transparency. It is desirable to have a metal-like conductivity and glass-like transparency.

We investigated the effect of chamber background pressure, argon flux, argon working pressure and post-deposition annealing treatment on the electrical, structural and optical properties of aluminum-doped zinc oxide, ZnO:Al front contact. To investigate the effect of each parameter, all other parameters were kept unchanged. Based on calibration runs, the sputter time for each condition was chosen to yield a ZnO:Al film having a nominal thickness of 600 nm. To verify the effect of the base pressure on the electrical and optical properties of ZnO:Al front contact, the sputtering chamber was vented to atmospheric pressure and then re-pumped to $1 \times 10^{-4}$, $1 \times 10^{-5}$, and $1 \times 10^{-6}$ Torr, respectively, for three sputtered samples. The deposition took place immediately after the set vacuum level reached. As shown in Fig. 4.3, the sheet resistance of the ZnO:Al thin film samples increases from $60 \ \Omega/\text{sq}$ up to $2 \times 10^6 \ \Omega/\text{sq}$ as the chamber background pressure increases from $1 \times 10^{-6}$ to $1 \times 10^{-4}$ Torr. The increase in sheet resistance as a function of increase in chamber
background pressure is attributed to the presence of impurities contributed by residual gas in the chamber.

The primary components of residual gas in the deposition chamber are reported to be water, nitrogen, oxygen and light hydrocarbons [34]. As the chamber background pressure increases, the residual gas in the chamber continue to have relatively higher percentages. Thus, the residual gas atoms and ions strongly contaminate the growing film and thus strongly influence their properties.

Due to the polycrystalline nature of the sputtered ZnO:Al films and its relatively small grain size, the density of grain boundaries is expected to be very high. Therefore, the residual gas atoms and ions that are absorbed at the grain boundaries can affect the conductivity properties of thin films because the absorbed atoms and ions can attract free carriers, thus reducing the carrier density.
available for conducting. Furthermore, the absorbed O\textsuperscript{-} ions can also establish electrostatic potential that further inhibits the free carriers from transporting between grains, hence reducing the carrier mobility [35]. Therefore, a low background pressure before sputtering is essential for obtaining a high quality ZnO:Al film.

### 3.2.2 Effect of Argon Flux on the Properties of ZnO:Al Films

![Graph](image)

**Figure 3.4:** Sheet resistance (solid sphere) and transmittance (open circles) are plotted as a function of the gas flow rate in (a) and the associated transmission spectra at different gas flow rate are displayed in (b).

The performance of the sputtered ZnO:Al film was found to be dependent on the argon gas flow rate. As displayed in Fig. 4.4, the sheet resistance of the ZnO:Al film resistance reduces from 500 to 60 Ω/sq as the Ar flow rate increases from 10 to 30 sccm. Further increase in the gas
flow rate from 30 to 50 sccm has little influence on the film conductivity. This is because, when
the gas flow rate is low, the degree of ionization very high, any increase in incoming gas will
result in an increase of ionized particles [36].

*Figure 3.5:* XRD spectra for three AZO films sputtered at the flow rate of 10 sccm (a), 25
sccm (b), and 50 sccm (c) are displayed.

During the ion bombardment, kinetic and vibration energy dissipates as the formation of
heat. Since no substrate heating was applied during sputtering process in this study, this
bombardment induces heating effect which had a considerable influence on the crystallization of
the sputtered ZnO:Al thin films. More substrate heating is expected for a high concentration of
ionized particles, leading to a big grain size that lowers resistivity. However, as the gas flow rate
further increases, the degree of ionization drops as a large amount of neutrals present in the
chamber. Therefore, too high gas flow rate will have no benefit in improving the conductivity of
the sputtered ZnO:Al thin films.
On the other hand, the film transmittance decreases monotonically as the Ar flow rate increases as shown in Fig. 4.5 (a) as open circles. The transmittance was calculated by integrating the transmission curves from 500 (the absorption edge of CdS) to 1200 nm (the absorption edge of CIGS) as displayed in Fig. 4.4 (b). The XRD patterns at different Ar gas flow rate as shown in Fig. 4.6, indicate that all the sputtered films exhibit preferential (002) orientation. The (002) orientation corresponds to Wurtzite structure, suggesting the free energy of (002) plane is lowest in ZnO films which results in the easy formation of the film pointing in the c-axis direction, perpendicular to the substrate surface.

The (002) orientation is preferred because it results in smoothest ZnO:Al film. The film sputtered at the flow rate of 10 sccm is not well crystallized based on the intensity of the main peak (002) and the existence of many other small peaks. The (002) peak intensity greatly enhanced as the flow rate increased to 25 sccm. This enhancement is also in agreement with the observed sharp decrease in resistance. When the flow rate up is further increased to 50 sccm, the intensity of the (002) peak remains unchanged. However, other small peaks from other orientations such as (101) increases, indicating that although the (002) direction is the preferred growth orientation in all cases; other orientations also exist and tend to be strong at high gas flow rates. Therefore, a good balance between the film conductivity and film transmittance lies at a gas flow rate of around 25 ~ 30 sccm.

3.2.3 Effect of Argon Working Pressure on Properties of ZnO:Al Films
The dependency of electrical sheet resistance and transmittance as a function of Ar sputter pressure is given in Fig. 4.6. The lowest reported sheet resistance 60 Ohm/sq corresponds to the lowest Ar sputter pressure of 3.0 mTorr. As the Ar sputter pressure is increased from 3.0 mTorr to 10 mTorr, the ZnO:Al sheet resistance monotonically increases to 200 Ohm/sq. The sheet resistance is inversely proportional to the product of the carrier concentration and the mobility [37]. Therefore, the increase in sheet resistance as a function of increasing working pressure could be attributed to the decrease in carrier concentration or mobility. It is important to note the film growth rate decreases as a function of increasing working pressure, hence the average grain size of ZnO:Al size is smaller, which increases the grain-boundary scattering, reducing the mobility. Furthermore, the ZnO:Al films are chemically active. The oxygen atoms which may be trapped at the grain boundaries could attract electrons from the conduction band, and reduce the carrier concentration.

![Graph showing sheet resistance and transmittance as a function of Ar working pressure.](image)

**Figure 3.6:** Measured values of sheet resistance and transmittance percentage of a ZnO:Al films as a function of Ar working pressure
In contrast, the transmittance of the ZnO:Al films decreases as a function of increasing working pressure. Bai et al., attribute decrease in transmittance as a function of increasing working pressure to the size of the ZnO:Al grains. The composition of the ZnO:Al becomes nonstoichiometric as the grainsize decreases, resulting in light scattering loss and the destruction of coherence between incident light and transmitted light, as well as disappearing of interference fringes, which lead to decrease in transmittance.

3.2.4 Effect of Post-Deposition Annealing Treatment on Properties of ZnO:Al Films

Finally, we investigated the effect of post-deposition annealing treatment in hydrogen atmosphere on both the conductivity and transmittance of sputtered ZnO:Al films. The as-deposited ZnO:Al films were heat-treated in Ar atmosphere with 5% H\textsubscript{2} concentration, by varying the annealing temperature from room temperature to 500 °C while keeping the annealing time constant at 60 min. Fig. 4.7 shows the dependency of annealing temperature on the resistance of ZnO:Al films.

At room temperature, the sheet resistance of the ZnO:Al films is relatively high, 55 Ohm/sq. This high sheet resistance is attributed to depletion regions formed by the adsorption of negatively charged species on grain boundaries [38]. As the annealing temperature reaches 200 °C, the sheet resistance decreases by more than 50%, reaching 25 Ohm/sq. The decrease in sheet resistance is attributed to desorption of the negatively charged species, mainly oxygen from the grain boundaries which act as trapping sites and form the potential barriers during the hydrogen treatment. The negatively charged species form depletion regions near the grain boundary surfaces,
decreasing the conductance of the film. These depletion regions in the ZnO:Al films can be removed by the passivation of the gain boundary surfaces during the post-deposition annealing in hydrogen atmosphere. Hydrogen is a highly reducing agent and can therefore easily reduce O from the grain boundaries of ZnO:Al films. However, as the annealing temperature increases, this beneficial annealing effect becomes less pronounced. As the annealing temperature increases from 200 °C to 400 °C, we observe an increase in sheet resistance from 25 Ohm/sq to 50 Ohm/sq.

The annealing time is found to play a crucial role in controlling the film conductivity at high temperatures. Morales-Masis et al., showed longer annealing time may result in desorption of more O\textsuperscript{-} ions from the grain boundaries, which can then react with OH atoms to form H\textsubscript{2}O atoms and condense on top of the ZnO:Al film, reducing the conductance of the ZnO:Al film. As the

![Figure 3.7: Measured values of sheet resistance and transmittance of a ZnO:Al film. The first data point at 25 °C is for as sputtered at a gas flow rate of 30 sccm, a working pressure of 3 mTorr, and a background pressure of 1×10\textsuperscript{-6} Torr, and other data points are for the annealed at different temperatures.](image)
annealing temperature further exceeds 400 °C, the film conductivity degrades. High annealing
temperature may damage the glass substrate and the film structure since the melting point of soda-
lime glass substrate is approximately 550 °C. The post-annealing treatment is also found to modify
the optical properties of the ZnO:Al films. As the annealing temperature is increased from 25 °C
to 500 °C, the transmittance of ZnO:Al films monotonically increased from 84% to 96%. Kormer
et al., attributed this to hydrogen doping suppressing the deep band defects, hence improving the
bandgap energy of ZnO:Al films. This is in conjunction with the findings of Oh et al., who reported
increased the bandgap energy of ZnO:Al thin films from 3.54 to 3.70 eV just by increasing the
post-annealing treatment time.

3.3 Conclusion

Molybdenum back contact film was fabricated with a bilayer structure. The lower layer
was deposited with high sputter pressure which resulted in a with tensile stress with high sheet
resistance, small grain size with increased intergranular voids. The upper layer was deposited in
low pressure which yielded Mo film with compressive stress, exhibiting increased the grain size
and shape and reduced the intergranular voids. ZnO:Al films were fabricated under low sputter
pressure which produced large ZnO:Al grain size with diminished intergranular voids which
increases transmittance of light due to reduced grain boundary scattering of light. Finally, post-
deposition annealing treatment in hydrogen atmosphere is found to enhance the conductance of
the film, which is attributed to desorption of the negatively charged species, mainly oxygen from
the grain boundaries which act as trapping sites and form the potential barriers. The post-annealing
treatment is also found to increase transmittance of ZnO:Al films, which is attributed this to
hydrogen doping suppressing the deep band defects, hence improving the bandgap energy of ZnO:Al films.
Chapter 4: Optimization of CuIn$_x$Ga$_{1-x}$Se thin films by Sputtering and Selenization

This chapter presents investigation of deposition parameters to optimize the uniformity, morphology and homogeneity of CuInGa precursor and CuIn$_x$Ga$_{1-x}$Se$_2$ thin films. CuInGa film was deposited using magnetron sputtering, and selenization process was performed by two step chemical vapor deposition method. Section 4.1 shows CuInGa precursor film sputtered sequentially as In/CuGa/In had the smoothest morphology and the best CuInGa homogeneity. In section 4.2, we introduce the design and assembly of chemical vapor deposition system in order to perform uniform films with reproducible results. In section 4.3, we describe the chemical processes involving the two-step selenization. Section 4.3.1 shows the optimized device performance achieved by tuning the Cu/In composition. Section 4.3.2 shows increase in Se flux facilitates In$_2$Se$_3$ and Ga$_2$Se$_3$ phases, resulting in compact CIGS films with larger grains. In Section 4.3.3, we show thermally evaporated selenization results in enhanced device performance. In Section 4.4, we summarize the results presented in this chapter.

