Preparation Of Efficient CuIn1-xGaxSe2-ysy/Cds Thin-film Solar Cells By Optimizing The Molybdenum Back Contact And Using Diethylselenide as Selenium Precursor

2006

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PREPARATION OF EFFICIENT CuIn_{1-x}Ga_{x}Se_{2-y}S_{y}/CDS THIN-FILM SOLAR CELLS BY OPTIMIZING THE MOLYBDENUM BACK CONTACT AND USING DIETHYLSELENIDE AS SELENIUM PRECURSOR

by

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Major Professor: Neelkanth G. Dhere.
ABSTRACT

High efficiency CuIn$_{1-x}$Ga$_x$Se$_{2-y}$S$_y$ (CIGSS)/CdS thin-film solar cells were prepared by optimizing the Mo back contact layer and optimizing the parameters for preparing CIGSS absorber layer using diethylselenide as selenium source. Mo is used as back contact layer in I-III-VI$_2$ compound thin-film solar cells. The Mo film was sputter deposited on 2.5 cm x 10 cm soda-lime glass using DC magnetron sputtering for studying the adhesion to the substrate and chemical reactivity of Mo with selenium and sulfur containing gas at maximum film growth temperature. Mo being a refractory material develops compressive and tensile stresses depending on the deposition conditions. Films deposited at a sputtering power 300 Watts and $0.3 \times 10^{-3}$ Torr working argon pressure develop compressive stresses, while the films deposited at 200 Watts and $5 \times 10^{-3}$ Torr pressure develops tensile stresses. Four sets of experiments were carried out to achieve an optimum deposition cycle to deposit stress free Mo. In a series of experiments, initially Mo with a thickness of 138 nm was deposited at 300 W power and $0.3 \times 10^{-3}$ Torr pressure to create compressive stresses. In a second experiment Mo with a thickness of 127 nm was deposited at a power of 200W and a pressure of $5 \times 10^{-3}$ Torr. In a third experiment, two high power cycles were sandwiched between three low power cycles with a total film thickness of 330 nm. In a fourth experiment two low power cycles were sandwiched between three high power cycles resulting in an effective thickness of 315 nm. It was found that the deposition sequence with two tensile stressed layers sandwiched between three compressively stressed layers had the best adhesion, limited reactivity and compact nature.

A new selenium precursor was developed to prepare CIGSS absorber layers. The organometallic compound, diethylselenide (DESe) a lower toxicity material has a potential to
provide selenium during selenization. Metallic precursors Cu-In-Ga were deposited by DC magnetron sputtering followed by furnace annealing in the temperature range of 475°C to 515 °C in the presence of a dilute DESe atmosphere. The films were grown in an indium rich regime. Systematic approaches lead to the optimization of each step involved in the preparation of the absorber layer. Initial experiments were focused on obtaining the range of maximum temperatures required for the growth of the film. The following experiments included optimization of soaking time at maximum temperature, quantity of metallic precursor, and amount of sodium in terms of NaF layer thickness required for selenization. The absorber surface was coated with a 50 to 60 nm thick layer of CdS as hetero-junction partner by chemical bath deposition. A window bi-layer of i:ZnO/ZnO:Al was deposited by RF magnetron sputtering. The thickness of i:ZnO was increased to reduce the shunt resistance to improve open circuit voltage. The cells were completed by depositing a Cr/Ag front contact by thermal evaporation. Having optimized the process parameters, CICSS/CdS thin-film solar cells with efficiencies greater than 13% were prepared on glass substrates. The performance of the cells was co-related with the material properties and areas of improvement were identified. The research presented here introduces a novel and lower toxicity selenium precursor and proves its potential to prepare device quality absorber. The material and the process parameters optimized during the research can be taken up by an industry for commercial production of CIGSS/CdS thin-film solar cells.
ACKNOWLEDGMENTS

I would like to take this opportunity to express my deepest gratitude towards Dr. Neelkanth G. Dhere, for giving me this opportunity to work on this project. I enjoyed working under his supervision and appreciate his constant guidance and encouragement. I would like to thank Dr. Helge Heinrich, Dr. Christine Klemenz, Dr. Gabriel Braunstein and Dr. Arvinda Kar for serving on my final examination committee and for their invaluable suggestions. This research work was supported by National renewable Energy Laboratory (NREL). I would like to thank the following people for their assistance on this project: Helio Moutinho and Bobby To from National Renewable Energy laboratory. Special words of thanks go to Mr. Anant Jahagirdar, Mr. Sachin Kulkarni, Mr. Vinay Hadagali, Mr. Shirish Pethe, Ms. Jyoti Shirolkar, Mr. Upendra Avchat, Mr. Parag Vasekar, Mr. Bhaskar Kumar, Mr. Santosh Khatri, Mr. Ashwani Kaul, Mr. Dhaval Shah, Mr. Mike Murphy, Mr. Joshua Newland and all other people at Florida Solar Energy Center (FSEC).

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<tr>
<th>ACRONYM</th>
<th>Definition of Acronym</th>
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<tbody>
<tr>
<td>CIS</td>
<td>Copper indium diselenide</td>
</tr>
<tr>
<td>CIGS</td>
<td>Copper indium gallium diselenide</td>
</tr>
<tr>
<td>CIGS2</td>
<td>Copper indium gallium disulfide</td>
</tr>
<tr>
<td>CIGSS</td>
<td>Copper indium gallium selenide sulfide</td>
</tr>
<tr>
<td>CdS</td>
<td>Cadmium sulfide</td>
</tr>
<tr>
<td>ZnS</td>
<td>zinc sulfide</td>
</tr>
<tr>
<td>i:ZnO</td>
<td>intrinsic zinc oxide</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>Aluminum doped zinc oxide</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>In</td>
<td>indium</td>
</tr>
<tr>
<td>Ga</td>
<td>Gallium</td>
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<tr>
<td>Se</td>
<td>Selenium</td>
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<tr>
<td>S</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Mo</td>
<td>molybdenum</td>
</tr>
<tr>
<td>DESe</td>
<td>Diethylselenide</td>
</tr>
<tr>
<td>FCC</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>FF</td>
<td>Fill Factor</td>
</tr>
<tr>
<td>R&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Series resistance</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
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<td>-------------------------------</td>
</tr>
<tr>
<td>$R_p$</td>
<td>Shunt resistance</td>
</tr>
<tr>
<td>kV</td>
<td>Kilo volts</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volts</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron Probe Micro Analysis</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>XEDS</td>
<td>X-ray Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>nm</td>
<td>Nano meter ($10^{-9}$ meter)</td>
</tr>
<tr>
<td>µm</td>
<td>Micro meter ($10^{-6}$ meter)</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
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<tr>
<td>X</td>
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CHAPTER ONE

INTRODUCTION

The near future the world’s energy requirement will be reaching a terra-watt figure. This challenge can be met only by economical processes. With lots of concerns expressed over the lasting of oil, renewable energy sources are attracting great attention. Among the available renewable energy sources, photovoltaic show high potential to meet this challenge. The major concern in the photovoltaic industry is to find a way to reduce $/peak watt number below $1.00 to make the technology economically viable and widely acceptable. Keeping this goal in mind the research activities are focused on developing highly efficient materials capable of being produced through an economical process. CuIn_{1-x}Ga_xSe_{2-y}S_y is one such material that is highly efficient and can be deposited as thin-films. Sputtering is the technique capable of providing high yield and higher production rates. The research presented in this work is a small step towards attaining the long-term goal of producing terra-watt energy. All the experiments were carried out on substrate size of 10 cm x 10 cm which could very well form a mini-module. Working on large-area substrates bridges the gap between the laboratory and the industrial results. The problems and their remedies in the laboratory settings would be directly applicable to the industrial shop floor issues. Before venturing into the experimental and the technical discussion related to the preparation of CIGSS thin-film solar cell a brief introduction is made to the physics of solar cells. Chapter one starts with developing an understanding for bandgap formation and goes upto the current generation using p-n junction devices. Chapter two presents fundamental understanding about the material that goes in to form a complete CIGSS/CdS thin-film solar cell.
Chapter 3 presents the initial work to optimize the deposition process for depositing a compact, well adherent and less reactive Mo back contact. Later, in chapter four a metal-organic compound called diethylselenide (DESe) was developed as a source of selenium to replace normally used H\textsubscript{2}Se gas during the selenization. The process developed with DESe overcomes the toxicity and stringent safety issues associated with H\textsubscript{2}Se gas. Finally, a CIGSS/CdS thin-film solar cell with conversion efficiency of 13.73% was prepared through a potential pilot plant facility at Florida Solar Energy Center.
1.1 Overview of photovoltaic

Silicon has ruled and will continue to rule as the material for solar cells. Solar cell technology can be divided into two categories thick-films and thin-films. Crystalline silicon (c-Si) was the first generation solar cell that falls in the category of thick-films. Crystalline silicon is an indirect bandgap semiconductor with a bandgap of 1.12eV. Being an indirect bandgap semiconductor, a minimum thickness of 100 µm is required for the maximum absorption of the solar spectrum. Si technology flourished very fast as a lot of the information was available from the microelectronic industry. Silica is available in vast amounts, however the process to produce device-quality grade Si is costly. Laboratory efficiency of 24.4% [1] has been achieved so far on a small area cell while the highest reported module efficiency has been 22.7%. Present-day crystalline-Si technology is approaching its lower limit in terms of production costs. However, to meet the energy requirement of the future a new technology has to be developed. Thin-film technology developed with an aim of lowering the cost of PV manufacturing by reducing the material required and developing high-yield techniques. Thin-film solar cells are referred to as second generation solar cells. From the various materials under consideration, only four thin-film technologies namely amorphous silicon (a-Si) and poly crystalline hetero-junction systems CdS/CuxS, CdS/CdTe and CdS/CuInSe₂, entered pilot production. As of now only a-Si contributes significantly to the world PV. Activities in the CdS/CuₓS stopped at the beginning of the eighties due to stability issues and a-Si became the frontrunner in the thin-film technology. The highest potential with regards to cost reduction and high efficiencies is provided by the hetero-junction solar cell based on CdTe and CuInSe₂ absorbers. Both materials look back to around 35 years of research and development with ‘promising material’ at every stage [2]. The
highest reported cell and module efficiencies for CdTe are 16.5% [3] and 10.7 [4] respectively. CuInSe₂ and its alloys with sulfur and gallium are reaching the theoretical limit as cell efficiency of 19.5% [5] has been achieved on glass substrate. Modules with efficiency 13.4% are already in production. Third generation solar cell are the intellectually engineered cells capable of achieving efficiencies beyond the theoretical limit. Quantum well and quantum dots solar cells are the examples of this category [6]. They work on the concept of creating multiple bandgaps in a single junction cell. Organic solar cells are another category that is in its infant stage. At present these cells are not highly efficient however they form the cheapest of all the existing technologies.

1.2. Basics and operation of a solar cell

A solar cell is a p-n junction diode capable of producing electricity when light is incident on it. This makes it the most important renewable energy source capable of harvesting the abundantly available sunlight to solve the world energy crisis. P and n type semiconductors are obtained by doping with impurities such as boron and phosphorous respectively in silicon or by naturally occurring point defects such as vacancies, interstitials and antisites as in copper indium diselenide thin-film solar cells. The majority carriers in p-type semiconductor are holes while electrons are the majority carriers in n-type semiconductors. When a p and n-type semiconductor is joined together, the free electrons from n-type migrate over the metallurgical junction to fill in the holes in the p-type semiconductor. A region is created wherein all the electrons and holes are recombined; it is called a depletion zone. Due to the rapid movements of electrons across the junction a negative charge is developed at the edge of the depletion zone in the p-type
semiconductor while a positive charge is developed on the other edge of the depletion zone ending in the n-type semiconductor. As a result, an in-built electric field is created within the material called a built-in voltage. It is this potential that drives the photo-generated electrons to the external circuit. The product of current and voltage is power that can be used to run varied applications.

1.3 Physics of Solar cells

Air mass (AM) is the measure of how absorption in the atmosphere affects the spectral content and intensity of the solar radiation entering the earth. In space the radiation intensity or the solar constant is 1.353 kW/m² and is referred to as AM 0. The absorption of the spectrum increases with the increase in the thickness of the atmospheric layer. For the thickness \( l_0 \) of the atmosphere, the path length \( l \) through the atmosphere for radiation from the sun incident at an angle \( \theta \) relative to the normal to the earth’s surface is given by

\[
 l = \frac{l_0}{\cos \theta} ,
\]

Where, \( \theta \) = angle of incidence, \( \theta = 0 \) if sun is exactly overhead.

The ratio \( l/l_0 \) is called air mass co-efficient. The performance of solar cells is evaluated at AM 1.5 condition corresponding to the solar constant of 1 kW/m². The solar constant on the earth’s surface is always lower than that in space due to the spectrum absorption by the atmosphere. This absorption is almost entirely caused by gases of low concentration in the infrared region of the solar spectrum, by water vapor (H₂O), carbon dioxide (CO₂), laughing-gas
(N₂O), methane (CH₄), fluorinated hydrocarbon, as well as by dust and in ultraviolet region of the spectrum by ozone and oxygen. A simple way of representing Air Mass value at different earth location is given by the simple equation,

\[ AM = \left(1 + \frac{S}{H}\right)^{1/2} \]

Where, \( S \) = Length of the shadow cast by an object of height \( H \) at that location.

### 1.3.1. Band structure in semiconductors

An atom of a solid is electrically neutral. The positive charge of a nucleus is compensated by negatively charged electrons. The electrons are acted upon by a Coulomb potential exerted by the nucleus, rendering electrons to posses certain allowed energies. Electron of a free atom can occupy one of the series of energy levels below \( E = 0 \), given by the approximation [7]

\[ E_n = -\frac{Z^2 m_o q^4}{8 \varepsilon_o^2 h^2 n^2} \]

Where,

- \( q \) - charge of electron;
- \( Z \) – atomic number;
- \( m_o \) - mass of free electron;
- \( \varepsilon_o \) – permittivity of free space or dielectric constant;
- \( h \) – Plank’s constant; and
- \( n \) – positive integer representing energy levels.
At equilibrium not all the electrons fill the lowest energy level. According to Pauli’s exclusion principle each energy level can have a maximum two electrons with opposite spins. These energy levels are further compounded in shells governed by quantum numbers given by classical quantum mechanic theory.

When atoms are isolated from each other the electron in individual atoms occupies the energy level given by equation 1. However as the atoms start coming close to each other the atomic core of the first atom exerts a force on the electron of the second atom disturbing the potential and consequently the energy levels of the electron. The effect is of prime importance for the highest occupied energy levels. Energy level $E_n$ of an atom contains two electrons. When two similar atoms are brought together the energy level $E_n$ cannot accommodate 4 electrons as it violates Pauli’s exclusion principle. As a result of this interaction the energy level $E_n$ is disturbed and it also splits into two slightly separated energy levels. As the atoms come closer the perturbation and also the splitting increases. If N numbers of atoms interact then the original energy level $E_n$ is split into N different allowed energy levels accommodating 2N electrons. When the atomic spacing equals the crystal lattice spacing, the regions of allowed energy level are typically separated by a forbidden energy gap in which electrons cannot exist.

Henceforth in the discussion the band structure will be represented in single lines indicating valence band maxima and conduction band minima separated by band-gap. In an intrinsic semiconductor at 0°C temperature, the valence band is completely filled while the conduction band is completely empty.
Figure 1: Band structure, Filled energy levels forms valence band while the allowed unfilled energy levels form the conduction band

As the temperature increase some of the electrons gain enough energy to cross over the forbidden gap and go to the conduction band. The effect of temperature on the occupancy of electrons in an energy level is given by the Fermi Dirac distribution function given by the equation [7]

\[
f(E) = \frac{1}{e^{\frac{E-E_f}{kT}} + 1}
\]

Where

\( f(E) \) = Fermi Dirac function determining the probability of electron occupancy at energy level ‘E’ at temperature ‘T’ reported in Kelvin;

K is Boltzmann constant (8.62 x 10\(^{-5}\) eV/K);

\( E_f \) – is a constant known as Fermi energy.
The fermi energy is defined as the highest filled energy level at absolute zero temperature. It is also defined as the energy level where the probability of charge carrier occupancy is 50%. For an intrinsic semiconductor, the Fermi level is at the center of the forbidden gap. Doping a semiconductor with an n-type impurity results in free electrons that introduce an additional energy level within the forbidden gap close to the conduction band. Addition of phosphorus (donor impurity) in silicon results in an energy level called donor level \( E_d \) that is 0.045 eV below the conduction band. Thermal energy at room temperature is \( kT = 0.026 \) eV. Though the thermal energy is less than 0.045 eV it is seen that the impurities are well ionized at room temperature in silicon. At low temperature \( E_f \) lies between the lower conduction band edge and \( E_d \). However at room temperature as the impurity ionizes more electrons occupy energy levels in the conduction band and hence the \( E_f \) shifts towards the intrinsic Fermi level such that \( E_f < E_d \) while \( E_f > \) intrinsic Fermi level. On similar lines, the Fermi level shifts towards the valence band with the addition of acceptor impurities. At high energy levels such that \( E - E_f \gg kT \). This makes \( \exp (E - E_f) \gg 1 \) and hence Fermi function tends to Boltzmann function.

\[
f(E) = e^{-(E-E_f)/kT}
\]

The density of allowed states is zero in the forbidden gap while it is non zero in the allowed energy bands. Density of states can be calculated by solving the time-independent Schrödinger equation. All the complexity of the periodic potentials of the component atoms has been incorporated into the effective mass.
The density of states at energy E near the conduction band edge is given by [9]

\[ g_c(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3} cm^{-3} eV^- \] \hspace{1cm} (4)

Similarly density of states at energy E near the valence band edge is given by [9]

\[ g_v(E) = \frac{m_p^* \sqrt{2m_p^*(E_v - E)}}{\pi^2 \hbar^3} cm^{-3} eV^- \] \hspace{1cm} (5)

Where

- \( m_n^* \) is effective mass of electron;
- \( m_p^* \) is effective mass of hole;
- \( E_c \) is conduction band minima;
- \( E_v \) is valence band maxima.

Now, the carrier concentration at any energy level is the product of probability of occupancy and the number of available states. Therefore electron concentration in the conduction band in the energy increment of dE can be written as [7]

\[ n_o = \int_{E_v}^{E_c} g_c(E) f(E) dE \] \hspace{1cm} (6)
On substituting with respective equations and solving the integral, we get [7]

\[ n_o = N_e e^{(E_f - E_v)/kT} \] ................................................................. (7)

Where

\[ N_e = 2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} \] ................................................................. (8)

\( N_e \) is a constant at fixed \( T \) known as effective density of states in the conduction band

Similarly, hole concentration in valence band can be calculated by [7]

\[ p_o = \int_{-\infty}^{E_f} g_p(E)[1 - f(E)]dE \] ................................................................. (9)

\[ p_o = N_v e^{(E_f - E_v)/kT} \] ................................................................. (10)

\[ N_v = 2\left(\frac{2\pi m^* kT}{h^2}\right)^{3/2} \] ................................................................. (11)

\( N_v \) is a constant at fixed \( T \) known as effective density of states in the valence band

The entire argument can be schematically represented for an intrinsic, n-type and p-type semiconductor as shown in Figure 2, Figure 3 and Figure 4 respectively.
Figure 2: Carrier occupancy in intrinsic semiconductor

Figure 3: Electrons occupancy in n-type semiconductor
1.3.2. P-N Junction (Homojunction)

The formation of an electric field when p and n type semiconductors are brought together to form a junction is the heart of operation of a p-n junction. When n-type and p-type semiconductors are brought in intimate contact with each other, the thermal equilibrium of individual systems is lost and in the event of re-establishing the thermal equilibrium for the combined system the electrons flow from n-type semiconductor to p-type semiconductor and holes from p-type semiconductor to n-type semiconductor. As these carriers move across to the oppositely doped material, they leave behind uncompensated dopant atoms. The positive ions on the n-type semiconductor and negative ions on the p-type semiconductor near the junction result in an electric field built-up. This field creates a potential barrier between the two semiconductors
as shown in Figure 5. This region of absence of charge carriers is called depletion region as mentioned earlier. When equilibrium is reached, the magnitude of the field is such that the tendency of electrons to drift from the n-type region into the p-type region is exactly balanced by the tendency of electrons to drift in the opposite direction under the influence of the built-in field. At equilibrium the Fermi level is constant throughout the entire system. For homojunction diodes the magnitude of the potential barrier associated with the built-in field can be found by considering the difference in the Fermi levels of the initially separated materials.

At equilibrium electrons and holes currents are zero. At this condition the electric field \( E \) generated by diffusion of charge carriers is given by the following relation. It can be noted that the electric field is maximum at the junction \([9]\).

\[
E = -\frac{kT}{qn} \frac{dn}{dx} \quad \text{................................................................. (12)}
\]

Where

- \( k \) is the Boltzmann constant;
- \( T \) is the temperature in Kelvin;
- \( q \) is the charge of an electron;
- \( n \) is free electron concentration in equilibrium;
- \( \frac{dn}{dx} \) is change in electron concentration.
Figure 5: Built in potential when n and p type semiconductor are brought in intimate contact

The built-in voltage can be obtained by integrating the electric field from p-region to n-region [9].

\[ V_B = \int_{p\text{-side}}^{n\text{-side}} E \, dx \] \hspace{1cm} \text{..............................................................} (13)

On solving the integral

\[ V_B = \frac{kT}{q} \ln \frac{N_A N_D}{n_i^2} \] \hspace{1cm} \text{..............................................................} (14)

Where
\( N_A \) is acceptor concentration;
\( N_D \) is donor concentration;
\( n_i \) is intrinsic carrier concentration.

The width of depletion region is determined by impurity concentration and total voltage which is the sum of built-in voltage and applied voltage. At equilibrium the applied bias is zero and so the depletion width depends only on the built-in voltage.

Total depletion width is given by the relation [9].

\[
d = d_i + d_p = \sqrt{\frac{2\varepsilon_s V_B (N_A + N_D)}{q(N_A N_D)}} \quad \text{..........................................................} (15)
\]

Where
\( d_n \) is depletion width on n-type material;
\( \varepsilon_s \) is permittivity of the material.

Under non-equilibrium condition when voltage \( V \) is applied across the p-n junction the equation modifies as [9]

\[
d = \sqrt{\frac{2\varepsilon_s (V_B - V_a) (N_A + N_D)}{q(N_A N_D)}} \quad \text{..........................................................} (16)
\]

The depletion width increases with the application of an external voltage \((V_a)\) in reverse biased condition \((-V_a)\) while it decreases in forward bias condition \((+V_a)\).
1.3.5 Hetero-junction

Figure 6: Heterogeneous band diagram of ZnO/CdS/CIGS thin-film solar cell

Where,

The numbers 1, 2, 3 and 4 refers to MoSe$_2$, CIGS, CdS and ZnO respectively.

Eg1, Eg2, Eg3 and Eg4 – Bandgap

qX2, qX3 and qX4 – electron affinity

q$\Phi$w2, q$\Phi$w3 – work function

q$\Phi$i – Built-in potential at p-n junction

$\Delta$Ec2/3 – Conduction band offset between CIGS and CdS

$\Delta$Ev2/3 – Valence band offset between CIGS and CdS
\( \Delta Ec^{3/4} \) – Conduction band offset between CdS and ZnO

\( \Delta Ev^{3/4} \) – Valence band offset between CdS and ZnO

The physics of a solar cell discussed so far was related to homo-junctions. CIGS/CdS is a hetero-junction device; hence it is important to understand the additional features involved in the band diagram. Hetero-junction can improve the performance of the solar cell. To form a hetero-junction, two semiconductors of different bandgaps are brought together such as p-type CIGS and n-type CdS as shown in Figure 6. In the case of heterojunction system, along with the bandgap, the electron affinities of the individual semiconductors are different due to the difference in their respective work functions. For vacuum level to remain continuous at the interface, a discontinuity must occur in the conduction band as well as valence band at the interface. The discontinuity in the conduction band at the interface can be written as [7]

\[ \Delta Ec^{2/3} = X_2 - X_3 \]

The discontinuities at the interface affect the near-by space-charge regions. In the neutral region of each material away from the interface the separation between the conduction band edge and the Fermi level is determined by doping in that material [7].

\[ Ec^3 - E_f = kT \ln \left( \frac{N_{c3}}{N_{D3}} \right) \] .............................. (17)

Where, \( N_{c3} \) – density of state in conduction band of CdS, \( N_{D3} \) – donor dopant density [7]

\[ Ec^2 - E_f = Eg^2 - (E_f - Ev^2) = Eg^2 - kT \ln \left( \frac{N_{v2}}{N_{a2}} \right) \] .............................. (18)
Where, $N_{v2}$ - density of state in valence band of CIGS, $Na_2$ - acceptor dopant density.

Therefore, the total difference in the conduction band edge between the neutral regions in the two semiconductors does not depend on electron affinities and is given by [7]

$$Ec2 - Ec3 = Eg2 - kT \ln \left( \frac{Nc3Nv2}{Nd3Na2} \right)$$  

Now to retain the same value of Ec2-Ec3 between the neutral regions with positive non-zero $\Delta Ec2/3$ at the interface, the total bending of the energy bands must increase by $\Delta Ec2/3$. The built-in potential also increases with positive $\Delta Ec2/3$ as the individual work function $\Phi w2$ and $\Phi w3$ changes. The greater bending of the energy bands with different electron affinities implies that the depletion region widens and hence the $V_{oc}$.

The importance of the spike as a barrier to the electron flow from n-type to p-type depends on the fraction of the built-in potential dropped on each side. If the acceptor concentration in p-type material is low as compared to the donor concentration in the n-type material, the majority of band bending occurs in the p-type material side and the top of the spike is lower than the conduction band edge in the neutral region of the p-type material. The barrier to electron flow from n-type to p-type is then just the difference in the conduction band edges in the neutral region of the two materials. However, if the doping in the p-type material is higher compared to the n-type material then the majority of band bending occurs in the n-type material and the top of spike can be higher than the conduction band edge in the neutral region of the p-type material. In this case the barrier to electron flow from n to p type is greatly increased.
1.3.3. Current –voltage relationship

A solar cell under no illumination is a simple p-n junction diode. When forward bias is applied to the diode, excess electrons are injected in the p region while excess holes are injected in the n region. This results in a reduction of the potential barrier across the junction making it possible for more charge carriers to cross over to opposite regions. A relation can be mathematically developed that indicates that the minority carrier concentration increases exponentially with the applied voltage. Due to the short life time (microsecond) of the injected minority carriers the recombination rate is high and the statement does not hold true. However, it has been experimentally proven that the relationship is valid at the depletion layer boundaries [7].

\[ n_p = n_{po} e^{qV_a/kT} \]  
\[ p_n = p_{no} e^{qV_a/kT} \]

Where

- \( n_p \) is the injected minority carrier concentration in p region;
- \( n_{po} \) is the minority carrier concentration for thermal equilibrium;
- \( p_n \) is the injected minority carrier concentration in n region;
- \( p_{no} \) is the injected minority carrier concentration for thermal equilibrium.
The excess minority carrier concentration decreases exponentially with the distance away from the junction as shown in Figure 7. The decay depends on both the diffusion constant and lifetime [7].

\[
\hat{n} = \hat{n}_o e^{-x/\sqrt{D_n \tau_n}} \tag{22}
\]

\[
\hat{p} = \hat{p}_o e^{-x/\sqrt{D_p \tau_p}} \tag{23}
\]

Where

- \(D_n\) and \(D_p\) are the diffusion constants for electron and hole minority carriers;
- \(\tau_n\) and \(\tau_p\) are the lifetime of electron and hole minority carriers;
- \(\hat{n}\) is the injected electron carrier concentration in p-region;
- \(\hat{n}_o\) is the injected electron carrier concentration at depletion width edge;
- \(\hat{p}\) is the injected hole carrier concentration in n-region;
- \(\hat{p}_o\) is the injected hole carrier concentration at depletion width edge as shown in Figure 7.