4.1 Preparation of CuInGa Precursor Film with Structural and Chemical Homogeneity

Fabricating high quality CuIn$_x$Ga$_{1-x}$Se$_2$ solar cell modules requires a smooth surface morphology, and uniform chemical homogeneity [39, 40]. The morphology and uniformity of CuIn$_x$Ga$_{1-x}$Se$_2$ films is dependent on the deposition conditions of the Cu-In-Ga precursor film. The deposition conditions and sequence of copper, indium and gallium metallic layers affect the
homogeneity, surface morphology of the CuInGa film, as well as the phase formation of the CuInGa$_{1-x}$Se$_2$ films during the chalcogenization process. Moreover, stacking density of the CuInGa precursor film directly affects the chalcogenization rate and time [41]. Thus, a thorough investigation of the deposition conditions which would yield smooth surface morphology and uniform homogeneity of CuInGa precursor film is the first step to fabricate high quality devices.

![Figure 4.1: CuGa top and cross sectional scanning electron microscope images and the sputter yield.](image)

In this section, we present investigation of sputtering conditions to produce smooth CuInGa surface morphology, with structural and chemical homogeneity. We first investigated the CuGa and In deposition conditions independently, and then investigated the optimal conditions to deposit the CuInGa precursor film. CuInGa precursor film that has a low stacking density selenizes more rapidly since selenium can diffuse into the film easily. Hence a low sputtering power, 1.31 W/cm$^2$, 

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic % Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>76.5</td>
</tr>
<tr>
<td>Gallium</td>
<td>23.5</td>
</tr>
</tbody>
</table>
was used during the deposition of CuGa and In films with a moderate working pressure, 5 to 10 mTorr, and with 30 sccm Ar flow rate. We first obtained the sputter yield for both the CuGa and In film. The sputter yield, correlation between the sputtering time and film thicknesses at 1.31 W/cm² was derived from the calibration runs under two different DC sputtering time conditions. For both CuGa and In layers, the thickness increased almost linearly with time.

The top view and cross sectional SEM images of CuGa film deposited at 1.31 W/cm² and 5 mTorr is shown in Fig. 4.1. The size of the CuGa grains is between 25 to 50 nm, with a very smooth surface morphology. EDX analysis reveals a slight compositional change of the Cu-Ga film after deposition. The Cu:Ga compositional ratio of the CuGa film is slightly higher, 76.5:23.5, than that of the Cu:Ga ratio, 80:20 in the CuGa target. The change in Cu-Ga compositional ratio

**Figure 4.2:** In top and cross sectional scanning electron microscope images and the sputter yield.
is due to Cu atoms scattering more severely than the Ga atoms because to its higher scattering angle during the sputtering process [42]. It is important to note the CuGa film is smooth with no disruption at the CuGa/Mo interface. The smooth CuGa morphology is due to similar surface energies of Mo and Cu. The surface energies of Mo and Cu are 1.90 J/m² and 1.79 J/m², respectively [43]. Hence, there is no disruption between the Mo and Cu films. Ga, however, has a lower surface energy of 1.10 J/m² than that of Mo and Cu. However, the concentration of Ga is not high enough to affect the morphology of CuGa film or the CuGa/Mo interface.

Similarly, the top view and cross sectional SEM images of In film is shown in Fig. 4.2 along with its sputter yield graph. The indium metal layer has large grains that are separated from each other, resulting in a rough surface morphology. Because of the rough surface of the indium film, its thickness is approximated. The rough surface morphology of In film is due to having a high-surface tension, a low melting temperature and poor wettability [44]. The surface energy of In, 0.675 J/m² is drastically different than that of Mo, 1.9 J/m². As a result, In atoms do not adhere to the surface of Mo, but instead form clusters on the Mo film. As the film thickness increases, the In clusters grow, covering the surface of the Mo film. The surface energy of In is dependent on the temperature:

$$\gamma_{In} = 568.0 - 0.04 \, T - 7.08 \times 10^{-5} \, T.$$  \hspace{1cm} (4.1)

Hence, one way to have matching In/Mo surface energy is to increase the temperature of the substrate during In deposition. However, increasing the substrate temperature will result in Ga-In eutectic reaction, since both In and Ga have low melting points of 156.6 °C and 29.6 °C,
respectively. Another way to reduce the size of the indium grains and the surface roughness is to increase the sputtering pressure and reduce the In film thickness by reducing the sputtering time. In order to reduce the size of indium grains and the surface roughness, we increased the In sputtering working pressure from 5.0 mTorr to 10.0 mTorr. Presence of argon plasma reduces the size of the indium grains through collision with indium grains. After increasing the argon working pressure, the resulting size of the indium grains reduces to 1-2 µm. During the CuInGa precursor growth, we also reduced the sputtering time of In film, which resulted in smoother In surface morphology.

Next, we investigated the deposition sequence of CuGa and In layers to yield the smoothest CuInGa precursor film with smooth surface morphology and uniformity. First, we deposited Cu-In-Ga multilayer precursor stacked with a structure of SLG/Mo/CuGa/In as shown in Fig. 4.3a. SEM images and EDX analysis revealed two different phases in the resulting CuInGa precursor film: a Cu-rich phase at the bottom of the film, and an In-rich phase scattered over the surface of the CuGa layer, forming island like structures. As indicated earlier, CuGa and Mo have matching surface energies of 1.90 J/m² and 1.79 J/m², respectively. Hence, there is no disruption between the Mo and CuGa films. The surface energy of In, 0.675 J/m² is drastically different than that of Mo, 1.79 J/m² and Cu, 1.90 J/m². Consequently, In atoms do not adhere on the surface of Mo/CuGa, but instead form clusters. The film is not thick enough to allow In clusters to form a uniform In film on the CuGa layer. So instead, we deposited Cu-In-Ga precursor film sequentially with a structure of SLG/Mo/In/CuGa as shown in Fig. 4.3b. The film is found to have a smoother surface morphology. At the bottom of the film, large indium grains formed island like structures due to mismatch of surface energies of Mo and In. On top of the In clusters, we deposited the CuGa layer. The fine grains of CuGa film with grainsize varying from 25 nm to 50 nm filled the
valleys created by the large indium clusters, forming a relatively smoother precursor film. The SEM images still reveal a rough surface morphology.

Finally, we deposited the multilayer precursor with a stacking structure of SLG/Mo/In/Cu-Ga/In. We lowered the deposition time of In and deposited a sandwich structure of In/CuGa/In. We first deposited the In layer. Reducing the In deposition time reduced the size of In clusters. Then, the CuGa films was deposited, which filled the valleys created by the indium clusters.

Figure 4.3 a) Top view and cross sectional SEM image of Mo/CuGa/In structure, b) Top view and cross sectional SEM of Mo/In/CuGa structure, c) Top view and cross sectional SEM of Mo/In/CuGa/In structure.
Finally, we deposited a thin layer of In on top of the In/CuGa structure. The In grains of the top In layer further filled the valleys created by the first In layer. This structure yielded the smoothest morphology.

In summary, we fabricated CuInGa precursor with a smooth surface morphology, and uniform homogeneity. We first investigated CuGa and In deposition conditions independently to calculate the CuGa and In sputter yields. We found that the morphology and uniformity of CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ films is dependent on the deposition sequence of Cu-In-Ga alloy precursors. The deposition sequence of copper, indium and gallium metallic layers affect the homogeneity, surface morphology of precursor films, and also phase formation of the CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ films during the chalcogenization process. We found that the multilayer precursor with a stacking structure of SLG/Mo/In/Cu-Ga/In yielded the smoothest morphology.

4.2 Chemical Vapor Deposition System for Selenization

Chemical vapor deposition system was first utilized by the Grindle et al. for the fabrication of CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ films [45]. A typical CVD setup involves a gas supply system, a reactor system, exhaust system and a control system [46]. Inside the LPCVD reactor is the reaction chamber. The reaction chamber consists of a source zone where the Se powder is evaporated, and a sample zone where the CuInGa precursor is reacted with Se vapor. The control system regulates the reaction time, temperature and the gas supply system. While the gas supply system provides the carrier gasses to carry the Se source vapor into the sample zone in the reaction chamber, the exhaust system serves to remove the waste gases through rotary pump and reduces the reaction chamber pressure required for the process.
The primary issue involving CVD systems is fabricating uniform films. In order to produce uniform CuIn$_x$Ga$_{1-x}$Se$_2$ films, the Se vapor flow must be precisely controlled so the Se vapor diffusion rate into the CuInGa precursor could be regulated. Moreover, the reactor chamber pressure must be controlled to ensure sufficient Se vapor pressure in the reactor chamber to produce CuIn$_x$Ga$_{1-x}$Se$_2$ films with the correct stoichiometry. Furthermore, fabrication of uniform CuIn$_x$Ga$_{1-x}$Se$_2$ films also require a sophisticated CuInGa precursor fixture. The fixture should exhibit smooth surface, high melting point, and be an excellent conductor of heat in order to maintain a uniform surface temperature during reactions, and sustain stability during heating and cooling temperatures. Furthermore, the geometry of the CuInGa fixture should be adjusted in order for Se vapor to diffuse uniformly throughout the CuInGa precursor film. Another issue is obtaining reproducible results. In order to obtain reproducible results, not only should the carrier gas flow, Se vapor flow, reactor chamber pressure must be controlled, but the gas supply system and exhaust system must be well maintained from rusting and clogging due to condensation of Se vapor and waste gas.

In this section, we present the approaches we undertook to fabricate uniform films with reproducible results. In order to fabricate reproducible CuIn$_x$Ga$_{1-x}$Se$_2$ films, the selenium flux in the reaction chamber must be constant during each experiment. Failure to maintain constant selenium flux in each experiment will result in CuIn$_x$Ga$_{1-x}$Se$_2$ films with different Se stoichiometry. Hence, the selenium flux entering the chamber and exiting the chamber must be regulated by the insertion of a mass flow regulator. Furthermore, reproducible CuIn$_x$Ga$_{1-x}$Se$_2$ films require constant selenium vapor pressure during each experiment. A slight change in selenium vapor pressure will alter the Se vapor presence on the surface of the CuInGa precursor which will also alter the CuIn$_x$Ga$_{1-x}$Se$_2$ stoichiometry and hence the resulting film properties. Thus, a pressure
regulator must be installed to the CVD system in order to maintain constant pressure during each experiment. Next, during each reaction, after exiting the reaction chamber, the unreacted residual Se vapor condenses in the exhaust system. This condensation of Se vapor starts clogging the exhaust system, altering the Se flux and pressure in the CVD system. Hence, a sophisticated exhaust gas collection system must be installed in order to capture residual Se vapor and maintain a constant Se pressure and flux in the reaction chamber. Furthermore, in order to fabricate uniform CuIn$_x$Ga$_{1-x}$Se$_2$ films, the configuration and geometry of the CuInGa fixture should be adjusted in the reaction chamber for Se vapor to be deposited evenly throughout the CuInGa precursor. Failure to deposit Se evenly will result in nonuniform CuIn$_x$Ga$_{1-x}$Se$_2$ films. Moreover, uniformity of CuIn$_x$Ga$_{1-x}$Se$_2$ films depend on the thermal conductivity of the fixture being used. High thermal conductivity materials would enable faster heat transfer from the reaction chamber onto the precursor. Hence, the substrate fixture material, configuration and geometry must be optimized in order to obtain uniform CuIn$_x$Ga$_{1-x}$Se$_2$ films.