![Figure 7: Distribution of excess minority carriers in forward bias condition](image-url)
The current flowing is the sum of the hole and electron currents at any point. However it is convenient to take the sum at the junction, where the currents are known. The slope of the curve determines the current contribution by each minority charge carrier. The hole current at the junction is given by [7]

\[
I_p = qA \sqrt{\frac{D_p}{\tau_p}} \hat{p}_o \tag{24}
\]

Where, A is the junction area

The electron current at the junction is given by [7]

\[
I_n = qA \sqrt{\frac{D_n}{\tau_n}} \hat{n}_o \tag{25}
\]

The total current is the sum of hole and electron currents [7]

\[
I = I_p + I_n = qA \left( \sqrt{\frac{D_p}{\tau_p}} \hat{p}_o + \sqrt{\frac{D_n}{\tau_n}} \hat{n}_o \right) \tag{26}
\]

We know that \( n_p = n_{po} + \hat{n}_o \) and also \( p_n = p_{no} + \hat{p}_o \)

\[
n_{po} = n_i^2 / N_A \tag{27}
\]

\[
p_{no} = n_i^2 / N_D \tag{28}
\]

Where

\( n_i \) is the intrinsic carrier concentration
Therefore,

\[ \hat{n}_o = n_{po} \left( e^{qV_o/kT} - 1 \right) \approx \frac{n_i^2}{N_A} \left( e^{qV_o/kT} - 1 \right) \] .......................... (29)

\[ \hat{p}_o = p_{po} \left( e^{qV_o/kT} - 1 \right) \approx \frac{n_i^2}{N_D} \left( e^{qV_o/kT} - 1 \right) \] .......................... (30)

From equation 19, 20, 26, 27, 28 and 29, the total current can be written as [7]

\[ I = qAn_i^2 \left( \sqrt{\frac{D_p}{\tau_p N_D}} + \sqrt{\frac{D_n}{\tau_n N_A}} \right) \left( e^{qV_o/kT} - 1 \right) \] .......................... (31)

If the applied voltage is negative i.e. reverse biased condition, we get a current called reverse saturation current [7].

\[ I_o = -qAn_i^2 \left( \sqrt{\frac{D_p}{\tau_p N_D}} + \sqrt{\frac{D_n}{\tau_n N_A}} \right) \] .......................... (32)

From relation 31 and 32

\[ I = I_o \left( e^{qV_o/kT} - 1 \right) \] .......................... (33)

Under illuminated conditions there is an extra current due to a photo generated current;

Therefore the above equation changes to [7]

\[ I = I_o \left( e^{qV_o/kT} - 1 \right) - I_L \] .......................... (34)

Where,

I_L is photogenerated current shown in Figure 8.
When light is shined on a cell not connected to the external circuit, the generated free charge carriers flow across the built-in electric field and built up charge on the other side of the cell. The charge build up by free carriers continues to increase till it just balances the built-in field. At this stage the built-in field will not be able to separate charge carriers. The corresponding built up potential is called open circuit voltage ($V_{oc}$) and it is the maximum voltage a cell can provide. It is given by the relation [8]

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{I_{sc}}{I_o} + 1 \right) \approx \frac{kT}{q} \ln \frac{I_{sc}}{I_o}$$

(35)
With series and shunt resistance becoming effective the nature of the I-V curve changes as shown in the Figure 9. The modified I-V relationship is given by equation 36. Therefore the data obtained from the I-V curve can be used to calculate series and shunt resistances [8].

$$\ln \left( I + \frac{I_L}{I_o} - \frac{V - IR_S}{I_o R_p} + 1 \right) = \frac{q(V - IR_p)}{kT} \quad \text{.................. 36}$$

As the resistance reduces more current will flow and the voltage will reduce. At short circuit condition the current is maximum and the voltage is zero. This value of current is called short circuit current ($I_{sc}$) generally represented as short circuit current density ($J_{sc}$) and it is the maximum current density a cell can produce.

At $V_{oc}$ and $J_{sc}$, the power is zero. The maximum power is the optimum combination of voltage and current. Fill Factor (FF) is another important factor in efficiency measurement of solar cell. The FF is defined as the ratio of peak power to the product of $V_{oc}$ and $J_{sc}$. It represents
the squareness of the I-V curve at the maximum power point and is given by equation 37 [9]. A good cell should have a FF over 70%.

$$\text{FF} = \frac{V_{m.p} \cdot I_{mp}}{V_{oc} \cdot I_{sc}}$$ .................................................................37

Where,

$V_m$ and $I_m$ is the voltage and current of the maximum power point Figure 8.

The photovoltaic conversion efficiency of a solar cell is given by the relation [9]

$$\eta = \frac{V_{oc} \cdot I_{sc} \cdot \text{FF}}{P_{in}}$$ .................................................................38

Where,

$P_{in}$ is the incident power taken as 100 mW/cm$^2$ for a laboratory measurement corresponding to the AM 1.5 solar spectrum.

### 1.3.4 Device parameters

The device parameters on the basis of which a cell’s efficiency is defined are short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$) and fill factor (FF). These values solely depend on the material used and its quality. The factors on which $J_{sc}$ depends are; 1) light absorption; it is the ability of a semiconductor to absorb sunlight, normally referred to as absorption co-efficient ($\alpha$). This value depends on the type of bandgap of the semiconductor. A direct bandgap semiconductor such as CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) can effectively absorb 90% of the light within 1 µm thickness ($\alpha = 10$-5 cm). An indirect bandgap semiconductor such as silicon requires additional energy provided by phonon in the form of lattice vibration to transfer an electron from
the valence band to the conduction band, hence its $\alpha = 10^{-2}$ cm. Therefore to effectively absorb 90% of the light, a thicker layer is required (~100 $\mu$m). 2) Drift and diffusion; Absorption of the photons depends on the direct/indirect bandgap material and their energy. Higher energy photons are absorbed within the built-in electric field while the lower energy photons are absorbed away from the electric field. Almost every electron-hole pair generated within the electric field region could be separated and contributed to the current. The field-driven movement of the free carriers within the built-in field is called drift. The charge carriers generated away from the electric field do not lose their energy instantly and fall back into the bound state. The amount of time for which they remain active is called their lifetime. Within the lifetime if the charge carrier does not encounter the built-in field it recombines and does not contribute to the current. However, if during its lifetime it comes under the influence of the built-in electric field it can cross over to other regions and produce a current. The average distance a charge carrier can travel towards the built-in field before getting recombined is called diffusion length. The diffusion length depends on the crystal quality of the material. Defects such as impurities resulting in interstitials or lattice strain, vacancies and grain boundary can reduce the diffusion length. The $V_{oc}$ depends on the built-in voltage of the device. Recombination centers located within the field greatly reduce the $V_{oc}$. These recombination centers are called shunts. For a highly efficient cell the current lost by shunts should be minimum i.e. the shunt resistance should be high towards $+\infty$. In contrast to the recombination center in the bulk, the recombination centers within the built-in electric field result in continuous recombination of charge carriers as a result of which the $V_{oc}$ is drastically reduced [11]. Another mechanism of current loss and mostly the voltage loss is series resistance. Series resistance losses occur because free carriers separated by the built-in fields have to travel some distance to reach a metal contact. At the back of the cell, this distance may
be purely vertical and quite small, may be less then a micron. But the front contact is usually a grid to avoid shadowing. To reach the grid fingers, carriers must move sideways along distances of several millimeters and can lose substantial energy to resistance in the process. This resistance can be reduced by making the top layer from a semiconductor with a high density of free carriers. These kinds of semiconductors are called transparent and conducting oxides.

All the factors mentioned in the above discussion can be measured by current-voltage (I-V) and quantum efficiency (QE) measurements. QE is the measure of the effectiveness of a cell in converting light of various energies into electricity. If a cell shows very fine response to high-energy photons and poor response to low-energy photons in QE measurements then it means the charge carriers generated within the built-in electric field are effectively absorbed while the charge carriers generated away from the field in the bulk undergo recombination [11]. This indicates that the diffusion length has to be improved by improving the crystal quality of the absorber or the defects need to be passivated through some mechanism. QE measurements showing poor response to high energy and good response for lower energy indicates the presence of a layer opaque to high energies and transparent to low energies or reflects high-energy light preferentially. Such a layer could be removed or altered to improve the performance. The cells with a mediocre QE response indicate several problems. The obvious ones are the losses due to the reflection of the incident spectrum or large recombination losses at the junction that are removing a fraction of electrons independent of the energy of their original photons [11].
CHAPTER TWO

MATERIALS REVIEW

2.1 Copper Indium Gallium Selenide (CuIn_{1-x}Ga_{x}Se_{2})

I-III-VI$_2$ compounds are proving to be promising materials to meet the energy requirement of the world. CuInSe$_2$ (CIS) and its alloys with Ga and S have shown long-term stability and highest conversion efficiency of 19.5% [5]. CIS has a direct bandgap of 1.02 ± 0.01 eV at room temperature with a temperature co-efficient of -2± 1 x 10$^{-4}$ eV/K in the lower temperature regime [12]. The typical absorption coefficient is larger than 10$^5$/cm for 1.4 eV and higher photon energies [13]. The band gap of CIS can be increased continuously over a wide range by increasingly substituting In by Ga. The band gap increases as a function of Ga content [14]. Similarly, one can also increase the band gap by substituting S for Se. The excellent radiation hardness property makes it a suitable material for space applications [15]. It has been shown by Guillemoles that the interface of CIGS with back contact and CdS are highly stable [16]. A wide variety of techniques has been used to fabricate CIS. These include three-source evaporation [17][18], laser ablation [19][20], flash evaporation [21][22], vapor transport [23], spray pyrolysis [24][25], sputtering [26], liquid phase epitaxy [27][28], electrodeposition [29][30] screen printing [31] and selenization of metallic layers [32][33][34]. Among the various ways of preparing CIGSS/CdS thin-film solar cells, co-evaporation and sputtering techniques are the most promising. Sputtering is an established process for very high-throughput manufacturing. ARCO Solar, now Shell Solar pioneered, the work in CIS using the sputtering technique [11]. The two stage process developed by ARCO Solar consisted of sputtering of a copper and indium
layer on Mo-coated glass as the first step. In the second step, the copper-indium layers were exposed to a selenium-bearing gas such as hydrogen selenide (H$_2$Se) mixed with argon. The hydrogen selenide breaks down and leaves selenium, which reacts and mixes with the copper and indium in such a way to produce very high-quality CIS absorber layer. Sputtering technology has the added advantage of being easily scalable and adaptable to roll-to-roll production on flexible substrates. In the early 90’s, a nontoxic selenization process was developed at the FSEC’s PV Materials Lab to avoid use of extremely toxic H$_2$Se gas. The two stage selenization process involved deposition of a copper-indium layer with excess copper. The elemental stack was selenized by heating the substrate in the presence of selenium vapors obtained by thermally evaporating elemental selenium. Selenization of the copper-rich film helped improve the adhesion with the Mo back contact. The copper-rich film was further deposited with indium and re-selenized to produce an efficient thin-film CIS absorber [35]. The process was further modified by addition of gallium and optimizing the Ga content to achieve a cell efficiency of 9.02% [36]. As of now, CIGSS absorbers are prepared by rapid thermal processing of a metallic precursor with elemental selenium in close space and conventional furnace annealing in selenium vapor obtained from diethylselenide (DESe) [37][38]. Sulfurization of the selenized film to form CIGSS and of metallic precursors to form CuIn$_{1-x}$Ga$_x$S$_2$ (CIGS2) is carried out in diluted H2S gas [32].

2.1.1 Crystal Structure

CuInSe$_2$ and CuGaSe$_2$, the material that forms the alloy Cu(In,Ga)Se$_2$, belongs to the semiconductor I-III-VI$_2$ material family that crystallizes in tetragonal chalcopyrite structure and
is stable from room temperature up to 810°C [39]. The chalcopyrite structure of CIS is similar to ZnS structure in which Zn atoms are replaced alternatively by Cu(I) and In(III) atoms. Each Cu and In atom has four bonds with Se(VI) atom. In turn each Se atom has two bonds to Cu and two to In (Figure 10). Since the strength of the I-VI and III-VI bonds are in general different, the ratio of lattice constants c/a is not exactly 2. The quantity 2-c/a (which is −0.01 in CuInSe$_2$, +0.04 in CuGaSe$_2$) is a measure of the tetragonal distortion in chalcopyrites. The bandgap energies of I-III-VI$_2$ are considerably smaller than those of their binary analogues because the Cu 3d band, together with the Se 4p band, forms the uppermost valence band in the Cu-chalcopyrite, which is not so in II-VI compounds. However, the system of Cu-chalcopyrite covers a wide bandgap of energies from 1.02 eV in CuInSe$_2$ up to 2.4 eV in CuGaSe$_2$, covering most of the visible spectrum. Any desired alloy between these compounds can be produced, as there is no miscibility gap in the entire system.

Figure 10. (a) CuInSe$_2$ chalcopyrite (b) Binary equivalent ZnS crystal structure
The CIS tetragonal structure is very much similar to a stack of two FCC structures, where \( c \sim 2a \). Since the FCC structure usually grows with closed packed (111) planes, CuInSe\(_2\) will grow in (112) close packed plane. CuInSe\(_2\) exhibits 142d symmetry, its atomic coordinates are as follows: four copper atoms at \((0,0,0); (\frac{1}{2},\frac{1}{2},\frac{1}{2}); (\frac{1}{2},0,\frac{3}{4}); \) and \((0,\frac{1}{2},1/4)\); four indium atoms at \((0,0,\frac{1}{2}); (\frac{1}{2},\frac{1}{2},0); (\frac{1}{2},0,\frac{1}{4}); \) and \((0,\frac{1}{2},\frac{3}{4}); \) and eight sulfur atoms at \((u,1/4,1/8); (-u,3/4,1/8); (\frac{1}{4},u,7/8); (\frac{1}{4},-u,7/8); (\frac{1}{2} + u,3/4,5/8); (\frac{1}{2}-u,1/4,5/8); (\frac{1}{4},u + \frac{1}{2},3/8); \) and \((\frac{1}{4},\frac{1}{2}-u,3/8)\) where \( u = c/a \). The lattice parameters for a CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\) film with Ga content, \( x \) of 0 is, \( a = 0.578 \) nm and \( c = 1.162 \) nm [40] and they decrease linearly with increase in \( x \) [40][41].

### 2.1.2 Phase diagram

The phase diagram provides the alloy composition, the allowed deviation from the stoichiometry and the process temperature for producing a good-quality absorber layer. Figure 11 shows a ternary elemental composition diagram of Cu, In and Se. CIS absorber grown with excess supply of selenium has a composition that lies on or near the tie line of Cu\(_2\)Se and In\(_2\)Se\(_3\). It is interesting to note that the order defect compounds (ODC) such as CuIn\(_3\)Se\(_5\), Cu\(_2\)In\(_4\)Se\(_7\), Cu\(_3\)In\(_3\)Se\(_9\) lie on the same tie line and have the same chalcopyrite structure. The ODCs are formed by regular arrangements of point defects in the chalcopyrite crystal structure. This complex ternary diagram can be reduced to a simpler pseudo-binary phase diagram along the tie line between Cu\(_2\)Se and In\(_2\)Se\(_3\) (Figure 12) [42]. As seen from the phase diagram the \( \alpha \)-phase (CuInSe\(_2\)) lies in a very narrow range of 24 to 24.5% of copper at room temperature. At growth temperature between 500°C to 550°C the \( \alpha \)-phase exists in the range of 22 to 24.5 at% Cu. As per
the phase diagram the cooling of slightly Cu-poor composition indicates the presence of additional \( \beta \)-phase (CuIn\(_3\)Se\(_5\)). This ODC is built by ordered arrays of defect pairs of Cu vacancies and indium on copper anti-sites. Some groups have reported the formation and benefits of having such ODC on top of the absorber layer [43]. This layer has a bandgap of 1.3eV higher than the bulk CIS bandgap. Having a higher bandgap semiconductor at the metallurgical junction helps in increasing \( V_{oc} \) [44]. When the absorber layer is grown in Cu-rich regime an additional phase, Cu\(_2\)Se is formed. This layer is metallic in nature and has to be removed before depositing the hetero-junction partner. It has been found that the addition of a control amount of gallium or sodium widens the \( \alpha \)-phase field making it possible to have single \( \alpha \)-phase at room temperature in the range of 22 to 24.5 at% Cu. Another phase that occurs in the phase diagram is the \( \delta \)-phase called sphalerite which is stable at high temperature. A congruent solid-solid phase transition occurs at 810\(^\circ\)C between the disordered \( \delta \)-phase and the ordered chalcopyrite \( \alpha \)-phase. The reason to grow CIS/CIGS/CIGSS in a copper-poor regime is evident from the phase diagram (Figure 12) as the homogeneity of the \( \alpha \)-phase extends over a range of composition towards copper poor at growth temperature while it is none towards the copper-rich side [39].
Figure 11: Ternary elemental composition diagram of Cu-In-Se [42].

Figure 12: Pseudo-binary phase diagram along the tie line between Cu$_2$Se and In$_2$Se$_3$ represented in terms of Cu atomic % [42].
2.1.3 Intrinsic defect doping of CIGS

The most important characteristics of CIGS material is to accommodate a large amount of compositional variation without appreciable change in the electronic properties. Highly efficient solar cells can be fabricated with Cu/(In+Ga) ratio of 0.7 to slightly less than 1. This phenomenon can be explained on the basis of defect chemistry of CIS. It has been shown that the formation energy of defects such as copper vacancies $V_{Cu}$ and defect complexes two copper vacancies in combination with indium on copper antisite ($2V_{Cu}+In_{Cu}$) is low [45]. $V_{Cu}$ is a shallow acceptor that contributes to the p-type conductivity of CIGS. The $2V_{Cu}+In_{Cu}$ defect prevents degenerate doping in indium-rich material. Isolated $In_{Cu}$ acts as a deep donor while the combination with $2V_{Cu}$ has no deep level and is electrically neutral. Because of a high amount of $2V_{Cu}+In_{Cu}$ complexes, they interact with each other and further reduce the formation energy. Thus the creation of such defect complexes can compensate for Cu-poor/In-rich composition of CIGS without adverse effects on photovoltaic properties. Doping of the CIGS semiconductor is controlled by intrinsic defects. Samples with p-type conductivity are grown if the material is copper poor and annealed under high Se vapor pressure, where as Cu-rich material with Se deficiency tends to be n-type [46][47]. Thus Se vacancy ($V_{Se}$) is considered to be the dominant donor in n-type CIGS and also compensating donor in p-type CIGS while $V_{Cu}$ is dominant acceptor in Cu-poor p-type material. Cu-poor material has $In_{Cu}$ antisite donor defects along with $V_{Cu}$ acceptors, resulting in heavily compensated n- or p-type material. In the case of excess Cu, dominant defects are $Cu_{In}$ antisite and In vacancy ($V_{In}$) acceptors, which both contribute to a strongly p-type material.
CIGS grain boundaries, which are parallel to the current-flow direction, can easily be modified electronically by dopants such as oxygen, and by low-temperature post-processing heat treatments, without affecting the bulk chemistry. As a result, grain boundaries can be made more p-type and thus are electronically benign since the minority carriers (i.e. electrons) cannot reach the grain boundaries to recombine [48].

2.1.4 Bandgap engineering by Ga addition and post sulfurization

Incorporation of Ga leads to an increase in the bandgap of CIS [14] by increasing the energy of the conduction band as shown in Figure 13 [45]. The increase in bandgap with gallium amount is governed by the relation $E_g (\text{eV}) = 1.010 + 0.626x - 0.167x(1-x)$ [49]. Gallium tends to diffuse towards the back contact and form CGS [48]. CGS is a wide bandgap semiconductor with a bandgap of 1.68 eV. The bandgap gradient created between CIS and CGS creates a back surface field (BSF) that acts as a mirror for the electrons moving towards the back contact. The BSF greatly suppresses the back contact recombination and increases the open circuit voltage [50]. Also the formation energy for a Ga$_{Cu}$ defect is higher than the formation energy of In$_{Cu}$. This destabilizes the formation of defect pairs of 2V$_{Cu}^+$In$_{Cu}$ thereby reducing the tendency for the formation of ODC [51] and enhancing the $\alpha$-CIGS region.

Sulfurization of metallic precursors is a well-developed process to produce a high-bandgap (1.55eV) absorber. The Hahn-Meitner-Institut of Germany has developed a similar process using elemental sulfur [52]. Sulfurization is considered as a bandgap engineering treatment for the selenide absorber. The open-circuit voltage $V_{oc}$ mainly depends on the band gap in the space charge region.
Post sulfurization treatment leads to the formation of CIGSS or CIGS2 layer at the interface. Having a wider bandgap of 1.55eV at the p-n junctions helps in increasing the $V_{oc}$. During post sulfurization treatment the sulfur atoms occupy already existing selenium vacancies or replace selenium because of the higher reactivity of sulfur compared to selenium, thereby reducing the compensating donors and also passivating the surface [53].
2.1.5 Effect of Na addition

The highest efficiencies of Cu(In, Ga)Se$_2$, CIGS, thin-film solar cells have been obtained by using soda lime glass as substrate material. Soda lime glass contains significant amounts of sodium in the form of NaO$_2$. It has been shown that the presence of sodium during growth of the CIGS absorber layer is beneficial for the device performance. Among the available sodium containing precursor, NaF is non-hygroscopic, stable in air and evaporates stoichiometrically [54]. Selenization of the film containing sodium results in the formation of NaSe$_x$ compounds that retard the growth of the CIGS phase thereby incorporating selenium in the film [55]. Sodium has a tendency to reduce detrimental point defects. It reduces compensating donors by filling selenium vacancies V$_{se}$ and therefore increases the p-type conductivity. Sodium also replaces In$_{Cu}$ antisite defects further reducing the compensating donors [56]. Apart from reducing the compensating donor sodium also replaces copper vacancies thereby reducing the formation of ODC and increasing the $\alpha$-phase region. Sodium has also been shown to passivate the surface and grain boundaries by promoting incorporation of oxygen [57]. Sodium also promotes of increase in grain size and preferred (112) orientation of CIGS films [54]. The overall effect of sodium incorporation during grain growth is an increase in efficiency by enhancements of fill factor and open circuit voltage. Addition of sodium also results in Cu-poor film with higher charge carrier mobility. This helps in fabricating higher efficiency cells without KCN treatment.
2.2 Buffer layer – Cadmium sulfate (CdS)

CdS is one of the most extensively investigated semiconductors in thin-film form and a large variety of deposition techniques have been utilized to obtain solar cell quality layers of CdS [58]. It is a heterojunction partner in CIGS2 with a bandgap of 2.45 eV, forming a n-type semiconductor. Cross section images of the CuInSe2/CdS interface shows that CdS can grow epitaxially on CIS [59]. It also serves as a window layer that allows the light to pass through it with relatively small absorption. Also, because the carrier density in CdS is much larger than in CIGS, the depletion field is entirely in the CIGS film where electron-hole pairs are generated. As a result, minority carrier recombination at the metallurgical interface is minimized [48]. CdS films are usually grown by chemical bath deposition (CBD). The crystal structure can be varied depending upon the deposition parameter [60]. CdS deposited by the CBD route has wurtzite crystal structure with the c axis perpendicular to the substrate plane. This film grows in a closed packed plane (0001) in the close-packed direction <0001>. A 500 Å film has yellow to orange color and when grown on CIGS a bluish to purple color is seen. The optical absorption edge of solution grown CdS films is the same as that of corresponding bulk material. Deposition of CdS buffer layers on the CIGS absorber is generally carried out in an alkaline aqueous solution of pH>9, consisting of cadmium salt (CdSO4), a complexing agent (NH3) and a sulfur precursor (SC(NH2)2 Thiourea). The complexing agent slows down the reaction and prevents the formation of Cd(OH)2. The concentration of thiourea is usually much higher than the metal precursor. The deposition is carried out in the temperature range of 60 to 80 °C where thiourea hydrolyzes and decomposes releasing S2- ions. The net reaction for the formation of CdS is
Cd\((\text{NH}_3)_4\)^{2+} + SC(\text{NH}_2)_2 + 2\text{OH}^- \rightarrow \text{CdS} + \text{H}_2\text{NCN} + 4\text{NH}_3 + 2\text{H}_2\text{O}

There are several benefits of the CdS layer:

1. CBD deposition of CdS provides conformal coverage of the rough polycrystalline absorber surface.
2. The layer protects against damages and chemical reactions resulting from subsequent ZnO deposition process.
3. The chemical bath removes the natural oxide from the film surface thus, it re-establishes positively charged surface states and, as a consequence, the natural type inversion at the buffer/absorber interfaces.
4. Cd also diffuses to a certain extent into the Cu-poor surface layer of the absorber material, where it possibly forms Cd$_{Cu}$ donors, thus providing additional positive charges that enhance the type inversion of the buffer (CdS)/absorber interface [61].
5. From the electrical point of view the CdS layer optimizes the band alignment of the device [62] and builds a sufficiently wide depletion layer that minimizes tunneling and establishes a higher contact potential that allows higher open circuit voltage [63].

2.3 Transparent conducting oxide window bilayer– intrinsic ZnO and Zinc oxide doped with aluminum (ZnO:Al)

Highly resistive intrinsic ZnO (i:ZnO) is used as a buffer layer. A very thin layer of i:ZnO (50-90 nm) prevents the direct contact of transparent and conducting oxide (ZnO:Al) and CIGSS absorber or even Mo back contact and thereby eliminates the shunt paths. The thickness of i:ZnO is very critical. If the layer is thinner than the critical value, it may lead to increase in leakage
currents. An excessively thicker layer gradually reduces the current density due to an increase in series resistance. The coverage of the i:ZnO layer greatly influences the $V_{oc}$ and the FF [64]. ZnO is a low-cost and abundant material having a bandgap of 3.3 eV making it transparent to the visible spectra. It can be easily doped with group III elements such as Al, B [65] and Ga [66] for high conductivity. Therefore ZnO:Al is frequently used as a transparent and conducting front contact in thin-film solar cells with CIGS absorber. ZnO:Al targets usually contain 2-wt% Al$_2$O$_3$ to make it highly conducting. It has hexagonal wurtzite structure with n-type conductivity because of non-stoichiometry.

RF sputtering (13.65 MHz) is generally used for deposition of i:ZnO while RF or DC plasma can be used for the deposition of ZnO:Al. The electrical conductivity of pure ZnO is due to intrinsic defects, i.e. oxygen vacancies ($V_O$) and zinc interstitials (Zn$_i$) that act as shallow n type donors [67][68]. Incorporation of electrically active defects in sputtered deposited ZnO layers depends critically on sputter deposition parameters such as pressure, gas flux, RF power and the distance between the target and the substrate. Oxygen depletion of the sputter plasma leads to the deposition of metallic zinc along with zinc oxide. In order to obtain transparent layers, oxygen is added to the sputter gas or the layers are deposited on heated substrates where the free zinc is re-evaporated. However, the use of excessive quantities oxygen or very high temperatures prevents the formation of the defect related donors and results in highly resistive layers [69]. Thus, the addition of oxygen must be controlled precisely [70].