The schematic diagram of our CVD system is shown in Fig. 4.4. A dual zone MTI OTF-1200X-II-UL chemical vapor deposition furnace with dimensions 590 mm(L) x 380 mm (W) x 520 mm (H) and temperature range 100-1200 C was used as the reactor. The reaction chamber consists of an 800 mL quartz tube in which both the Se source powder and the samples. The quartz tube was sealed using vacuum flanges. The gas supply system and exhaust system were connected through ¼” thick stainless steel pipes, while a series of needle valves were installed to manually control the carrier gas flow and the pressure within the CVD system.

Fabrication of CuIn$_x$Ga$_{1-x}$Se$_2$ films with reproducible stoichiometry requires precise control of selenium flux and selenium vapor pressure in the reactor chamber during each experiment. A slight change in the selenium vapor pressure in the reactor chamber alters the
selenium vapor pressure, hence the number of selenium molecules diffusing into the CuInGa precursor film which changes the resulting selenium content in the CuIn$_x$Ga$_{1-x}$Se$_2$ film. Furthermore, a slight change in selenium flux alters the selenium diffusion rate into the CuInGa precursor film which changes the selenium content as a function of the film depth, and the thickness of the MoSe film at the Mo/ CuIn$_x$Ga$_{1-x}$Se$_2$ interface.

In order to control and maintain a constant selenium flux, we installed an MFC-A digital mass flow controller in the CVD system at position (A) as shown in the schematic diagram. The digital mass flow controller regulates the selenium flux entering and exiting the reactor chamber by automatic valves. The valves dilate and contract in order to maintain the desired Se flux throughout the experiment. Furthermore, in order to control the selenium vapor pressure, we installed the NIST traceable digital vacuum gauge and controller in order to measure and regulate the pressure in the reactor chamber as shown in position (B) in the schematic diagram. We avoided

![Figure 4.4: Schematic diagram of the Chemical Vapor Deposition System.](image-url)
installing the flow controller and the vacuum gauge on the exhaust system of the CVD setup to avoid the unreacted Se residual vapor from contaminating the electronic equipment of the flow controller and the vacuum gauge. Moreover, a number of needle valves were installed in order to manually control both the Se flux and Se vapor pressure in the reactor chamber if there was a drastic change in the Se flux or the chamber pressure.

Production of unreacted residual Se gas is inevitable during the selenization process. After exiting the reactor chamber, the unreacted residual Se vapor starts to condense inside the needle valves and inside the pipe walls as well as inside the exhaust system. Condensation of Se eventually clogs the valves, pipes and the exhaust system which causes contamination and change the flow and pressure inside the CVD reactor. In order to prevent this, we installed the exhaust gas collection system to trap the unreacted residual Se vapor. The exhaust gas collection system consisted of 30 cm long ¼” thick stainless steel pipe which was partially bent as shown in position (D) in the schematic diagram. During each selenization process, the bent portion of the pipe was placed in an ice bath. As a result, all the unreacted Se vapor condensed and trapped on the cold walls of the pipe. Trapping all the unreacted Se in this pipe prevented the CVD system from Se vapor contamination. Moreover, after each reaction, the pipe was uninstalled and cleaned with a pipe brush. Installing the gas collection system prevented CVD contamination and clogging of the exhaust system which also enabled us to obtain reproducible results.

Moreover, in order to fabricate uniform CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ films, the configuration and geometry of the CuInGa fixture should be adjusted in the reaction chamber for Se vapor to be deposited evenly throughout the CuInGa precursor. Failure to deposit Se evenly will result in nonuniform CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ films. Moreover, uniformity of CuIn$_{x}$Ga$_{1-x}$Se$_{2}$ films depend on the thermal conductivity of the fixture being used. High thermal conductivity materials enable faster
heat transfer from the reaction chamber walls onto the precursor, which allows the CuInGa precursor.

Furthermore, fabrication of uniform CuIn$_{x}$Ga$_{1-x}$Se$_2$ films depend on the thermal properties of the CuInGa precursor fixture. Since CuIn$_{x}$Ga$_{1-x}$Se$_2$ phases are temperature dependent, the fixture should exhibit homogenous temperature throughout its surface. Hence, the precursor fixture should exhibit high thermal conductivity so the heat transfer from the chamber walls onto the fixture would be fast and the surface of the fixture would exhibit homogenous temperature. In order to test which material is best suitable as the precursor fixture, we investigated fixtures made up of copper, nickel, aluminum and graphite plates. All the plates were polished and trial experiments were performed to observe the uniformity of the CuIn$_{x}$Ga$_{1-x}$Se$_2$ films. The results revealed the most uniform CuIn$_{x}$Ga$_{1-x}$Se$_2$ films were produced by the graphite precursor fixture. The thermal conductivity of copper, nickel aluminum and graphite are 401, 90, 205 and 470 W/mK, respectively. Because of high thermal conductivity and its softness, we manually crafted sample fixture from a graphite block.

Moreover, the configuration and geometry of the CuInGa fixture should be adjusted in the reaction chamber in order for Se vapor to be deposited evenly throughout the CuInGa precursor. Failure to deposit Se evenly will result in nonuniform CuIn$_{x}$Ga$_{1-x}$Se$_2$ films. The reaction chamber is an 800 mL horizontal quartz tube. Hence, the direction of Se flow is horizontal to the surface of the CuInGa precursor. Since the flow is horizontal to the surface of the CuInGa precursor, Se will not be deposited uniformly on the precursor. So, we prepared a batch of six CuInGa precursor samples with dimensions: 1”x3”. Each sample was then loaded into the CVD furnace and selenization was carried out. During the reaction, the angle of the CIG precursor film was lifted from the horizontal to an angle $\theta$, thus changing the selenium flow angle with respect to the sample.
orientation. The images of the CuInGaSe deposited at different fixture holder angler is shown in Fig. 4.5.

When the CuInGa precursor film was held horizontal, selenium flux was parallel to the surface of the film. As a result, selenium does not seem to penetrate and diffuse into the CuInGa precursor film, thus leaving a very nonuniform film as can be seen by the discoloration of the CIGS film. As the CuInGa fixture angle varied from 0 to 90 degrees, we saw more uniformity and homogeneity throughout the films as can be seen by the uniform color of the films. We adjusted the angle of the substrate holder to approximately 90 degrees so Se vapor strikes the surface of the film almost perpendicularly, hence diffusing well into the film whereby producing uniform films.

In summary, in this section, we describe the design and assembly of our chemical vapor deposition system to fabricate uniform films with reproducible results. We also present the design and insertion of crucial components to control the reactor chamber pressure, carrier gas and Se

\textbf{Figure 4.5: Morphology and uniformity of the CuInGaSe absorber films as a function of CuInGa precursor fixture angle. The angles varied from 0 to 90 in 15 degree increments.}
vapor flow. Furthermore, we discuss the use of critical components for preventing the exhaust system from being contaminated due to condensation of waste gas, in order to reproducible experiments. Moreover, we present the design and geometry of our CuInGa precursor fixture in order to produce both uniform and reproducible CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films. Finally, we adjusted the angle of the substrate fixture to approximately 90 degrees so Se vapor strikes the surface of the film almost perpendicularly, hence diffusing well into the film whereby producing uniform films.

4.3 Fabrication of CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} Devices by two-step Selenization Process

The highest efficiency CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} devices have been fabricated using the coevaporation method implemented by Boeing since the early 1980s [47]. The coevaporation method involves evaporation of Cu, In, Ga, Se from separate elemental sources onto substrates coated with a Mo back electrode. The devices are completed with an n-type CdS layer followed by a conductive ZnO current-carrying layer [48]. Although the CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} solar cell efficiency of 21.7% has been achieved with the co-evaporation method, the industrial application of this method is restricted due to uniformity issues over large areas, reproducibility, high cost, expensive vacuum equipment [49]. The issue of uniformity over large areas, reproducibility, high cost and expensive vacuum equipment has been solved by the alternative two-stage method implemented by ARCO Solar. The two-stage method provides efficient material utilization, simple device requirement, higher throughput and compositional uniformity than coevaporation [50]. Companies currently using the two-step method include Showa Shell, Avancis, Miasole, Honda Soltec and Energy Photovoltaics. The two-stage method involves deposition of Cu, In, Ga using magnetron sputtering technique
followed by reaction with Se atmosphere at high temperatures to yield CuIn$_x$Ga$_{1-x}$Se$_2$ films. The reaction chemistry and kinematics during the selenization process can be described by a sequence of reactions involving Cu, In and Ga. These compounds then react with Se and form a series of binary compounds In$_2$Se$_3$, CuSe$_2$, Ga$_2$Se$_3$ which then react to form CuIn$_x$Ga$_{1-x}$Se$_2$. The CuIn$_x$Ga$_{1-x}$Se$_2$ formation mechanism then follows [51]:

\[
Cu + 2Se \leftrightarrow CuSe_2
\]

\[
2In + 3Se \leftrightarrow In_2Se_3
\]

\[
2Ga + 3Se \leftrightarrow Ga_2Se_3
\]

\[
In_2Se_3 + 3Se \leftrightarrow CuInSe_2
\]

\[
Ga_2Se_3 + Cu_2Se \leftrightarrow CuGaSe_2.
\]

The primary issues involving the two-step process includes producing uniform CuIn$_x$Ga$_{1-x}$Se$_2$ films. Since the reaction rates of Cu/Ga with Se vapor is much faster than In/Ga with Se vapor, two separate phases CuInSe$_2$ and CuGaSe$_2$ form within the film. Consequently, during the conventional Se vapor selenization, In-related phases form at the top of the film, while the Ga-related phases are inevitably buried at the bottom of the film. As the Ga-related CuGaSe$_2$ grains aggregate near the backside, the resulting device behaves like CuInSe$_2$, which yields low open circuit voltage, $V_{oc}$, and low conversion efficiency of the device. The second issue involving
conventional selenization is, evaporated selenium has large molecular chains, Se\textsubscript{x} where x>5, which results in difficulty of Se to diffuse into the CuInGa precursor film. Furthermore, Se molecular chains exhibit low chemical reactivity. Consequently, the CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films end up having selenium deficiency and result in random local non-stoichiometry and deteriorating uniformity and film structure, leading to low conversion efficiency.

In the following sections, we first present the investigation of the effect of In, Ga, Cu stoichiometry on the CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} device performance. Next, we present the investigation to improve chemical and structural homogeneity as a function of Se flux. Finally, we present the investigation to increase Se chemical reactivity and diffusivity into the CuInGa precursor by cracking the Se molecular chains with increased Se source temperature.