In case of ZnO:Al it has been shown by Hall measurements that resistivity is influenced to a large extent by carrier density and only slightly by mobility; low resistivity corresponds to higher carrier density and vice versa. Mobilities in the range of 10 to 30 cm$^2$/Vs are typical for RF sputtered ZnO doped with aluminum [70][71]. Doping of ZnO is a critical process as
excessive doping enhances the free carrier absorption preventing the low energy photon from contributing to the current. These transparent conducting oxides (TCO) are sequentially deposited on CdS film with initial layer of 500 Å of highly resistive intrinsic ZnO followed by 5000 Å of ZnO: Al.
CHAPTER THREE

OPTIMIZATION of MOLYBDENUM BACK CONTACT

3.1 Introduction

Molybdenum is one of the most important materials used as back ohmic contact for CIS/CIGS/CIGSS thin-film solar cells. A variety of metal/CIS contacts have been investigated, including Mo, Pt, Au, Au/Be, Al, Ni, Ag, and Cu. These studies show that Pt, Ni, Au, and Mo all form fairly reproducible, low-resistance contacts to CIS. When annealed at elevated temperatures Au and Pt show significant diffusion into the CIS [72], while Mo and nickel contacts seem to improve with high-temperature treatment [73]. Other evidence shows that both Mo and tungsten films deposited on CIS inter-diffuses in the bulk at 600 °C [74]. The contact properties of CIS films formed at high temperatures (600 °C and above) on metallic thin-films are likely to be quite different [74]. Moreover for polycrystalline CIS solar cells, the metallic back contact forms the substrate upon which the absorber layer is formed. Because of its relative stability at the processing temperatures, resistance to alloying with Cu and indium, and its low contact resistance to CIS, Mo has emerged as the dominant choice for the back contact layer to CIS and CIGSS solar cells [75]. Mo develops residual stresses. Mo being a refractory material, exhibits a correlation between sputtering gas pressure (argon) and developed residual stress when deposited using DC magnetron technique [76]. Gross stress may be determined by visual inspection in that highly compressed films tend to buckle up, frequently in zigzag patterns, whereas films under extreme tensile stress develop a system of stress lines that look like scratches [77]. It is suggested that such stress reversals are dependent on energetic bombardment by reflected neutrals and /or
sputtered atoms. The working gas pressure is expected to moderate the flux and energy of these particles. At relatively low pressures, the arriving atom has high kinetic energy and the resulting film has dense microstructure, experiencing compressive stress. This compressive stress is explained by atomic peening caused by the impact of energetic particles. At relatively high pressures, less energy is provided to the film because of scattering and the resulting film exhibits an open porous microstructure. Inter-atomic attractive forces producing tensile stress can act most effectively in such structures.

3.2 Sample Preparation

Mo deposition was carried out by DC magnetron sputtering in a vacuum chamber with base pressure of $3 \times 10^{-6}$ Torr using a combination of a mechanical pump and a cryo pump [32]. Depositions were carried out from a Mo target of dimensions 30 cm x 10 cm. The distance between the target and substrate was maintained at 6 cm throughout for all depositions. The substrates were moved linearly along 10-cm width of the target with the help of a PC-controlled stepper motor. The thickness variation was in the range of $\pm 3\%$ along the 30-cm length of the target [78]. Earlier, preliminary experiments were carried out on a 25 µm thick titanium foil to obtain qualitative information about the stresses developed under various parameters of deposition. Thin flat strips of a titanium foil of dimension 1 cm x 15 cm were attached to a glass substrate along the 30-cm length of the target gluing them with vacuum compatible tape only at the two ends [79]. The length and the corresponding bend displayed by the titanium foil were along the 30-cm length. Depending on the stress developed the nature of bend in the foil was either convex or concave. Later to obtain quantitative information, wafer bending and XRD
analysis were carried out. Mo depositions were carried out on 125 mm silicon wafers with 100 orientation. The thickness of the silicon wafers was 500 µm and polished on one side. Measurement of stress was carried out by measuring the change in curvature of the wafer using a Flexus (Tencor FLX-2320) surface profilometer. Initially, the curvatures of the uncoated wafers were measured. These values were used as a reference for measuring the change in curvature and thereby calculating the stress in the deposited film. Four deposition cycles were selected for the purpose of this experiment. Argon was used as a sputtering gas and its flow rate, and hence its pressure, was varied with a mass flow controller. Silicon wafers used for deposition were mounted in the vacuum chamber on the day before deposition. The wafer was kept in $5 \times 10^{-6}$ Torr vacuum overnight to ensure a clean surface. Based on the parameters such as power, pressure and time, four deposition cycles were designed. In the first experiment, a Mo layer having a thickness of 138 nm was deposited at 300 W of sputtering power and $3 \times 10^{-4}$ Torr of Ar pressure (cycle A). In the second experiment, a Mo thickness of 127 nm was deposited at a power of 200 W and Ar pressure of a $5 \times 10^{-3}$ Torr (cycle B). Two more experiments were carried out by using alternate layers to reduce the overall stress. In a third experiment, two Mo layers deposited using high power/low argon pressure cycles were sandwiched between three Mo layers deposited using low power/high argon pressure cycles to achieve a total film thickness of 330 nm (cycle C). In a fourth experiment, two Mo layers deposited using low power/high Ar pressure cycles were sandwiched between three Mo layers deposited using high power/low Ar pressure cycles to obtain an effective thickness of 315 nm (cycle D). Along with the silicon wafer, a 2.5 cm x 10 cm sodalime glass piece was also mounted for measuring the thickness of the film, to check adhesion using simple adhesive tape and for morphology and composition analyses. The residual stress was measured by the wafer bending technique. Crystal structure and
morphology were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Sheet resistance was measured using a four-point probe measurement technique. The extent of sulfur diffusion in Mo layer was analyzed by Auger electron spectroscopy (AES) in conjunction with argon ion sputtering.

### 3.3 Results and Discussion

Initially, a simple bending foil technique was used to estimate the amount of stress present in the foils. This was a crude approach for qualitative understanding of the stress build up by varying the deposition parameters. Loads were applied to the concave and convex region of the foil and weight required to make the foil flat similar to its position prior to deposition was measured. The required load, height of curvature and the stress developed in the film are provided in Table 1.

<table>
<thead>
<tr>
<th>Power / Argon Pressure</th>
<th>Height of curvature</th>
<th>Loads applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>300W / 0.3 x 10^{-3} Torr (cycle A)</td>
<td>0.88 mm</td>
<td>450 mg</td>
</tr>
<tr>
<td>200W / 5 x 10^{-3} Torr (cycle B)</td>
<td>0.48 mm</td>
<td>130 mg</td>
</tr>
<tr>
<td>Alternate cycles (cycle C &amp; D)</td>
<td>Flat film</td>
<td>--------</td>
</tr>
</tbody>
</table>

From the data of applied loads as well as the curvature of the foil it was observed that the stress developed during cycle A was comparatively higher than that developed during cycle B. From the amount of load required for flattening the foil, it was observed that the stress developed
in cycle A was approximately 3 times that of stress developed in cycle B. Depositions carried out using cycle C and D showed a flat substrate indicating a very small residual stress. As mentioned earlier, for quantitative measurements a wafer-bending technique was used. The stress in the film was calculated from the following equation [80].

$$\sigma = \frac{[E/(1-\nu)]}{[h^2/6Rt]}$$

Where,

$\sigma$ is the film stress (Pa)

$E/(1-\nu)$ is the biaxial elastic modulus of the substrate (1.805E11Pa for 100 Si)

$h$ is the substrate thickness (m)

$t$ is the film thickness (m)

$R$ is the radius of the curvature (m) of the substrate

Table 2 summarizes the stress values in the individual high power / low pressure and low power / high pressure cycles as well as in the combination cycles. The cycle A measured tensile stress of 300 MPa while cycle B measured compressive stress of 91 MPa along 30-cm length of the target. On the other hand, earlier work at the FSEC PV Materials Lab and some publications [81] report the nature of stress to be compressive for high power cycle and tensile for low power cycle. The deposition process for cycles A and B was repeated with higher thicknesses of 260 nm for cycle A’ and 300 nm for cycle B’. Stress values obtained along 30-cm length of target were 120 MPa (compressive) and 69 MPa (compressive) respectively. These values were not consistent with the earlier reported values for lower thickness. The stress values for cycle C were comparatively lower in both the directions over that observed in cycle D, suggesting the benefits of using cycle C for depositing Mo back contact.
Table 2: Nature and amount of stress build up during selected deposition cycles.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Thickness (nm)</th>
<th>Stress along 30-cm length of target (MPa)</th>
<th>Stress along 10-cm width of target (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>127</td>
<td>300 (tensile)</td>
<td>20.5 (compressive)</td>
</tr>
<tr>
<td>A' (repeated)</td>
<td>260</td>
<td>69 (compressive)</td>
<td>330 (compressive)</td>
</tr>
<tr>
<td>B</td>
<td>138.8</td>
<td>91 (compressive)</td>
<td>100 (compressive)</td>
</tr>
<tr>
<td>B' (repeated)</td>
<td>300</td>
<td>120 (compressive)</td>
<td>162 (compressive)</td>
</tr>
<tr>
<td>C</td>
<td>330</td>
<td>35.8 (tensile)</td>
<td>18.5 (compressive)</td>
</tr>
<tr>
<td>D</td>
<td>315.3</td>
<td>103.7 (tensile)</td>
<td>19.6 (compressive)</td>
</tr>
</tbody>
</table>

Figure 14: XRD pattern of as-deposited Mo film, from cycle C.
X-ray diffraction was carried out to measure the total strain in the lattice created due to sputter deposition during cycle C and D. Figure 14 represents the XRD pattern of film deposited using cycle C, while Figure 15 represent XRD pattern obtained from film deposited using cycle D. Table 3 summarizes the analysis of the data obtained from the Figure 14 and Figure 15.

Table 3: Data collected from XRD patterns of the films.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Mo(110) intensity (counts)</th>
<th>FWHM Mo(110)</th>
<th>Fe(110)/Mo(110)</th>
<th>Interplanar d(110) Å</th>
<th>Lattice parameter ‘a’ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>81</td>
<td>1.54</td>
<td>34.5%</td>
<td>2.25</td>
<td>3.18</td>
</tr>
<tr>
<td>D</td>
<td>85</td>
<td>1.26</td>
<td>24.7%</td>
<td>2.24</td>
<td>3.167</td>
</tr>
</tbody>
</table>
Lattice parameter of powdered and annealed Mo is 3.16 Å. Amount of induced strain can be computed using the simple relation,

\[
\text{Strain } \% = \frac{\Delta a}{a} \times 100
\]

Strain induced by cycle C = 0.63%, cycle D = 0.22%.

From the values of induced strain, intensity, Fe (110) to Mo (110) peak intensity ratios and FWHM it can be concluded that the film deposited, starting and ending with 300W / 0.3 x 10\(^{-3}\) Torr (cycle D) appears more crystalline as well as comparatively denser.

Sheet resistance measurements were carried out using a four-point probe measurement technique on the films deposited in all cycles at four different locations per wafer at identical position for each wafer. Adhesion of the film to the substrate was studied by simple adhesive tape test. Adhesive tape strips of same lengths were glued on the wafer and stripped with approximately equal amount of force. The film deposited in cycle C peeled off completely from Mo/substrate interface, while it remained adherent in other cycles. The sheet resistance values and adhesion observations are summarized in Table 4. The stress in the film from the cycle C was lower as seen from wafer bending analysis, however peeling off occurred probably because the first film in contact with the substrate was less compact. Similar effect was not observed for the film in cycle B because the film thickness in cycle C was higher as compared to the film thickness in cycle B. Small pieces of dimension 1 cm x 1 cm were cut from the films deposited on a glass substrate and sulfurized at 475 °C for 20 minutes to see the reactivity of Mo film. The films turned purple and energy dispersive spectroscopy revealed the presence of sulfur in all the films, indicating reactivity of Mo in sulfur atmosphere at operating temperature. The extent of sulfur incorporation in the film was analyzed by AES in conjunction with argon ion sputtering.
Table 4: Sheet resistance and adhesion observations.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Sheet resistance (Ω/sq.)</th>
<th>Adhesion observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (127 nm)</td>
<td>3.32</td>
<td>Well adherent</td>
</tr>
<tr>
<td>A’ (260 nm)</td>
<td>2.20</td>
<td>Well adherent</td>
</tr>
<tr>
<td>B (138 nm)</td>
<td>13.5</td>
<td>Well adherent</td>
</tr>
<tr>
<td>B’ (300 nm)</td>
<td>17.5</td>
<td>Well adherent</td>
</tr>
<tr>
<td>C (330 nm)</td>
<td>2.20</td>
<td>Peeled off</td>
</tr>
<tr>
<td>D (315 nm)</td>
<td>1.46</td>
<td>Well adherent</td>
</tr>
</tbody>
</table>

Figure 16: (a), (b), (c), (d). AES depth profiling showing sulfur incorporation in Mo films.
Figure 16 shows the depth profile of the elemental composition in individual films. It was observed that the sulfur diffused to a depth of 25 nm (Figure 16-a) in high power cycle A while it diffused to a depth of 35 nm (Figure 16-b) in the low power cycle B. This was expected as the film deposited in cycle A was more compact compared to that deposited in cycle B. Sulfur diffusion depth in Mo film of cycle C was 25 nm (Figure 16-c) and the corresponding value for cycle D was 15 nm (Figure 16-d). The results for cycle C and D can be justified as the top surface layer in cycle D was more compact than that in cycle C. Since it was desired to have minimum incorporation of sulfur in the Mo film, it was concluded that the Mo deposition sequence in cycle D is more suitable for back contact deposition.