4.3.1 The influence of Cu, In, Se stoichiometry on CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} device performance

In CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} solar cells, the [Cu]/[In] ratios have a significant influence on the structural, morphological, optical and electrical properties \cite{52} \cite{53}. Furthermore, high efficiency CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films are obtained with Cu/In ratios ranging from 0.8 to 0.9. Thus, we first investigated the influence of [Cu]/[In] ratio on the CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} device performance. A series of seven CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films were fabricated with various [Cu]/[In] ratios, prepared by precursor deposition using magnetron sputtering, followed by selenization process. The CuInGa precursor film was stacked with Mo/In/CuGa/In, while different [Cu]/[In] ratios were achieved by changing CuGa and In deposition times hence film thicknesses during CuInGa precursor deposition. During CuInGa deposition, indium sputter time was held at 800 s in order to obtain a film thickness of
916 nm, while CuGa sputter time was varied from 600 s to 900 s in 50 s intervals in order to obtain film thicknesses from 166 nm to 228 nm. The films were then selenized with the procedure listed in Section 4.3.

The CuInSe$_2$ films with different CuGa and In thicknesses, hence [Cu]/[In] ratios were then turned into complete devices, and the open circuit voltage and the light generated current density were measured under solar illumination. The results of $V_{oc}$ and $J_{sc}$ are displayed in Fig. 4.6. The

![Graph showing $V_{oc}$ and $J_{sc}$ vs. CuGa film thickness.](image)

**Figure 4.6:** $V_{oc}$ and $J_{sc}$ of CuIn$_x$Ga$_{1-x}$Se$_2$ films as a function of varying In and Cu content

The highest $V_{oc}$ and $J_{sc}$ of 405 mV and 8.1 mA/cm$^2$, respectively is obtained for the CuIn$_x$Ga$_{1-x}$Se$_2$ film with In film thickness equal to 916 nm and CuGa thickness equal to 197 nm. This is the CuIn$_x$Ga$_{1-x}$Se$_2$ film with the optimal [Cu]/[In] ratio composition. As the CuGa film thickness was decreased, the CuIn$_x$Ga$_{1-x}$Se$_2$ film entered Cu-poor and In-rich phase. Consequently, the $V_{oc}$ decreased from 405 mV to 380 mV and $J_{sc}$ decreased from 20.80 mA/cm$^2$ to 15.64 mA/cm$^2$ as the CuGa film
thickness decreased from 184 nm to 166 nm. Similarly, as the CuGa film thickness was increased, the CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) film entered Cu-rich and In-poor phase. A drastic decrease in \(V_{oc}\) and \(J_{sc}\) is observed as the CuGa concentration was increased in the CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) film. The \(V_{oc}\) decreased from 405 mV to 5 mV and \(J_{sc}\) decreased from 20.80 mA/cm\(^2\) to 0.51 mA/cm\(^2\) as the CuGa thickness was increased from 184 nm to 228 nm, respectively.

The change in \(V_{oc}\) and \(J_{sc}\) as a function of [Cu]/[In] ratio is attributed to the change of phases and structures in the CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) system [54]. The possible CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) phases are given in the pseudobinary system phase diagram in Fig. 2.4. As shown in the figure, the possible phases in the CuInSe\(_2\) system are, \(\alpha\), \(\beta\), \(\delta\), \(\alpha + \beta\), \(\alpha + \text{Cu}_2\text{Se}\) which result from stoichiometry variation from Cu\(_2\)Se to In\(_2\)Se\(_3\) due to [Cu]/[In] ratio and the chalcogenization temperature. Between the [Cu]/[In] ratio and the selenization temperature of 550 °C we utilized, the possible phases are \(\alpha\), \(\alpha + \beta\), \(\alpha + \text{Cu}_2\text{Se}\).

The structure of the CuInSe\(_2\) films with various Cu/In ratios were investigated by Fianti, et al [55]. The XRD spectra obtained by Fianti, et al., shows the films with high Cu/In ratio, or high Cu concentration formed CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) phase along with Cu\(_x\)Se\(_y\) phase. This corresponds to \(\alpha + \text{Cu}_2\text{Se}\) phase in the pseudobinary system. The Cu\(_x\)Se\(_y\) phase is formed due to excess presence of Cu in the CuInGa precursor, which reacts with Se to yield Cu\(_x\)Se\(_y\). The decrease in \(V_{oc}\) and \(J_{sc}\) in CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) is attributed to presence of Cu\(_x\)Se\(_y\) phase behaving like a metal. Furthermore, a decrease in bandgap of around 0.98 eV was found, which limits absorption of photons. As the Cu concentration increased in the CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) film, the film behaved like a conductor as opposed to semiconductor due to the abundance of Cu\(_x\)Se\(_y\) phase, which explains the decrease in \(V_{oc}\) and \(J_{sc}\).
Moreover, the XRD spectra obtained by Fianti, et al., reveals the presence of a single CuIn$_x$Ga$_{1-x}$Se$_2$ phase for the device with the maximum $V_{oc}$ and $J_{sc}$. This is the $\alpha$-phase in the pseudobinary system. The highest $V_{oc}$ and $J_{sc}$ is obtained by Cu/In ratio equal to 0.55. The optimal $V_{oc}$ and $J_{sc}$ can be attributed to the best crystalline quality and absence of impurities in the CuIn$_x$Ga$_{1-x}$Se$_2$ film. The single phase CuIn$_x$Ga$_{1-x}$Se$_2$ film with Cu/In ratio equal to 0.55 also exhibited the highest reported bandgap of 1.34 eV.

As the [Cu]/[In] ratio decreased the CuIn$_x$Ga$_{1-x}$Se$_2$ films became In-rich and Cu-poor, entering the $\alpha + \beta$ phase [56]. As the Cu/In ratio decreases, both the surface and the bulk of the film becomes In and Ga rich, and Cu poor. The excess In and Ga atoms occupy Cu vacancies ($V_{Cu}$) and form ($2V^{-}_{Cu} + In^{2+}_{Cu}$) defects. As the Cu/In ratio decreases, the presence of the defect pair cluster will be more abundant. The presence of ($2V^{-}_{Cu} + In^{2+}_{Cu}$) defect clusters leads to formation of ordered defect compounds including CuIn$_5$Sena, CuIn$_3$Se$_5$, Cu$_2$In$_4$Se$_7$ and Cu$_3$In$_5$Se$_9$ as a repeat of single defect pairs ($2V^{-}_{Cu} + In^{2+}_{Cu}$) unit of CuIn$_x$Ga$_{1-x}$Se$_2$. Fianti, et al., detected the presence of both CuInSe$_2$ phase and ordered defect compound phases in the In-rich CuIn$_x$Ga$_{1-x}$Se$_2$ films. These ordered phases form impurities in the CuIn$_x$Ga$_{1-x}$Se$_2$ film. These ($2V^{-}_{Cu} + In^{2+}_{Cu}$) defects, which can be converted from shallow donors into deep level electron traps under photoexcitation serve as recombination centers, reducing the mobility and carrier concentration, hence the device performance. Simulation reveal that the ($2V^{-}_{Cu} + In^{2+}_{Cu}$) defects which behave as shallow donors in the ground state, can capture two electrons and become deep defect-localized states with a substantial energy barrier for trapped electrons to re-emit into the conduction band, under photoextitation

\[(In, Ga)Cu^{2+} + 2e \leftrightarrow (In, Ga)Cu^{0} \quad (4.6)\]
Simultaneously, the \((2V^-_{Cu} + In_{Cu}^{2+})\) defects can capture free holes to back transit into the substitutional configuration,

\[
(In, Ga)Cu^0 + h \leftrightarrow (In, Ga)Cu^{2+} + e
\] (4.7)

leading for non-radiative recombination. If the surface of the CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) film is Cu poor, this \((2V^-_{Cu} + In_{Cu}^{2+})\) defect may also behave as interface defect.

Moreover, Lee, et al., attribute the change in \(V_{oc}\) and \(J_{sc}\) as a function of \([Cu]/[In]\) ratio to the crystalline size of the CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) films [54]. Cross-sectional SEM images revealed Cu-excess films exhibited smaller crystalline size with intergranular voids. In contrast, In-excess films exhibited larger crystalline size, but still exhibited intergranular voids. The reduction of \(J_{sc}\) with increasing \([Cu]\) content and \([In]\) content may be as a result of decrease in charger carrier transport due to the intergranular voids. CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) films with the best device performance revealed dense and large crystalline size with no intergranular voids and smooth surface morphology, which may explain the optimal current density, \(J_{sc}\).

We can conclude that all the CuIn\(_x\)Ga\(_{1-x}\)Se\(_2\) films with different \([Cu]/[In]\) ratios exhibited chalcopyrite structure. The films with excess Cu content or high Cu/In ratio, formed CuInSe\(_2\) phase along with Cu\(_x\)Se\(_y\) phase. This corresponds to \(\alpha + Cu_2Se\) phase in the pseudobinary system. The decrease in \(V_{oc}\) and \(J_{sc}\) in CuInSe\(_2\) is attributed to presence of Cu\(_x\)Se\(_y\) phase behaving like a metal. As the \([Cu]/[In]\) ratio decreased the CuInSe\(_2\) films become In-rich and Cu-poor, entering the \(\alpha + \beta\) phase. The excess In lead to formation of \((2V^-_{Cu} + In_{Cu}^{2+})\) defect development in CuInSe\(_2\). With increasing In content, the presence of the defect pair cluster became more abundant leading to
formation of CuIn$_5$Se$_8$, CuIn$_3$Se$_5$, Cu$_2$In$_4$Se$_7$ and Cu$_3$In$_5$Se$_9$ ordered defect compounds. Moreover, the CuInSe$_2$ films with the best device performance reveals the presence of a single CuInSe$_2$ phase in the film.

### 4.3.2 The Influence of Selenium Flux on CuIn$_x$Ga$_{1-x}$Se$_2$ Device Performance

As noted in Section 4.3, one of the main issues involving the two-step process includes producing CuIn$_x$Ga$_{1-x}$Se$_2$ films with structural and chemical homogeneity. The reaction rates of Cu/Ga with Se vapor is much faster than In/Ga with Se vapor, resulting in formation of two separate phases CuInSe$_2$ and CuGaSe$_2$ within the film, leading to structural and chemical inhomogeneity in the CuIn$_x$Ga$_{1-x}$Se$_2$ films. [57] As a result, In-related phases form at the top of the film, while the Ga-related phases are buried at the bottom of the film [58]. As the CuInSe$_2$ phase forms at the top of the film, the resulting device behaves like CuInSe$_2$, which yields low open circuit voltage, $V_{oc}$, and low conversion efficiency of the device.

Numerous methods have been utilized to improve the structural and chemical inhomogeneity resulting from formation of CuInSe$_2$ and CuGaSe$_2$ phases during conventional selenization process. One method to improve the structural and chemical inhomogeneity resulting from CuInSe$_2$ and CuGaSe$_2$ is depositing thinned CuInGa precursor film, followed by conventional selenization to yield CuIn$_x$Ga$_{1-x}$Se$_2$ film with thickness less than 1 µm. The thin precursor allows easier diffusion of Se into the film, thereby bonding with In atoms as well as Ga atoms and resulting in homogeneous CuIn$_x$Ga$_{1-x}$Se$_2$ phase. Another method is depositing CuInGaSe film from a single target source, followed by conventional selenization. The sputtered
CuInGaSe precursor film already exhibits uniformly distributed Se atoms throughout the film. After annealing in Se vapor, the CuInGaSe film is found to exhibit structural and chemical homogeneity. Moreover, rapid thermal selenization of selenium containing Cu-In-Ga-Se precursors or is also favorable method for fabricating uniform CuInGaSe films. While the reaction time can be maintained at 5-10 min, the resulting CuInGaSe films have been found to exhibit structural and chemical homogeneity.