The morphology of the films deposited at different combinations of operating conditions (power and pressure) was also studied by scanning electron microscopy (SEM). High-power cycle A and low-power cycle B films were also deposited on glass substrates. The film deposited using cycle A was densely packed and showed less porosity (Figure 17-a). This resulted in a decrease in film resistivity, the film deposited using cycle B had porous (fish-like) grain morphology and significant inter-granular voids (Figure 17-b). The higher resistivity was a direct result of this sputter-induced porosity. Figure 17 (c) and (d) indicated compact morphology for cycles C and D. It is interesting to note that the morphology in cycle C appears comparatively rough than that in cycle D. This is expected as cycle C contains three cycles of porous films as shown in Figure 17 (b) while cycle D contains three cycles of comparatively denser structure as shown in Figure 17 (a). On the basis of SEM observations and resistivity values it was concluded to use cycle D, as it provides compact, a uniform and less resistive Mo film as back contact. These observations support the argument made from XRD analysis.
Figure 17: (a) SEM image of sample deposited at 300W / 0.3 x 10^{-3} Torr at 20,000 X, (b) deposited at 200W / 5 x 10^{-3} Torr at 20,000 X, (c) & (d) image of film deposited at low power and high power cycles at 65,000 X.

### 3.4 Summary of the chapter

The overall conclusion for the selection of deposition cycle for Mo back contact was based on the observation made in the individual analysis. The wafer bending technique suggested that the cycle C consisting of two layers deposited at 300W / 0.3 x 10^{-3} Torr sandwiched between three layers of 200W / 5 x 10^{-3} Torr develops a comparatively lower stress. XRD, SEM, AES, adhesion and sheet resistance measurement suggested that the film deposited in cycle D was crystalline, compact, inert, well adherent to the substrate and more conducting
compared to the one deposited in cycle C. It was, therefore, decided to use cycle D, composed of
two layers deposited at a sputtering power of 200 W and a Ar pressure of $5 \times 10^{-3}$ Torr
sandwiched between three layers deposited at a sputtering power of 300 W and a Ar pressure of
$3 \times 10^{-4}$ Torr as the sputtering sequence for depositing a Mo back contact layer. From a
commercial production stand point, a process involving five cycles is not advisable. The entire
five-layer sequence was, therefore, reduced to three layers. Here the first and third layer was
deposited by the high power cycle with thicknesses corresponding to the total thickness of three
individual high power cycles ($300 \text{ W} / 3 \times 10^{-4}$ Torr). The middle layer was deposited by the
low-power cycle with a thickness equal to the total thickness of two individual low power ($200
\text{ W} / 5 \times 10^{-3}$ Torr) cycles.
CHAPTER FOUR

PREPARATION AND OPTIMIZATION OF CIGSS/CDS THIN-FILM SOLAR CELLS USING DIETHYLSELENIDE AS SE SOURCE

4.1 CIGSS/CdS thin-film solar cell for space application

The start of the space era was ignited by the development of rockets, light-weight materials and electronics. This odyssey was propelled by the human thirst for knowledge and adventure. Space endeavor relies on materials with outstanding properties – they must survive in an environment that combines ionizing radiation, extreme temperatures, and micrometeorites. Certain missions add extra threats: low earth and geostationary orbits inflict ferocious ozone-induced degradation, while deep space missions involve high levels of ionizing radiation and eventually extremely low temperatures.

The main requirements for space materials are: light weight (to reduce mission costs); resistance to ionizing radiations (accelerated electrons, protons and ions); multifunctional capabilities; smart features; self healing capability and outstanding thermal stability. Out of the available candidates, CuIn$_{1-x}$Ga$_x$Se$_2$ and CuIn$_{1-x}$Ga$_x$S$_2$ are attractive because of their high resistance to radiation damage. Tuttle et al have shown in their study that no degradation was observed even when the cells were subjected to a fluence of $10^{15}$ 1-Mev electrons [82]. CuInGaSe$_2$ cells demonstrate more than 5 times the specific power at 20 to 40 % of the manufacturing costs while the power density is 70-91 % of crystalline cell technology [82]. When it comes to the substrate to be lightweight, flexible and robust, there are various candidates such as polyamide sheets, e.g. Kapton, Apical and Upilex and thin metallic foils. It is difficult to use a polyamide sheet over 400$^\circ$C whereas high quality cells are grown at a temperature of
around 475°C [83]. Moreover, organic sheets need a rigid frame and mesh because of their tendency of to sag, therefore, CIGS/CIGS2 on thin and ultra-lightweight metallic foil is the potential combination for the fabrication of ultra-lightweight solar cells for space power application.

4.2 Thin foil substrate

Fabrication of CIGSS based thin-film solar cells on a flexible and ultra-lightweight substrate possesses a great advantage of increasing the duration of space mission and improving fuel economy by reducing the pay load of satellite. At this stage it is essential to understand the basic property requirement of the substrate material for it to be successfully used in preparing high-quality devices. The properties to be considered are: vacuum compatibility – in sputtering technique the thin elemental layers are deposited in vacuum better than 5 x 10^{-6} Torr. Therefore it is essential that the substrate should not degas during vacuum deposition steps and contaminate the layers. Thermal stability – high efficiency cells are processed at temperatures greater then 475°C. Higher temperature promotes grain growth thereby reducing the grain boundary planar defects that would otherwise act as recombination centers. It is required for substrates to maintain chemical stability at such high temperatures. Suitable thermal expansion – the thermal coefficient of expansion of CIS is ~9 × 10^{-6}/K in the temperature interval of interest. A CIS film deposited on a substrate with a lower thermal expansion coefficient, such as borosilicate glass, will be under increasing tensile stress during cool down. Typically, such films exhibit voids and microcracks [84]. When the thermal expansion coefficient of the substrate is higher than that of the film material, like for polyimide, it will result in compressive stresses in the thin-film
material, which may lead to adhesion failures. Chemical inertness – the substrate should not corrode in reactive ambient during selenization and sulfurization. It should be reasonably stable against environmental attacks during long-term exposure especially from water vapor diffusing into the PV module. It should not decompose during CdS deposition nor release undesired impurities to the absorber layer. Cost and weight effective – the substrate should be economically manufacturable, require minimum manufacturing energy consumption, readily available in abundant quantity and lightweight. Measuring the properties of the potential substrate material such as aluminum, titanium, Mo, copper, stainless steel and polyimide sheets, it is observed that stainless steel satisfies most of the requirements. Calculations have shown that with the reduction of the SS substrate thickness from 127 µm to 20 µm, the specific power increases from 133 W/kg to 769 W/kg with 10 % efficiency cells [85]. Since thinner sheets require more rolling steps, commercially available thinner sheets tend to be relatively rougher which affects the performance of the cell. A smooth substrate surface is required for three reasons. First, abrupt changes in the surface topography such as spikes or cavities may lead to shunt paths between the front and back contact. Second, the increase in the surface area due to surface roughness may increase the amount of impurities diffusing in the absorber layer. It has been postulated that Fe and other elements from steel diffusing into the absorber increase series resistance by increasing front and back contact resistance due to alloying effect. This diffusion of substrate components also decreases the shunt resistance by forming electrically conducting phases which mostly segregate along CIGSS grains [86]. Third, the roughness may cause non-conformal coverage of the surface by the diffusion barriers or insulation layers. The smooth insulating layer facilitates the monolithic contact. A highest efficiency of 17.4% has been reported for the co-evaporation technique on a SS substrate [87].
4.3 Diethylselenide (DESe): A low-toxic alternative for selenization

DESe is a volatile liquid having a vapor pressure of approximately 29 Torr at room temperature. DESe was selected as a source for selenium instead of H₂Se because of two reasons,

1) Toxic limit and storage pressure: H₂Se gas is very toxic with the time weighted average threshold limit value (TWA-TLV) of 50 parts per billion (ppb) and must be stored at high-pressure (~20 Kgf/cm²) cylinders, while, diethylselenide [(C₂H₅)₂Se: DESe] with a (TWA-TLV) of 0.2 mg/m³ equivalent to 250 ppb is a safer alternative to H₂Se with a lower potential leakage risk. Therefore, the use of DESe leads to less stringent regulations on the exhaust system.

2) Price comparison: Rough estimates indicate that the selenization process using DESe would cost approximately the same or slightly less compared to that using H₂Se. The price of DESe is five times that of H₂Se per mole (market price June 2004). However, the partial pressure of DESe, which reflects the source material consumption, required for the selenization process has been found to be approximately three to four times lower than that of H₂Se, due to the higher decomposition rate of DESe compared to H₂Se. The actual DESe material consumption would be four to ten times less compared to that of H₂Se. Therefore, operational costs can be considerably higher when hydride gases are used.

4.4 Experimentation

Initially SS foils of thicknesses 127 µm and 25 µm with average surface roughness of 6.23 nm and 25.4 nm respectively were used for deposition. Deposition parameters were
maintained identical in both the cases. The Mo back contact and CuGa and indium metallic precursors were deposited by DC magnetron sputtering. Depositions were carried out from targets of dimensions 30 cm x 10 cm. The distance between the target and substrate was maintained at 6 cm throughout all depositions. The substrates were moved linearly along the 10-cm width of the target with the help of a PC-controlled stepper motor. To minimize the stress build up the Mo was deposited in alternate layers as discussed in chapter 2. The deposition timings were adjusted to deposit a total thickness of 0.35 µm. The metallic precursor such as Cu-Ga was deposited at 350 W and 1.5 x 10⁻³ Torr argon pressure while indium was deposited at 230W and 7 x 10⁻⁴ Torr argon pressure using DC magnetron sputtering. The deposition of metallic precursors was carried out in three steps, in the first step the substrate was moved over the copper-gallium target at a linear speed of 0.056 cm/sec, in the second step the substrate was moved over the indium target at a linear speed of 0.052 cm/sec, the third step involved the deposition of a thin layer of copper-gallium at a linear speed of 0.096 cm/sec. During parameter optimization this cycle was modified to obtain a stoichiometric composition. The modified cycle was also a three step sequence with a first and third layer of CuGa deposition at 0.07 cm/sec and 0.16 cm/sec while indium was deposited at a substrate speed of 0.03 cm/sec. The entire elemental stack sequence was first selenized at 400°C for 10 minutes followed by sulfurization at 475°C for 20 minutes. These parameters were used because good quality CIGS absorbers using H₂Se are prepared at 400°C [88] while earlier, a 10.4 % efficient CIGS2/CdS thin-film solar cell has been produced with a sulfurization process by annealing the elemental stack at 475 °C for 60 minutes [89]. The copper-rich film was etched in dilute KCN solution to obtain a near stoichiometric CIGSS chalcopyrite thin-film. For optimization of heat treatment parameter during selenization, experiments were carried out in temperature range of 450°C to 515°C while
the soaking time was varied between 10 minutes to 80 minutes. The amount of DeSe was also varied along with the CuGa amount. For better performance and intermixing of elements, experiments were performed with multiple layers (5 and 9 layer) of CuGa and indium. The morphology of the CIGSS absorber was studied by scanning electron microscopy. X-ray diffraction analysis was carried out to study the crystallinity of the absorber layer. Electron probe microanalysis was used to study the chemical composition of the absorber elements. Auger electron microscopy was carried out for studying the compositional gradient along the thickness of the film. Transmission electron microscopy was used on selective samples for studying the cross-sectional grain structure and interfaces.

4.5 Results and Discussions

In the following section, initial results obtained on metallic foils are discussed. These results were essential for the optimization of the parameters to obtain a high-quality absorber layer using the novel DESe selenium source.

4.5.1 Analysis of film grown on SS foils

A SEM image of a CIGSS film on a 25 µm SS substrate (Figure 18 & Figure 19) shows a comparatively porous structure with well defined grains of 0.5 µm diameter. The film on the 127 µm SS substrate (Figure 20 & Figure 21) is dense but the grains are not well resolved. This indicates that the hold time during selenization and sulfurization is not sufficient to form the single pseudo-pentanary phase.
Figure 18: SEM of CIGSS on a 25 µm SS substrate (X5500)

Figure 19: SEM of CIGSS on a 25 µm SS substrate (X20000)
XRD analysis of the film on a 25 µm substrate (Figure 22) indicates the formation of the chalcopyrite structure with compositional formula CuIn$_{0.93}$Ga$_{0.07}$Se$_{1.4}$S$_{0.6}$. The pattern obtained
on 127 µm substrates (Figure 23) indicates the presence of two phases, CIS and CuIn$_{0.5}$Ga$_{0.5}$Se$_{1.3}$S$_{0.7}$. During selenization/sulfurization the phase change occurs from binary to pseudo-pentanary, it is therefore necessary to increase the soaking time during the process to form the required phase for the layers on the thicker substrate. A normal trend of gallium diffusing towards the back contact is observed in a film grown on a 25 µm substrate (Figure 24). It is observed that the amount of gallium is higher in the film on 127 µm which is also indicated by XEDS data shown in Table 5. AES profile shown in Figure 25 for 127 µm substrate also indicates higher concentration of gallium in the film. It is also observed that the concentration profile of the elements does not follow the trend obtained on a 25 µm substrate. It is also observed that as the gallium concentration increases towards the back contact probably due to a stress gradient, the amount of indium decreases. Gallium and indium being group III elements tend to replace each other in the crystal lattice.