![Surface SEM images of CIGS films selenized at various N2 fluxes](image)

**Figure 4.7: The surface SEM images of CIGS films selenized at a) 30 sccm, b) 50 sccm, c) 100 sccm.**

In our investigation, in order to form CuIn$_x$Ga$_{1-x}$Se$_2$ films with structural and chemical homogeneity we increased the selenium flux during selenization process. Controlling and increasing the Se flux is expected to enable easier Se diffusion into the CuInGa precursor film, whereby reacting with In and Ga at the same rate, hence producing uniform CuIn$_x$Ga$_{1-x}$Se$_2$ film. A series of five CuIn$_x$Ga$_{1-x}$Se$_2$ films were selenized under identical conditions except for variation in the Se flux rate. During the selenization process, the source zone was heated to 380 °C to generate Se vapor, which was carried into the sample zone by the N$_2$ carrier gas. The N$_2$ carrier gas flux was increased from 30 sccm to 100 sccm in 10 sccm intervals which controlled the Se flux. The pressure was maintained at 30 mTorr during the entire 90 minute selenization process. The surface SEM images of the CuIn$_x$Ga$_{1-x}$Se$_2$ films selenized at various N$_2$ fluxes are shown in
Fig. 4.7. As the Se flux is increased from 30 to 50 to 100 sccm, the CuIn$_{x}$Ga$_{1-x}$Se$_2$ films became more compact, exhibiting larger grainsize and shape, less intergranular voids, indicating improvement in crystallinity. The figure shows the obtained open circuit voltage, $V_{oc}$, and short circuit current density, $J_{sc}$, of the films as a function of Se flux. When the Se flux is 40 sccm, the $V_{oc}$ and $J_{sc}$ are 374 mV and 13.59 mA/cm$^2$, respectively. As the Se flux is increased from 40 sccm to 100 sccm, a gradual increase in both $V_{oc}$ and $J_{sc}$ is obtained. As the Se flux reached 100 sccm, the $V_{oc}$ and $J_{sc}$ reached 432 mV and 23.5 mA/cm$^2$, respectively.

Han et al., attribute the increase in both $V_{oc}$ and $J_{sc}$ as a function of rising Se to formation of In$_2$Se$_3$ and Ga$_2$Se$_3$ during the early stages of the selenization process which leads to reaction of CuSe$_2$, In$_2$Se$_3$ and Ga$_2$Se$_3$ to form CuIn$_x$Ga$_{1-x}$Se$_2$ [59]. Since the reaction of Se with In is kinetically favored compared to that of Ga, if the Se vapor is insufficient, CuSe$_2$ and In$_2$Se$_3$ phases will be dominant. This will lead to unreacted Ga atoms. Hence, the resulting films end up having CuInSe$_2$.

![Figure 4.8: $V_{oc}$ and $J_{sc}$ of CuInGaSe$_2$ devices as a function a selenium flux rate.](image-url)
phase with unreacted Ga atoms. The rise in Se flux leads to an increase of Se atmosphere near the surface of the CuInGa precursor film and enables deeper Se penetration into the CuInGa precursor. This benefits the formation of Ga$_2$Se$_3$ phase, whose increase in magnitude pushes the reaction of Ga$_2$Se$_3$, In$_2$Se$_3$ and CuSe$_2$. These phases then react to form 2CuInSe$_2$ and 2CuGaSe$_2$ which in return result in formation of CuIn$_x$Ga$_{1-x}$Se$_2$.

Similarly, Park et al., attribute the increase in device performance as a function of increasing Se to improvement in CuIn$_x$Ga$_{1-x}$Se$_2$ crystallinity and formation of MoSe$_2$ film at the Mo/CuIn$_x$Ga$_{1-x}$Se$_2$ interface [60]. XRD spectra obtained by Park et al. show that all films selenized at low Se flux exhibited main peaks at [112], [220], [312] crystal orientations corresponding to CuIn$_x$Ga$_{1-x}$Se$_2$ phase, along with peaks corresponding to metallic phases such as Cu$_9$Ga$_4$ and Cu$_{16}$In$_9$. However, the intensity of these metallic phases diminished and disappeared as a function of increasing Se flux. This lead to formation of pure CuIn$_x$Ga$_{1-x}$Se$_2$ phase as a function of increasing Se flux. Moreover, as the Se flux increased, [103] peak appeared corresponding to MoSe$_2$ film formation at the Mo/CuIn$_x$Ga$_{1-x}$Se$_2$ interface. MoSe$_2$ layer is known to change the Mo/CuIn$_x$Ga$_{1-x}$Se$_2$ Shottky barrier to Mo/MoSe$_2$/CuIn$_x$Ga$_{1-x}$Se$_2$ Ohmic barrier, whereby increasing the device performance.

We can conclude that increasing the flux of Se during selenization leads to a more uniform structural and chemical homogeneity. Increasing the Se flux, enhances the reaction rates of Cu/Ga with Se and In/Ga with Se vapor, leading to formation of In$_2$Se$_3$ and Ga$_2$Se$_3$ phases form during the early stages of the selenization process. The In$_2$Se$_3$, Ga$_2$Se$_3$, CuSe$_2$ phases then react to form 2CuInSe$_2$ and 2CuGaSe$_2$, which then react to form the desired chalcopyrite CuIn$_x$Ga$_{1-x}$Se$_2$ phase.
4.3.3 The Influence of Cracked Selenium on CuIn_{x}Ga_{1-x}Se_{2} device performance

Thermally assisted Se vapor selenization process is highly desirable because it is non-toxic and of low cost. However, thermally assisted Se vapor has large molecular chains Se_{x}, x>5. During the selenization process, Se source atoms react with the nearest neighbor Se atoms and form polymeric rings up to 1000 atoms per ring. At higher temperatures, Se molecular chains reduce to Se_{6}, Se_{7} and Se_{8} rings. Consequently, the Se_{x} molecular chains exhibit low chemical reactivity and cannot penetrate deep into the CuInGa precursor film, resulting in large selenium consumption, selenium deficiency through the film, leading to randomly local non-stoichiometry and deteriorating uniformity and film structure. One strategy for increasing the activity of Se vapor is utilize argon-diluted H_{2}Se gas or hydrogen-assisted Se vapor. CuInGaSe films fabricated in the H_{2}Se atmosphere displayed superior structural and morphological properties as well as homogeneity. However, because H_{2}Se is expensive, highly toxic and explosive, hydrogen-assisted Se vapor is not preferred. Another method is to employ plasma-assisted Se technique to increase the activation energy of Se vapor. The activity of Se vapor is increased by coupling with a radio frequency (RF)-plasma treatment. Other alternative ways to increase the Se chemical activity is to increase the Se source zone temperature, also called thermal cracking process. Thermal cracking of Se is achieved by high-temperature heating of selenium clusters to decompose them into Se_{x}, x<5. The increase in temperature breaks the Se-Se bonds, thereby increasing the chemical activity of Se radicals.

In this section, we describe the effect of Se cracking temperature on the CuIn_{x}Ga_{1-x}Se_{2} device performance. A series of six CuIn_{x}Ga_{1-x}Se_{2} films were selenized under identical conditions.
except for variation in the Se source zone temperature. During the selenization process, the source zone temperature was increased from 200 °C to 550 °C in 50 °C increments. The Se vapor was carried into the sample zone by the N\textsubscript{2} carrier gas. While the N\textsubscript{2} carrier gas flux was held at 100 sccm, the pressure was maintained at about 30 mTorr during the entire selenization process.

![Graph showing open circuit voltage and short circuit current density as a function of selenium cracking temperature.](image)

**Figure 4.9:** \(V_{oc}\) and \(J_{sc}\) of CuInGaSe\(_2\) devices as a function of selenium cracking temperature.

Fig. 4.9 shows the obtained open circuit voltage, \(V_{oc}\), and short circuit current density, \(J_{sc}\), of the films as a function of Se cracking temperature. When the Se cracking temperature is 200 °C, the \(V_{oc}\) and \(J_{sc}\) are 325 mV and 10.5 mA/cm\(^2\), respectively. As the Se cracking temperature is increased from 200 °C to 550 °C, a gradual increase in both \(V_{oc}\) and \(J_{sc}\) is obtained. As the Se cracking temperature reached 550 °C, the \(V_{oc}\) and \(J_{sc}\) reached 525 mV and 24.10 mA/cm\(^2\), respectively. The increase in \(V_{oc}\) and \(J_{sc}\) is attributed to diffusion of Se into the CIG precursor film.
leading to significant phase variation of the CuInGaSe$_2$ films as a function of Se source temperature. Han et al., attribute the increase in both $V_{oc}$ and $J_{sc}$ as a function of Se cracking temperature to formation of In$_2$Se$_3$ and Ga$_2$Se$_3$ during the early stages of selenization process [59].

The XRD results obtained by Huang, et al., show the presence of Cu$_2$Se, CuSe, In$_4$Se$_3$ and Cu$_7$(In$_{1-x}$Ga$_x$)$_3$ phases when selenized at low Se source temperature around 150 to 250 C [61]. Similarly, XRD results obtained by Li, et al., reveal the presence of CuInSe$_2$, CuSe, CuSe$_2$ phases at Se cracking temperatures between 150 to 200 C [62]. Moreover, Cu$_3$Ga phase is also present, indicative of unreacted Ga. At higher temperatures, around 350 °C, the peak intensities corresponding to binary phases InSe, CuSe diminish indicating these phases are disappearing. Furthermore, at 350 °C, the XRD pattern starts to exhibit a low intensity peak displayed at 27.7 degree corresponding to CuGaSe$_2$ phase. This is the lowest Se source temperature which generates ternary Ga-phase in the film. At even higher temperatures, around 450 °C, all the binary phases disappear and the two ternary CuInSe$_2$ and CuGaSe$_2$ dominate throughout the film. As the Se source temperature exceeds 500 °C, the peak intensity of CuGaSe$_2$ continue to rise and broaden, suggesting more presence of CuGaSe$_2$ phase in the CIGS film. As the temperature reaches 550 °C, the CuInSe$_2$ and CuGaSe$_2$ peaks merge and shift to 26.9 degree, indicative of forming the (112) oriented chalcopyrite CuInGaSe$_2$ phase, which shows a moderate Ga-containing CIGS phase. The results show the thermal-assisted Se vapor selenization process reduce the reaction activation energy of Ga-Se, leading to formation of GaSe phase. This facilitates the formation of CuGaSe$_2$ phase, which then reacts with CuInSe$_2$ phase to form the chalcopyrite CuInGaSe$_2$ phase.

In conclusion, the increase in $V_{oc}$ and $J_{sc}$ is attributed to diffusion of Se into the CuInGa precursor film by breaking the Se-Se bonds in selenium molecules. Diffusion of Se into the CuInGa precursor film during the early stages of the selenization process, leads to formation of Ga-related
phases. The Ga-related phases enable formation of CuGaSe$_2$ phase which then react with CuInSe$_2$ to form the chalcopyrite CuInGaSe$_2$ phase. We can conclude increasing cracking temperature of Se lowers the activation energy of Se-Ga bonds.

4.4 Conclusion

In conclusion, we studied the parameters to optimize the uniformity, morphology and homogeneity of CuInGa films using magnetron sputtering. Our results show that CuInGa precursor film sputtered sequentially as In/CuGa/In had the smoothest morphology and the best CuInGa homogeneity. We then investigated the selenization parameters to optimize the CuIn$_{x}$Ga$_{1-x}$Se$_2$ device performance. During the selenization process, we varied the selenium flux angle, sputtering times, selenium flux rate and selenium zone temperature. Our results show that the most uniform CIGS films are produced when the Se flux is perpendicular to the surface of the CIG precursor. The device performance can be optimized by tuning the Cu/In composition. An increase in Se flux facilitates In$_2$Se$_3$ and Ga$_2$Se$_3$ phases, resulting in compact CIGS films with larger grains, leading to better device performance. We finally show thermally evaporated selenization results in enhanced device performance by selenium diffusion into the film, and lowering the activation energy of Se-Ga bonds.
Chapter 5: Optimization of the Defects and the Nonradiative Lifetime of GaAs/AlGaAs Double Heterostructures

This chapter presents investigation of deposition parameters that optimize the crystalline quality and therefore the internal radiative quantum efficiency of MBE-grown GaAs/AlGaAs double heterostructures (DH) using Raman spectroscopy and time-resolved photoluminescence (TRPL) measurements. The DH structures were grown at two different temperatures and three different As/Ga flux ratios to determine the conditions for an optimized structure with the longest nonradiative minority carrier lifetime. Moreover, we investigated the effect of the distributed Bragg reflector (DBR) between the substrate and DH structures on the defect density. Sections 5.2 and 5.3 present Raman scattering results which show an improvement in lattice disorder in both the GaAs and AlGaAs layers as the As/Ga flux ratio is reduced from 40 to 20 to 15 and substrate temperature is increased from 550 °C to 595 °C, which is consistent with the longest minority carrier lifetime from our TRPL results. Sections 5.4 and 5.5 reveal that incorporation of a distributed Bragg reflector layer significantly reduces the defect density in the subsequent layers due to a decrease in the density of defects in the GaAs/AlGaAs double heterostructures. Our results show that the combined analysis of Raman and TRPL spectra provide a powerful tool for understanding defect mechanisms and carrier dynamics in GaAs/AlGaAs DH structures since the conventional spectroscopy techniques including transmission electron microscopy (TEM) and electron diffraction analysis may not always reveal the defect mechanisms in structures as shown in Section 5.6. Section 5.7 summarizes the results presented in this chapter.
5.1 Experimental Description

GaAs/AlGaAs double heterostructures were grown at U.S. Army Research Laboratory by molecular beam epitaxy (MBE) on semi-insulating (100) oriented GaAs substrates with the following layers: 500-Å Al_{0.5}Ga_{0.5}As, 20-µm GaAs active region, 500-Å Al_{0.5}Ga_{0.5}As, and a 50-Å GaAs cap layer. The GaAs buffer layer was grown at 550°C and 595°C, and with As/Ga flux ratios of 15, 20 and 40, while the thicknesses of the DH layers were unchanged. A DH structure was also grown on top of a distributed Bragg reflector that comprises ten periods of a 598-Å GaAs/726-Å Al_{0.8}Ga_{0.2}As superlattice. In Raman scattering measurements, the samples were excited by the 514.5 nm line of an Ar^+ laser (2.0 µm, 10.0 mW), and the scattered signal was collected in backscattering geometry at room temperature. The time-resolved photoluminescence measurements were conducted at the U.S. Army Research Laboratory using 632 nm (250 kHz, 6.7 mW, 1.5 mm) in reflection geometry at room temperature. The time resolved photoluminescence spectra as well as the spectral analysis were provided by the U.S. Army Research Laboratory. Details on sample preparation and equipment specifications can be found in Chapter 2.

5.2 Effect of As/Ga Flux Ratio on the Defect Density of GaAs/AlGaAs Double Heterostructures

We first investigated the effect of As/Ga flux ratios of 15, 20, and 40 at 595 °C on the defect density and hence the internal radiative quantum efficiency of the MBE-grown GaAs/AlGaAs double heterostructures. In Fig. 5.1, the normalized Raman scattering spectra of the DH structures grown with As/Ga flux ratios of 15, 20 and 40 at 595 °C along with the spectrum of the GaAs substrate as a reference is shown. The Raman spectra suggest the scattering arises in the Al_{0.5}Ga_{1-x}As barrier and the GaAs layer, as the penetration depth of the 514.5 nm laser radiation is
approximately 1053 Å in GaAs [63]. The Al\textsubscript{x}Ga\textsubscript{1-x}As/GaAs DH Raman spectra exhibit the decomposed “GaAs-like” optical phonons assigned to the GaAs buffer layer, and the “AlAs-like” optical phonons assigned to the Al\textsubscript{0.5}Ga\textsubscript{0.5}As epitaxial layer. Selection rules, obtained by the Raman dispersion tensor analysis, only allow longitudinal-optical (LO) phonons to appear in the Raman spectrum for the Al\textsubscript{x}Ga\textsubscript{1-x}As/GaAs DH structure in the backscattering geometry [64]. Defects and impurities in the Al\textsubscript{x}Ga\textsubscript{1-x}As/GaAs DH, that are possibly associated with growth of Al\textsubscript{x}Ga\textsubscript{1-x}As, result in non-conservation of momentum, a breakdown of the selection rules for Raman scattering and the appearance of forbidden transverse-optical (TO) phonon modes and broadened coupled LO phonon-plasmon modes in the Raman spectra [65]. In the spectra, the intense dominant LO-GaAs mode located at 290 cm\textsuperscript{-1}, and the well-defined TO-GaAs mode localized near 266 cm\textsuperscript{-1} are identified. Furthermore, the LO-AlAs mode localized around 385 cm\textsuperscript{-1} is observed. The frequency position of the AlAs-like phonon located at 385 cm\textsuperscript{-1} coincides with the theoretical calculations for Al\textsubscript{x}Ga\textsubscript{1-x}As modes:

\[
\omega_{LO}^{GaAs}(x) = 290.2 - 36.7x \text{ cm}^{-1} \tag{5.1}
\]

\[
\omega_{LO}^{AlAs}(x) = 364.7 + 46.7x - 9.4x^2 \text{ cm}^{-1}. \tag{5.2}
\]

with aluminum content x=0.5 [66] [67]. Finally, the TO-AlAs mode near 364 cm\textsuperscript{-1} appears as a small shoulder on the lower frequency side of the LO-AlAs mode. The GaAs substrate exhibits a fairly narrow (Γ\textsubscript{0}=5.8 cm\textsuperscript{-1}) and symmetric (Γ\textsubscript{a}=2.8 cm\textsuperscript{-1}, Γ\textsubscript{b}=3.0 cm\textsuperscript{-1}) LO-GaAs phonon, and retains a small intensity TO-GaAs phonon, indicative of lattice disorder in the GaAs layer arising from slight disorientation from the (100) surface [68]. Compared to the GaAs substrate, the DH
structures grown with As/Ga flux ratios of 15, 20 and 40 exhibit broader LO-GaAs mode as well as a higher intensity TO-GaAs mode arising from compositional and lattice disorder. The highest level of lattice disorder in the GaAs layer is observed for the DH structure M1279, grown with As/Ga flux ratio of 40. However, an improvement in the lattice disorder in the GaAs is observed as a function of decreasing As/Ga flux ratio from 40 to 20 to 15, as the intensity of the defect activated TO-GaAs phonon diminishes monotonically.

Figure 5.1: Normalized Raman spectra of GaAs/Al$_{0.5}$Ga$_{0.5}$As DH structures grown at 595 °C with an As/Ga flux ratio of 15, 20 and 40.

In the spectra, the intensity of the defect activated TO-AlAs mode decreases drastically and the linewidth of the LO-AlAs mode becomes more symmetric as a function of decreasing
As/Ga flux ratio from 40 to 20 to 15. This indicates an obvious improvement in the crystalline quality in the Al$_{0.5}$Ga$_{0.5}$As layer as a result of decreasing defect density. Interestingly, the linewidth and the symmetry of the LO-GaAs mode also depend on the As/Ga flux ratio. Previous studies have attributed variation in the linewidth and symmetry of the LO-GaAs phonon to the compositional disorder in the Al$_x$Ga$_{1-x}$As layer due to the aluminum concentration [69]. Al$_x$Ga$_{1-x}$As structures with more aluminum content exhibited wider and more asymmetric LO-GaAs mode as a result to translational invariance being broken due to microscopic nature of lattice disorder [70].

![Figure 5.2: Time-resolved photoluminescence (TRPL) spectra of GaAs/AlGaAs DH structures grown at 595 °C with As/Ga flux ratio 15, 20 and 40.](image)

We reveal the lattice disorder in the Al$_x$Ga$_{1-x}$As is improved only when the As/Ga flux ratio is changed in the GaAs buffer layer. The linewidth of the LO-GaAs phonon reduced from 8.5 cm$^{-1}$, to 6.6 cm$^{-1}$ to 5.5 cm$^{-1}$ as the As/Ga flux ratio decreased from 40 to 20 to 15, respectively.
Similarly, an improvement in the symmetry of LO-GaAs phonon is observed when the As/Ga flux ratio was reduced from 40 ($\Gamma_a=3.9$, $\Gamma_b=4.6$) to 20 ($\Gamma_a=3.2$, $\Gamma_b=3.3$) to 15 ($\Gamma_a=2.8$, $\Gamma_b=2.7$). The decrease in defect activated TO-AlAs phonon, and the improvement of the linewidth and the symmetry of both the LO-AlAs and LO-GaAs modes are strong indications that an improvement in the lattice disorder of the GaAs layer improves the lattice disorder in the subsequent layers.