![XRD of CIGSS on 25 µm SS substrate](image)

Figure 22: XRD of CIGSS on 25 µm SS substrate
From the analysis of CIGSS films deposited on the metallic substrate it was clearly evident that the process parameters such as temperature, time, amount of DESe and the atomic concentrations of metallic precursors need to be optimized for growth of a highly crystalline layer. Since the preparation of CIGSS layer on metallic foils takes 3 more days than that on glass substrates, further optimization experiments were carried out on Mo coated glass substrates some of which were provided by Shell Solar Industries formerly Siemens Solar Industries.

Table 5: XEDS data at 15 KV measured on 25 and 127 µm stainless steel

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Cu (at %)</th>
<th>In (at %)</th>
<th>Ga (at %)</th>
<th>Se (at %)</th>
<th>S (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 µm SS</td>
<td>21.1</td>
<td>19.3</td>
<td>4.2</td>
<td>27.4</td>
<td>24.8</td>
</tr>
<tr>
<td>127 µm SS</td>
<td>19.0</td>
<td>15.8</td>
<td>12.7</td>
<td>14.9</td>
<td>33.9</td>
</tr>
</tbody>
</table>

Figure 23: XRD of CIGSS on 127 µm SS substrate
Figure 24: Depth profile of CIGSS on a 25 µm SS substrate

Figure 25: Depth profile of CIGSS on a 127 µm SS substrate
4.5.2. Parameter optimization

Initially, a temperature ramp of 6 °C/ minute was used for selenization/sulfurization of the elemental stack because it led to the minimum error between the set values and the actual values of the temperature controller. A series of experiments were performed for optimizing the heat treatment parameters such as temperature and soaking time at growth temperature to ensure complete selenization and formation of a device-quality absorber.

Metallic precursors CuGa and indium were sputter-deposited on Mo coated glass substrate for optimizing the process parameters. Power and pressure for precursor deposition was kept the same in all experiments discussed here. The speed at which the substrates moved over the targets of each precursor layer was varied in order to obtain desired rates of depositions, total thicknesses of each layer and consequently slightly Cu-poor composition.

4.5.2.1 To establish baseline parameters for preparing CIGS/CIGSS film

Purpose: To set initial parameters for selenization and sulfurization.

The elemental stack of metallic precursors was selenized at 400°C for 10 minutes in a combined DESe and argon pressure of 30 Torr and sulfurized at 475°C for 20 minute in a 4% H₂S/N₂ gas mixture [88] i:ZnO of 50 nm and ZnO:Al of 500 nm were deposited by RF magnetron sputtering at 200W and 300W respectively and argon pressure of 1.5 x 10⁻³ Torr. Ni/Al contact fingers were deposited using a metal mask by electron beam evaporation. EPMA carried out at 20 kV on the absorber layer measured the elemental concentration as Cu- 24.5 at%, In- 31 at%, Ga- 4.9 at%, Se- 15 at% and S- 24.5 at%.
Figure 26: SEM image of CIGSS prepared by selenization at 400°C and sulfurization at 475°C and etched in 10% KCN.

From SEM analysis (Figure 26) it was seen that the grain size was very small and the grains were not faceted. EPMA analysis at 20 kV was carried out to analyze the stoichiometry and it was observed that the amount of selenium (13.8 at%) was comparatively lower than that of sulfur (34.7 at%). This indicated that there was not enough Se in the selenization ambient or the temperature and soaking time were not adequate for completion of the reaction between metallic precursors and Se.

Purpose: To see if selenium incorporation increases in the presence of sodium and excess copper.

Two changes were made in this experiment. First the amount of CuGa was increased by increasing the time required for the substrate to move over the sputtering target allowing more
time to deposit. For this purpose the substrate movement speed was reduced from 0.048 cm/sec to 0.04 cm/sec. Secondly, a small amount of sodium was added in the form of a NaF layer. 3.4 mg of NaF was thermally evaporated by Joule heating onto the Mo surface. The complete evaporation of the specified quantity corresponds to 12 nm thick layer. Current flowing through the Mo boat having NaF was 160-165 ampere during evaporation. Some part of the film peeled off at the Mo/CIGSS interface. This peeling was probably due to improper cleaning or incomplete dissociation of the NaF layer at the interface. The film had a sheet resistance varying from 250 $\Omega/\Box$ to 300 $\Omega/\Box$ measured with the two probe method. The elemental composition of Cu-31 at%, In- 22.8 at%, Ga- 3.7 at%, Se- 15 at% and S- 27 at% was measured by EPMA at 20 kV. Overall the film was copper-rich with a Cu/In+Ga ratio of $>1.17$. The problem of incomplete selenization continued as the amount of Se in the films was consistently low. The effect of sodium and excess Cu was not realized. This indicated that the parameters used in the process were not adequate to produce device quality absorber.

**Purpose: To understand the effect of NaF layer position on peeling-off of the film**

A thinner layer of NaF (12 nm) was deposited on the precursor layer instead of Mo layer as it was believed to be one of the potential reasons for peeling observed in earlier experiment. The film appeared uniform after the selenization cycle and no peeling of the absorber film was observed. The SEM image (Figure 27) revealed underdeveloped, compact and non-distinct grains. It was again evident from EPMA analysis carried out at 20 kV that the proportion of selenium was considerably lower than that of sulfur. The elemental composition was Cu-28 at%, In- 21.5 at%, Ga- 3.5 at%, Se- 13 at% and S- 34 at%.
The important inference from the experiment was that the amount of selenium vapor during the growth process was not sufficient to completely selenize the film as well as dissociate the NaF at Mo interface that resulted in peeling.

Purpose: To increase the Se incorporation by supplying more selenium-containing vapor for longer time.

Soaking time at selenization temperature was increased by 5 minutes (400°C for 15 minutes) while sulfurization hold time was reduced by 5 minutes (475°C for 15 minutes). The sulfurization time was reduced to incorporate more Se than S in the films. Diluted DESe pressure was increased from the earlier value of 30 Torr to 60 Torr in order to increase the amount of Se. The heat-treated film had a sheet resistance in the range of 700 Ω/□ to 1200 Ω/□ measured by the two point probe.
Figure 28: AES depth profile shows the elemental distribution along the thickness of the sample

The sheet resistance value lower than 500 Ω/□ is considered as Cu-rich, between 500 Ω/□ and 1500 Ω/□ it is considered as slightly Cu-rich and the film gets Cu-poor with the increase in sheet resistance beyond 1500 Ω/□. EPMA data was not available, therefore it was observed from AES data shown in Figure 28 that selenium incorporation was not significant. Hence, further experiments were carried out for preparing only selenide absorber layer.

**Purpose:** To study the effect of higher heating rate and dwell at lower temperature

In the following experiment, the deposition parameters and the maximum temperature for selenization were kept un-changed, except that in this case a heating ramp of 20°C/minute was used instead of 6°C/minute and an additional dwell at 140°C for 30 minutes was used during
heating. During the measurement, it was realized that the Mo layer from the absorber layer interface to the substrate had completely reacted, leaving no Mo back contact for efficiency measurement. The thickness of these films was measured using a thickness profilometer and was found to be 1.3 to 1.5 µm. This thickness was almost half of the value intended (2.75 µm). SEM image (Figure 29) showed the formation of larger and distinct grains. XEDS was carried out at 20 kV, at the Material Characterization Facility of AMPAC (University of Central Florida) showed slightly Cu-poor film, Cu-23 at%, In- 25 at%, Ga- 3.1 at%, Se- 48 at%. Though the cells cannot be completed on the sample it was important to note that since the thickness was reduced the amount of selenium vapor per unit volume was adequate or slightly more than required. Adequate amount of Se vapor can be concluded from the formation of larger grains while Mo reactivity indicates excess amount.
Another example is shown in Figure 30-3 was selenized at 400°C/15 minutes and it showed a pattern after removing from the furnace. The pattern remained after etching. The entire film turned dark on oxidation treatment in solution of 1:1 proportion of H₂O₂/1%H₂SO₄. The film also peeled during CdS deposition (Figure 30-2). In both the films shown in Figure 29 and 31, the thickness of the absorber layer was in the range of 1.3 to 1.5 µm. Due to the lower thickness, Mo layer was completely reacted and no devices could be made on the film.

![Figure 30: 1- As deposited, 2- Selenized and CdS treated, 3- Selenized](image)

**Purpose: Thickness of the absorber was doubled to prevent complete Mo reaction**

The deposition timings were doubled so as to obtain higher thickness of the absorber film. CuGa was deposited in two layers; the first layer was deposited at a substrate speed of 0.02 cm/sec while the second layer was deposited at 0.07 cm/sec. An indium layer deposited at a substrate speed of 0.021 cm/sec was sandwiched between the two CuGa layers corresponding to Cu/(In+Ga)=2.5. This ratio of the precursor was used because sulfurization of absorber film in highly Cu-rich regime has yielded efficiencies above 10% [89].
A 5 cm x 10 cm strip from this deposition was selenized at 400°C for 10 minutes. The total pressure of diluted DESe in argon was 30 Torr. The temperature was ramped up at 20°C/min with no intermediate dwell. The sample showed patches of dark and light gray areas as
seen in Figure 31. The sheet resistance in the dark areas was 1.4 kΩ/□ and 1 kΩ/□ in the light gray areas. Overall, the film was slightly copper-rich which was evident from the CuSe whiskers seen in the SEM image (Figure 32).

**Purpose: To study the effect of reduced ramp rate**

In another experiment, the ramp rate was reduced to 6°C/minute while the deposition and selenization parameters were kept the same as the previous experiment. The film was comparatively uniform (Figure 33). The sheet resistance was 300 to 500 Ω/□ and the thickness was 3.8 to 3.9 µm. The SEM image is shown in Figure 34.

Figure 33: Photograph of the sample selenized at 400°C for 10 minutes with 6°C/min heating ramp.
The grain size varied from <1 µm to 2 µm in all the samples. Cells were prepared on the film and corresponding efficiency values were below 1% indicating that the process needs to be modified to optimize the parameters to obtain a good-quality absorber. The furnace hardware parameters were not suitable for higher ramp rates; however, installing new controllers would benefit in achieving higher ramp rate that may avoid the formation of harmful binary compounds such as Cu$_2$Se [90].

The important inferences of these set of experiments were; 1) The heating ramp of 6°C/minute could be used for reaching the growth temperature during selenization/sulfurization. However the process could be made more efficient at higher ramp rates. 2) The growth temperature to be increased above 400°C. 3) The total pressure of DESe and hydrogen needs to be increased above 30 Torr.
4.5.2.2 Establish a film growth temperature regime and soaking time in this regime for preparing crystalline CIGS/CIGSS absorber film

Purpose: To carry out selenization at 425°C with higher amount of DESe

The deposition parameters were maintained to be highly Cu-rich (Cu/(In+Ga)=2.5). This experiment was an effort to observe the behaviour of the film under different temperature and time values. The sample was selenized at 425 °C for 30 minutes. Diluted DESe was filled in the reaction tube of the furnace to a pressure of 60 Torr. On the surface of the film withered patches were observed (Figure 35). XEDS analysis at 15 kV revealed the patches to be indium rich indicating segregation of indium. Cu - 12 at%, In - 52 at%, Se - 36 at% and the amount of Ga was not in a detectable range as most of it goes to the back contact.

Figure 35: SEM of sample grown at 425 °C for 30 minutes in 60 Torr total pressure of DESe+H₂
In one of the earlier experiments, a similar elemental stack with highly Cu-rich condition was selenized at 400 °C for 30 minutes in 60 Torr DESe + H₂. On the surface of the film globules were observed (Figure 36). XEDS at 13 kV of these grains showed the composition to be Cu- 9 at%, In- 63 at% and Se- 28 at%. Comparing the composition and the morphology of the sample grown at 400°C and 425°C it can be inferred that with an increase in temperature the indium segregation reduces as the globules start disintegrating and the film appears to be more homogeneous.

Figure 36: SEM of sample grown at 400 °C for 30 minutes in 60 Torr total pressure of DESe+H₂

**Purpose: To identify the cause of film peeling**

The precursor deposition parameters were kept the same as in previous experiments. 60 Torr of total DESe and argon was used for the process. The film was selenized at 425°C for 60 minutes. After removing from the furnace the film appeared uniformly gray with some dark
patches on one side (Figure 37). During etching in 10% KCN the film completely peeled off (Figure 38). The well-reflecting appearance of the Mo surface indicated no reaction with Mo. It was believed that the excess copper in the film formed a Cu₂Se layer at Mo/CIGS interface that dissolved during etching resulting in peeling of the film. The other reason and more probable cause was an insufficient amount of Se due to which a well adherent CIGS layer could not form.
In-order to eliminate the possible effect of Cu$_{2-y}$Se the deposition parameters were changed. The amount of CuGa was reduced by increasing the speed of substrate movement over the CuGa target while the amount of indium was kept the same. Single layer of CuGa was deposited by linearly moving the substrate over the target at a speed of 0.04 cm/sec and indium was deposited at 0.021 cm/sec. These deposition parameters correspond to a slightly Cu-poor chemistry. The sample was cut in half and one part of it was selenized at 450°C for 30 minutes. However, the problem continued as the film peeled completely during etching in a similar way. On opening the DESe feeding set-up it was found that the DESe liquid was over, hence the peeling of the complete film during etching was a direct cause of absence of Se vapor during selenization.

Purpose: To see the effect of higher selenization temperature 475°C on cell performance

A part of the metallic precursor deposited strip with slightly Cu-poor stoichiometry was selenized at 475 °C for 30 minutes. A minute amount of oxygen was deliberately added as it prevents the segregation of indium during alloy formation. Oxygen was essential during the process, as the top layer of the metallic precursor was indium that was in direct contact with selenium vapor. In order to see the effect of temperature the total pressure of DESe and argon was fixed at 40 Torr. The amount of DESe provided was 10 to 12 times more than that used for the continuous process used by Chichibu et al. [37]. After the selenization treatment the sample appeared uniform gray with no patches. The selenized sample had a sheet resistance of 37-47 kΩ/□. After etching in 10 % KCN the change in sheet resistance was negligible. This was expected as the precursor deposition parameters were adjusted to obtain a near-stoichiometric composition (Cu/(In+Ga)=0.82).
Figure 39: SEM image of unetched absorber with absence of NaF layer.