To gain insight into the defect-induced changes in the Raman spectra, we also utilized time-resolved photoluminescence measurements to determine the minority carrier lifetime and internal radiative quantum efficiency of the GaAs/AlGaAs DH structures. Fig. 5.2 shows the natural logarithm of the TRPL spectra for the DH structures grown with As/Ga flux ratios of 15, 20 and 40 at 595°C. Upon excitation, all spectra exhibit a bimolecular and non-exponential decay for the first 40 ns due to fast surface recombination as a result of screening of the electric field in the surface depletion region [71] [72]. A single exponential decay follows immediately after the first 40 ns as a result of reaching low-injection regime conditions [73]. The effective minority carrier lifetime, the PL decay time, $\tau$ is determined by fitting a single exponential decay to the low-injection tail of the PL decay. For the structure grown with As/Ga flux ratio of 40, the effective minority carrier lifetime is determined to be 576 ns as shown in Table 5.1. As the As/Ga flux ratio was reduced to 20, the minority carrier lifetime increased to 871 ns, and an optimal value of 1120 ns was obtained for the DH structure grown with As/Ga flux ratio 15. Using the theory developed by Nelson and Sobers [74], we calculate the minority carrier nonradiative lifetime from the following equation.

$$\frac{1}{\tau} = \frac{1}{\tau_{nr}} + \frac{2S}{d}$$

(5.3)

where $d = 20 \mu m$ is the thickness of the GaAs layer, and $S=75 \text{ cm/s}$ is the GaAs/AlGaAs interface recombination velocity determined from previous measurements [75] [76]. Radiative
recombination has a negligible contribution to the effective minority carrier lifetime in the 20 µm undoped GaAs layer due to the self-absorption of emitted photons and the low carrier concentration in the undoped GaAs layer. Accordingly, the minority carrier nonradiative lifetime for the DH structure grown with As/Ga flux ratio 40 is 602 ns, and increased to 932 ns and 1200 ns for the DH structures grown with As/Ga flux ratio 20 and 15 respectively. A similar result is also observed for the nonradiative lifetime. Under the weak injection condition, theory [77] [78] shows that $\tau_{nr} = 1/(\sigma v_{th} N_t)$, where $\sigma$ is the carrier capture cross-section, $v_{th}$ is the carrier thermal velocity and $N_t$ is the deep trap density. Using known GaAs parameters [79] and the observed $\tau_{nr}$, we determine that for the DH that was grown with As/Ga flux ratio of 20 at 550°C, $N_t = 1.1 \times 10^{14}$cm$^{-3}$ while the optimized structure, grown with the As/Ga flux ratio equal to 15 at 595°C, has a reduced trap density, $N_t = 2 \times 10^{13}$cm$^{-3}$.

<table>
<thead>
<tr>
<th>Sample Name, As/Ga Flux ratio</th>
<th>Substrate growth temperature (°C)</th>
<th>Minority carrier lifetime (ns)</th>
<th>Nonradiative recombination lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1280, 15</td>
<td>595</td>
<td>1120</td>
<td>1200</td>
</tr>
<tr>
<td>1278, 20</td>
<td>595</td>
<td>871</td>
<td>932</td>
</tr>
<tr>
<td>1279, 40</td>
<td>595</td>
<td>576</td>
<td>602</td>
</tr>
</tbody>
</table>

Table 5.1: Minority carrier lifetime and nonradiative recombination lifetime of GaAs/AlGaAs DH structures grown at 595°C with As/Ga flux ratios 15, 20 and 40.

5.3 Effect of the Substrate Temperature on the Defect Density of GaAs/AlGaAs Double Heterostructures
Next, we investigated the effect of the substrate temperature on the density of defects in the GaAs/Al_{1-x}Ga_{x}As DH structures. Fig. 5.3 shows the normalized Raman spectra of the DH structures M1281 and M1278 grown at 550°C and 595°C respectively, with As/Ga flux ratio of 20. A drastic increase in the density of defects is observed in both the GaAs layer and the Al_{0.5}Ga_{0.5}As layer when the temperature was reduced from 595 °C to 550 °C as the defect activated TO-GaAs and TO-AlAs modes intensified. Similarly, the linewidth of the LO-AlAs and LO-GaAs phonons broadened and became less symmetric indicative of poor translational invariance and a decrease in the overall crystalline quality of the Al_{x}Ga_{1-x}As epitaxial layer.

![Normalized Raman spectra of GaAs/AlGaAs DH structures grown at 595 °C, and 550 °C.](image)

**Figure 5.3:** Normalized Raman spectra of GaAs/AlGaAs DH structures grown at 595 °C, and 550 °C.

The influence of the substrate growth temperature on the minority carrier dynamics was also investigated. As listed in Table 5.2, the minority carrier lifetime reduced from 871 ns to 250
ns as the substrate growth temperature is decreased from 595°C to 550°C. A similar result is also observed for the nonradiative lifetime.

5.4 Effect of the Distributed Bragg Reflector on the Defect Density of GaAs/AlGaAs Double Heterostructures

Moreover, we studied the effect of incorporating GaAs/Al$_{0.8}$Ga$_{0.2}$As Bragg reflector on the crystalline quality and deep trap defect density of GaAs/Al$_{0.5}$Ga$_{0.5}$As DH structures. Fig. 5.4 shows the normalized Raman spectrum of the GaAs/Al$_{0.5}$Ga$_{0.5}$As DH structure grown with an As/Ga flux

**Figure 5.4:** Normalized Raman spectra of GaAs/AlGaAs DH structures grown at 595 °C with and without a Bragg reflector.

Moreover, we studied the effect of incorporating GaAs/Al$_{0.8}$Ga$_{0.2}$As Bragg reflector on the crystalline quality and deep trap defect density of GaAs/Al$_{0.5}$Ga$_{0.5}$As DH structures. Fig. 5.4 shows the normalized Raman spectrum of the GaAs/Al$_{0.5}$Ga$_{0.5}$As DH structure grown with an As/Ga flux
ratio of 20 at 595°C with the Bragg reflector. The Raman spectrum of the DH with the Bragg reflector retains the GaAs like and AlAs like phonon as that of the structure without the Bragg reflector. However, both the defect activated TO-GaAs and the TO-AlAs modes appear with a lower intensity in the structure with the Bragg reflector. This is a strong indication that the density of structural defects is reduced by incorporating the GaAs/Al$_{0.8}$Ga$_{0.2}$As Bragg reflector. Furthermore, the linewidth of the LO-GaAs mode reduced from 6.5 to 6.3 cm$^{-1}$, and became more symmetric compared to the structure grown without the Bragg reflector. This is a strong indication that incorporating the Bragg reflector improves the crystalline quality of the subsequent layers in the DH structures.

Furthermore, we observed that both the minority carrier lifetime and nonradiative lifetime increased for the GaAs/AlGaAs DH structure grown with the Bragg reflector compared to that for the structure grown without it. The minority carrier lifetime increased from 871 ns to 919 ns, while the nonradiative lifetime increased from 932 ns to 987 ns as shown in Table 6.2. The increase in the minority carrier lifetime and nonradiative lifetime of the GaAs/AlGaAs DH structure is attributed to the decrease in defect density by the incorporation of the GaAs/AlGaAs Bragg reflector as evidenced in the Raman spectra. The decrease of defect activated TO-GaAs and TO-AlAs, indicative of a decrease in defect density, resulted in an increase of the minority carrier lifetime and the nonradiative lifetime by 5.2 % and 5.8 % respectively, compared to that of the structure grown without the Bragg reflector. TRPL measurements on other AlGaAs/GaAs DH structures, that were grown at 550°C with an As/Ga ratio of 40 with and without the Bragg reflector, show that the Bragg reflector increases the nonradiative lifetime from 209 ns to 539 ns. The growth of the Al$_{0.8}$Ga$_{0.2}$As Bragg reflector between the GaAs active layer and the substrate
improves crystalline quality, reduces deep trap density and increases the nonradiative lifetime of GaAs/AlGaAs DH structures.

5.5 Effect of the Distributed Bragg Reflector on the Defect Density of GaAs/AlGaAs Double Heterostructures of various GaAs thicknesses

Incorporation of the distributed Bragg Reflector improved the crystalline quality in both GaAs and Al$_{0.5}$Ga$_{0.5}$As layers. To investigate the degree of improvement in the GaAs and Al$_{0.5}$Ga$_{0.5}$As layers, we decreased the thickness of the GaAs layer from 20 µm to 2 µm and 1 µm. In this section, we report the results of an investigation of the effect of a DBR on the nonradiative lifetime in GaAs/AlGaAs DHs with 2 µm and 1 µm GaAs layer. Fig. 5.5 shows the observed Raman scattering spectra of the DH structures M1286 and M1165 with a 2 µm thick GaAs layer grown with and without the BR respectively. The spectrum of the GaAs substrate is also shown as a reference. Four optical phonon modes are identified in the spectra: the dominant LO-GaAs mode at 290 cm$^{-1}$, the TO-GaAs mode around 270 cm$^{-1}$, the well-defined LO-AlAs mode at 385 cm$^{-1}$, as well as the TO-AlAs mode localized around 360 cm$^{-1}$ appearing as a small shoulder on the lower frequency side of the LO-AlAs mode. The frequency positions of the LO-AlAs and LO-GaAs modes agree with the theoretical calculations for Al$_x$Ga$_{1-x}$As modes with aluminum content x=0.5. The frequency positions of the GaAs-like and AlAs-like phonons of the DH structures with a 2 µm GaAs layer grown with and without the BR coincide, suggesting the DBR does not induce any compositional change in the Al$_x$Ga$_{1-x}$As and the GaAs epitaxial layers.
In the spectra, a high-intensity TO-GaAs phonon is observed for both DH structures, indicative of lattice disorder in the GaAs layer arising from slight disorientation from the (100) surface. However, with the incorporation of the BR, the intensity of the TO-GaAs phonon is reduced compared to that of the DH grown without the BR, indicating restoring of lattice disorder in GaAs induced by the BR [80]. Moreover, both spectra retain the defect activated TO-AlAs mode on the low-frequency side of the LO-AlAs mode, indicative of structural defects in the Al$_{0.5}$Ga$_{0.5}$As layer. However, incorporation of the BR enhances the Al$_{0.5}$Ga$_{0.5}$As crystalline quality as evidenced by the reduction of the intensity of the TO-AlAs phonon.

**Figure 5.5:** Raman scattering spectra of GaAs/AlGaAs DH structures grown with $d=2\ \mu m$ with and without the Bragg reflector.
The enhancement of the Al$_{0.5}$Ga$_{0.5}$As crystallinity is further confirmed by the LO-GaAs mode line shape and symmetry. The GaAs substrate spectrum exhibits a narrow ($\Gamma_0 = 3.7$ cm$^{-1}$) symmetric ($\Gamma_a = 1.9$ cm$^{-1}$, $\Gamma_b = 1.8$ cm$^{-1}$) Lorentzian line shape. However, the LO-GaAs phonon of the DHs exhibit broader and asymmetric line shape. Asymmetric broadening of the LO-GaAs mode is attributed to the translational invariance in Al$_{0.5}$Ga$_{0.5}$As being broken as a result of microscopic nature of lattice disorder due to aluminum concentration. DH M1165 exhibits a broad ($\Gamma_0 = 4.6$ cm$^{-1}$) and asymmetric ($\Gamma_a = 2.2$ cm$^{-1}$, $\Gamma_b = 2.4$ cm$^{-1}$) LO-GaAs phonon. With the incorporation of the Bragg reflector, translational invariance is restored as the linewidth becomes narrower ($\Gamma_0 = 4.4$ cm$^{-1}$) and more symmetric ($\Gamma_a = 2.1$ cm$^{-1}$, $\Gamma_b = 2.3$ cm$^{-1}$). Similar behavior is observed for the linewidth LO-AlAs phonon. The linewidth of the LO-AlAs phonon becomes

\textbf{Figure 5.6: TRPL spectra of GaAs/AlGaAs DH structures grown with $d = 2$ µm with and without the Bragg reflector.}
narrower with the incorporation of the BR by 1.1 cm\(^{-1}\) indicating an overall improvement in the crystalline quality of the Al\(_{0.5}\)Ga\(_{0.5}\)As layer.

Fig. 5.7 shows the TRPL spectra of the DH structures with a 2 µm thick GaAs layer grown with and without the BR. We observe a significant increase in both the minority carrier lifetime and nonradiative lifetime for the DH structure with the Bragg reflector: The minority carrier lifetime showed a 61% increase from 131 ns to 212 ns and the nonradiative lifetime increased by 63% from 209 ns to 539 ns. A larger increase in the minority carrier lifetime is observed when the GaAs layer is reduced while keeping the growth parameters unchanged.

![Raman spectra of DH structures with and without BR](image)

**Figure 5.7:** Raman scattering spectra of GaAs/AlGaAs DH structures grown with \(d = 1 \mu m\) with and without the Bragg reflector.

Figure 5.8 shows that the Raman spectra of the DH structures M1288 and M1285 with a 1 µm GaAs layer grown with and without the BR. The DHs exhibit similar behavior to that of the
structures with 2µm GaAs layer. Incorporation of the BR enhances the crystalline quality of both the GaAs and AlGaAs layers, as the defect activated TO-GaAs and TO-AlAs phonons diminish. Furthermore, for the DH grown with BR the linewidth of the LO-GaAs phonon decreased by 0.6 cm\(^{-1}\), and the line shape became more symmetric \((\Gamma_a = 2.2, \Gamma_b = 2.1)\) compared to that grown without the BR \((\Gamma_a = 2.6, \Gamma_b = 2.3)\). The LO-AlAs phonon of the DH with the BR is closer to the theoretical value of 385.8 cm\(^{-1}\) than the DH without the BR suggesting better crystallinity in the Al\(_x\)Ga\(_{1-x}\)As layers. Fig. 5.8 shows the TRPL spectra of DH structures with 1 µm GaAs layer grown with and without the BR. The minority carrier lifetime increased by 68% from 101 ns to 170 ns and the nonradiative lifetime increased by 63% from 209 ns to 539 ns.

\[\text{Figure 5.8: TRPL spectra of GaAs/AlGaAs DH structures grown with } d = 1 \text{ µm with and without the Bragg reflector.}\]
Overall, the crystalline quality of the $\text{Al}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}$ layers have improved as can be seen by the reduction of the defect activated TO-$\text{GaAs}$ and TO-$\text{AlAs}$ phonon intensities, restoration of LO-$\text{GaAs}$ phonon linewidth and symmetry. The decrease in the forbidden TO-$\text{GaAs}$ and TO-$\text{AlAs}$ modes, improvement of linewidth and symmetry of the LO-$\text{GaAs}$ mode are strong indications that the density of structural defects in GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epitaxial layers is decreased with the incorporation of the GaAs/$\text{Al}_{0.8}\text{Ga}_{0.2}$As BR. This is consistent with the increased minority carrier lifetime and nonradiative lifetime in DH structures grown with the BR

**Figure 5.9:** TEM images of optimized sample M1280 and non-optimized sample M1281. Selected area electron diffraction patterns of optimized sample M1280 and non-optimized sample M1281.
hat has been attributed to the decrease in the defect density by the incorporation of the BR. It is important to note that growth of the Al$_{0.8}$Ga$_{0.2}$As Bragg reflector between the GaAs active layer and the substrate improves crystalline quality, reduces deep trap density and increases the nonradiative lifetime of GaAs/AlGaAs DH structures.

It is crucial to note that the differences in the crystal structure and nonradiative lifetime that are easily detected by Raman scattering and TRPL measurements are not readily observed by transmission electron microscopy (TEM) or possibly by deep-level transient spectroscopy (DLTS), since the deep level trap densities are very low. For example, TEM images of the optimized sample M1278 ($\tau_{nr}=1200$ ns) and a non-optimized sample M1281 ($\tau_{nr}=255$ ns) indicate smooth sharp interfaces with no visible dislocations and both samples exhibit excellent selected area diffraction images as shown in Fig. 5.10.

### 5.5 Summary

In conclusion, Raman scattering measurements were used to determine the changes of defect density as a function of As/Ga flux ratio, substrate growth temperature and due to incorporation of a distributed Bragg reflector between the substrate and the DHs. Furthermore, TRPL was utilized to determine the minority carrier lifetimes, the interface recombination velocity and the radiative recombination constant on a set of MBE-grown GaAs/AlGaAs double heterostructures. Raman scattering results show improvement in both compositional and lattice disorder in GaAs layer as the As/Ga flux ratio was reduced from 40 to 20 to 15. Improvement in compositional and lattice disorder in GaAs lead to a better crystalline quality in the subsequent Al$_{0.5}$Ga$_{0.5}$As layer, resulting in better heterojunction interface quality and hence longer minority carrier lifetime and longer non-radiative recombination time. We observed a similar behavior when
the substrate growth temperature was increased from 550 °C to 595 °C. As the compositional and lattice disorder improved for GaAs layer, Al$_{0.5}$Ga$_{0.5}$As crystalline quality improved, leading to longer minority carrier lifetime and minority carrier non-radiative recombination time as shown in the TRPL results. Moreover, we show that the growth of a GaAs/AlGaAs Bragg reflector between the GaAs substrate and the active DH layer lowered the intensity of defect activated TO-GaAl and TO-AlAs phonons, indicating an improvement in compositional and lattice disorder in both GaAs and Al$_{0.5}$Ga$_{0.5}$As layers leading to much longer minority carrier lifetime and minority carrier non-radiative recombination time. Our results show that the combined analysis of Raman and TRPL spectra provide a powerful tool for understanding defect mechanisms and carrier dynamics in GaAs/AlGaAs DH structures since the conventional spectroscopy techniques including transmission electron microscopy (TEM) and electron diffraction analysis may not always reveal the defect mechanisms in structures.
Chapter 6: Summary

CuIn$_x$Ga$_{1-x}$Se$_2$ is a promising chalcopyrite absorber material for high efficiency thin film solar cells due to its exceptional radiation stability, tunable direct bandgap, high absorption coefficient and low cost preparation methods. In the first part of this thesis, we present the systematic investigation of the deposition conditions to optimize the Mo back contact, ZnO:Al front contact using magnetron sputtering technique. Next, we present systematic investigation of deposition conditions to optimize the CuIn$_x$Ga$_{1-x}$Se$_2$ absorber film using the two-step deposition method. In the second part of this thesis, we present the use of Raman spectroscopy and time-resolved photoluminescence techniques to investigate and optimize the bulk and interface properties of photovoltaic devices.

First, we present the investigation of deposition parameters to optimize the structural, electrical, optical and adhesion properties of molybdenum, Mo back contact, and aluminum doped zinc oxide, ZnO:Al front contact. Our results show that Mo films deposited at high pressure exhibited tensile stress which lead to good adhesion, but suffered from high sheet resistance due to grain boundary scattering of small Mo grains size and grain density. In contrast, the Mo films deposited at low pressure exhibited compressive stress which lead to poor adhesion, but low sheet resistance due to large Mo grain size and grain density. Moreover, increase in sputter power resulted in lower sheet resistance due to increased grain size and shape, lower intergranular voids, reduced grain-boundary scattering, increased mobility and carrier concentration. Finally, increase in sputter time controlled the film thickness, hence the cross-sectional area of the film. The increased cross sectional area allowing more charge carrier to flow per unit time whereby reducing the sheet resistance. Similarly, our results reveal that ZnO:Al films fabricated under low sputter
pressure produced large ZnO:Al grain size with diminished intergranular voids, whereby increasing the transmittance of light due to reduced grain boundary scattering of light. Moreover, high argon flow rate lead to better crystallization of ZnO:Al film due to the ion bombardment during sputtering process which lead to kinetic and vibration energy dissipating as heat. This bombardment induced heating effect which had a considerable influence on the crystallization of the sputtered ZnO:Al thin films. Finally, post-deposition annealing treatment in hydrogen atmosphere is found to enhance the conductance of the film, which is attributed to desorption of the negatively charged species, mainly oxygen from the grain boundaries which act as trapping sites and form the potential barriers.

Second, we present the investigation of deposition parameters to optimize the uniformity, morphology and homogeneity of CuInGa precursor and CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films. We deposited the CuInGa precursor film using magnetron sputtering at room temperature to prevent the In-Ga eutectic reaction. This lead to rough surface morphology of the precursor due to mismatch of surface energies. In order to reduce the surface morphology and obtain uniform chemical homogeneity, we reduced the deposition time for In which yielded smoother surface roughness, and further deposited the precursor in the Mo/In/CuGa/In structure to ensure uniform chemical homogeneity. Next, we present our chemical vapor deposition system to fabricate uniform CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with reproducible results. In our chemical vapor deposition system, we incorporated a flow controller to control the selenium diffusion rate, hence the thickness of the Mo\textsubscript{x}Se\textsubscript{y} layer, and a pressure regulator to control the selenium vapor pressure in order to fabricate CuIn\textsubscript{x}Ga\textsubscript{1-x}Se\textsubscript{2} films with the right selenium content and the stoichiometry. We further incorporated a sophisticated exhaust gas collection system to trap the unreacted residual Se vapor, and prevent the CVD system from contamination and to obtain reproducible results. Moreover, we
used a graphite CuInGa precursor fixture and oriented it normal to the direction of selenium flux in order to fabricate uniform CuIn$_x$Ga$_{1-x}$Se$_2$ films. Next, we investigated the influence of [Cu]/[In] ratios on the CuIn$_x$Ga$_{1-x}$Se$_2$ device performance. Films with high [Cu]/[In] ratios exhibited the metallic Cu$_x$Se$_y$ phase which lead to the absorber film behaving like a metal, leading to low $V_{oc}$ and $J_{sc}$. Films with low [Cu]/[In] ratio lead to formation (2$V_{Cu}^- + In^{2+}_{Cu}$) defect development in CuInSe$_2$ due to excess indium. With increasing In content, the presence of the defect pair cluster became more abundant leading to formation of CuIn$_5$Se$_8$, CuIn$_3$Se$_5$, Cu$_2$In$_4$Se$_7$ and Cu$_3$In$_5$Se$_9$ ordered defect compounds. The CuInSe$_2$ films with the best device performance reveals the presence of a single CuInSe$_2$ phase in the film. Furthermore, our results reveal an increase in Se flux facilitates In$_2$Se$_3$ and Ga$_2$Se$_3$ phases, which then react to form pure CuIn$_x$Ga$_{1-x}$Se$_2$ phase, resulting in CuIn$_x$Ga$_{1-x}$Se$_2$ films with larger grains, and hence leading to better device performance. We also show selenium cracking helps to activate the early formation of Ga-Se phase during selenization, which leads to a pure CuIn$_x$Ga$_{1-x}$Se$_2$ phase with moderate Ga incorporation.

Third, we present the investigation of deposition parameters that optimize the crystalline quality and therefore the interval radiative quantum efficiency of MBE-grown GaAs/AlGaAs double heterostructures using Raman spectroscopy and time-resolved photoluminescence measurements. Our results reveal an improvement in lattice disorder in both GaAs and AlGaAs layers as the As/Ga flux ratio is reduced from 40 to 20 to 15 and substrate temperature is increased from 550 to 595 °C, which is consistent with the longest minority carrier lifetime from our time-resolved photoluminescence results. Moreover, we reveal that incorporation of a distributed Bragg reflector layer significantly reduces the defect density in the subsequent layers. Our results show that the combined analysis of Raman and TRPL spectra provide a powerful tool for understanding defect mechanism and carrier dynamics in GaAs/AlGaAs DH structures since the conventional
spectroscopy techniques including transmission electron microscopy and electron diffraction analysis may not always reveal the defect mechanisms in the structures.
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