Figure 40: SEM image of dilute KCN etched absorber
Table 6: EPMA at 20 kV, chemical composition of as selenized and KCN etched absorber prepared at 475°C for 30 minute and thickness of 3.6 µm

<table>
<thead>
<tr>
<th></th>
<th>Elem.</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>As selenized</td>
<td>at%</td>
<td>23.3</td>
<td>25.3</td>
<td>2.9</td>
<td>48.5</td>
</tr>
<tr>
<td>Selenized and KCN etched</td>
<td>at%</td>
<td>23.0</td>
<td>25.5</td>
<td>3.0</td>
<td>48.4</td>
</tr>
</tbody>
</table>

Chemical analysis (Table 6) shows a minute reduction in the copper and selenium content as the Cu$_{2-y}$Se was removed by etching treatment. The SEM image (Figure 39 & Figure 40) shows the absorber layer before and after etching. It was also noted that the grain size was in the range of 0.5 µm to 1.5 µm. The thickness of the film was 3.5 to 3.6 µm. This sample was further cut in half to produce two pieces of 5 cm x 5 cm. One of the pieces was etched while the other was used as selenized for CdS (50 nm thickness) deposition. i:ZnO (50 nm)/ZnO:Al (500 nm) and Ni/Al contact fingers were deposited with the earlier stabilized parameters. A PV conversion efficiency of 5.56 % was measured on the etched and CdS deposited sample while the unetched and CdS deposited sample provided lower values due to the presence of a Cu$_{2-y}$Se metallic phase at the interface.

Purpose: To reduce the thickness of the absorber layer keeping the growth parameters same and to observe the effect of NaF

The amount of precursors was reduced in order to obtain absorber thickness of approximately 2.75 µm. For this purpose the speed of the substrate moving over the respective targets was increased. Substrate speed over the CuGa target was 0.052 cm/sec while that over indium target was 0.027 cm/sec. A very thin layer of NaF (12 nm) was deposited on half of the sample while the other half was selenized as deposited.
Figure 41: SEM of selenized and etched sample.

Figure 42: SEM of NaF deposited, selenized and etched absorber
Table 7: EPMA at 10 kV, chemical composition of an absorber with and without NaF layer, prepared at 475°C for 30 minute and etched with 10% KCN

<table>
<thead>
<tr>
<th></th>
<th>Elem.</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>No NaF and etched</td>
<td>at%</td>
<td>20.8</td>
<td>29.3</td>
<td>1.2</td>
<td>48.8</td>
</tr>
<tr>
<td>NaF and etched</td>
<td>at%</td>
<td>21.0</td>
<td>30</td>
<td>1.3</td>
<td>47.9</td>
</tr>
</tbody>
</table>

The sample was selenized in 40 Torr of diluted DESe. The difference in the microstructures between both the films is shown in Figure 41 & Figure 42. Addition of sodium improved the grain size as well as, the grains were faceted. The resulting films had a thickness of approximately 2.8 μm. The amount of precursors was reduced proportionally during deposition, however EPMA data presented in Table 7 indicated the film to be indium rich. The sheet resistance of the film with NaF was in the range of 109 to 190 KΩ/□ while that of the film with no NaF layer was 500 KΩ/□ to 2 MΩ/□. The addition of sodium in the form of NaF helped in improving crystallinity.

Table 8: EPMA at 20 kV, chemical composition of as selenized and KCN etched absorber prepared at 500°C for 30 minute with 12 nm layer of NaF

<table>
<thead>
<tr>
<th></th>
<th>Elem.</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>As selenized</td>
<td>at%</td>
<td>22</td>
<td>26</td>
<td>3</td>
<td>49</td>
</tr>
<tr>
<td>Selenized and KCN etched</td>
<td>at%</td>
<td>21.9</td>
<td>26</td>
<td>3.1</td>
<td>49</td>
</tr>
</tbody>
</table>
Purpose: To study the morphology of a film grown at 500°C for 30 minutes with better elemental stoichiometry and a thin layer of NaF

In this experiment CuGa was deposited at substrate speed of 0.052 cm/sec while the amount of indium was decreased by increasing the substrate speed to 0.03 cm/sec. The Cu/(In+Ga) ratio improved from previous 0.72 to 0.75. A 12 nm layer of NaF was deposited by thermal evaporation Table 8. Selenization was carried out at 500°C for 30 minutes in 40 Torr dilute DESe atmosphere. The SEM image in Figure 43 shows well developed and faceted grains with an average size of 1.5 μm. The resulting film had a thickness of 2.7 to 2.8 μm. Cells were completed by depositing the remaining layers of CdS, i:ZnO, ZnO:Al and Ni/Al front contact. The best efficiency of 4.8% was achieved from this experiment. Corresponding device parameters were $V_{oc} = 400$ mV, $J_{sc} = 32$ mA/cm$^2$ and $FF = 38\%$

Figure 43: Etched film showing well faceted and large grains
Purpose: To see the effect of longer soaking period at the film growth temperature (500°C for 60 minute)

A similar metallic precursor layer used in the previous experiment was selenized at 500°C for 60 minutes in 40 Torr diluted DESe. The grains were highly faceted and could not be differentiated from one another with clear boundaries as seen in Figure 44. The elemental composition provided in Table 9 was used to calculate the Cu/(In+Ga) ratio to be 0.74. From EPMA and SEM images it was observed that the excess soaking affects the morphology however the elemental composition remains the same.

Figure 44: SEM image of film etched in 10% KCN showing highly faceted grains
Table 9: EPMA at 20 kV, chemical composition of as selenized and KCN etched absorber prepared at 500°C for 60 minute with thin layer of NaF

<table>
<thead>
<tr>
<th>Elem.</th>
<th>Cu</th>
<th>In</th>
<th>Ga</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>As selenized at%</td>
<td>22.4</td>
<td>25.77</td>
<td>2.49</td>
<td>49.32</td>
</tr>
<tr>
<td>Selenized and KCN etched at%</td>
<td>21.46</td>
<td>26</td>
<td>3.11</td>
<td>49.42</td>
</tr>
</tbody>
</table>

Figure 45: TEM cross-sectional view of a film selenized at 500°C for 60 minutes.
The TEM image (Figure 45) shows a porous structure (white) near the interface with the Mo back contact layer. The grains near the interface are comparatively smaller than those in the top part of the film. The grain size ranged from 1 to 2 µm. The porosity may be an artifact of sample preparation. It also indicates that the phase formed near the interface is poorly adherent with the matrix as it was removed during the focused ion beam milling for sample preparation. Gallium has the tendency to diffuse towards the back contact and form CGS that is defect free and well adherent to the back contact. An insufficient amount of gallium would lead to the formation of a poor-quality CGS phase reducing the adhesion with the matrix; therefore in the next experiment the amount of CuGa was increased. Silicon was detected along the edge of the pores. The exact origin of the silicon is not known. The probable source identified was from SiO₂ diffusion barrier layer between glass and Mo. During milling silicon can re-deposit on the region near the Mo surface and since the grains near the Mo surface fall apart silicon would remain on the edge. Another postulation was diffusion of silicon from the barrier coating or glass which is believed to be a rare probability. The matter needs further attention to identify the real cause. The cells prepared on this absorber had inferior device properties of $V_{oc}$– 280 mV, $J_{sc}$– 29.5, FF – 32.7 and efficiency of 2.7.

**Purpose: To study effect of 500°C for 30 minutes selenization cycle on a higher CuGa content metallic precursor**

The amount of CuGa was increased by 24% for this experiment by reducing the speed of the substrate moving over the CuGa target to 0.042 cm/sec. The amount of NaF and diluted DESe vapor was kept the same as in the previous experiment. The amount of indium was kept constant. The elemental stack was selenized at 500°C for 30 minutes.
Figure 46: Cross-section of the film having higher CuGa content and selenized at 500°C for 30 minutes

Figure 47: Topographic view of KCN etched film
Figure 46 shows the cross-section of the absorber. Small grains are seen at the interface with Mo while larger grains were observed towards the surface. The surface of the film appeared rough. The grain size was measured to be ~2µm (Figure 47) and it can also be seen that the grains were faceted. The cell was completed and the corresponding device parameters were; $V_{oc}$– 390mV, $J_{sc}$– 29.6 mA/cm$^2$, FF – 38.5 and eff. – 4.47%. There was an improvement in the cell performance with the increase in the CuGa amount. The soaking time at the growth temperature was increased in the next experiment to see the effect of higher dwell time on the absorber layer.

**Purpose:** To study the effect of higher soaking time (60 minutes) at 500°C

The deposition parameters were kept the same in this experiment. The total dwell time 60 minutes at maximum temperature was distributed between selenization (30 minutes) and sulfurization (20 minutes). A total time of 10 minutes was required for removal of Se-containing gas and refilling of sulfur containing gas. The process was carried out at 500°C. The cross-section view showes large grains along the thickness of the film. Higher soaking time helped in improving the grain size. TEM analysis was carried out in the sample as shown in Figure 48. The micrographs reveal a homogeneous CIGS absorber layer with fewer pores. The differences between the top and bottom layer are less pronounced. The grain size in the top part of the absorber layer was ~1µm in diameter, while grains in the lower part are typically 100 to 200 nm in diameter. The EDX analysis in Figure 49 reveals the formation of a Mo and Se-rich layer (probably MoSe$_2$) of 50 nm thickness above Mo layer. This layer appears gray in the Figure 48. The MoSe$_2$ layer formed at the interface between Mo and CIGS provides numerous advantages such as; (a) It forms an ohmic contact thereby eliminating resistive losses. Absence of MoSe$_2$
results in an undesired Schottky barrier at the back contact [91]. (b) MoSe$_2$ improves adhesion between Mo and the absorber layer. (c) The bandgap of MoSe$_2$ is 1.41 eV which is higher than for the bulk CIGS. This reduces recombination at the back contact providing simultaneously low resistivity for holes [91]. The increase in the amount of CuGa substantially reduced the porosity. It is believed that increasing the amount of CuGa prevented the formation of any volatile phase causing porosity. Adhesion of the film was also better by making more gallium available for the formation of a defect free CGS phase at the interface with Mo.

Figure 48: Bright-field transmission electron micrograph of the interface between Mo and CIGSS. A Mo and Se rich layer on top of Mo and a low fraction of pores is found. The adhesion between the Mo and the CIGSS layer appears to be good.
Figure 49: HAADF-STEM of the Mo-CIGSS interface (left) and XEDS line scan (right). A clear increase in the Se signal as well as Mo is found at the interface indication MoSe$_2$.

The important outcomes of the experiments discussed in the section 4.4.2.2; 1) A device quality- absorber is prepared at temperature above 475$^\circ$C. 2) The soaking time varies between 30 to 60 minutes, with better result obtained at 500$^\circ$C for 60 minutes.

**Purpose:** To optimize the elemental composition of metallic precursor

Cu/(In+Ga) ratio plays an important role in determining the performance of the cell. In order to enhance the intermixing of the elements the metallic precursors were deposited in multiple layers in a sandwich pattern. Further, the amount of CuGa was empirically reduced as the deposition parameters in the earlier experiment (substrate speed over CuGa target – 0.042
cm/sec) resulted in copper rich composition at ‘as selenized’ condition. The chemical compositions mentioned so far were obtained after KCN etch. The idea was to achieve Cu-poor chemistry at the ‘as selenized’ stage to eliminate etching step. The substrate movement speed that decides the atomic concentration of Cu was readjusted to 0.058 cm/sec. The indium concentration was maintained with the speed of 0.03 cm/sec. Total thickness of CuGa was divided in 5 equal layers while that of indium was equally divided in 4 layers. The substrate speed during each individual cycle of CuGa deposition was $0.058 \times 5 = 0.29$ cm/sec and for each cycle of indium it was $0.03 \times 4 = 0.12$ cm/sec to deposit each layer of equal thickness. The amount of DESe in each experiment was kept constant. Initially, 4 nm of a NaF layer was deposited on the Mo layer. The film was selenized at 475°C for 80 minutes. The film had features coming out of the film surface with a deep ring at its base. The chemical compositions of the selenized film and the features, measured by EPMA are given in Table 10.

Table 10: EPMA of film (43A) and features present on the film processed at 475°C for 80 minutes

<table>
<thead>
<tr>
<th></th>
<th>Cu (at %)</th>
<th>In (at %)</th>
<th>Ga (at %)</th>
<th>Se (at %)</th>
<th>Cu/(In+Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10kV (film)</td>
<td>21.36</td>
<td>28.31</td>
<td>0.95</td>
<td>49.36</td>
<td>0.73</td>
</tr>
<tr>
<td>20kV (film)</td>
<td>21.01</td>
<td>25.95</td>
<td>2.31</td>
<td>50.69</td>
<td>0.74</td>
</tr>
<tr>
<td>10kV (feature)</td>
<td>20.8</td>
<td>28.11</td>
<td>1.08</td>
<td>49.97</td>
<td>0.71</td>
</tr>
<tr>
<td>20kV (feature)</td>
<td>21.65</td>
<td>27.6</td>
<td>2.77</td>
<td>47.95</td>
<td>0.71</td>
</tr>
</tbody>
</table>
The chemistry of features varied slightly from that of the film. The features being indium rich were resistive and therefore did not cause shunting of the film. The efficiency of the cells prepared on such an absorber film measured between 4.6 to 5% with corresponding $V_{oc}$ of 370 mV.

The amount of Cu was increased by 13%. For this purpose, the speed at which the substrate was moved over the CuGa target was modified to 0.052 cm/sec. There were five layers of equal thickness. The amount of indium was kept constant by maintaining substrate speed at 0.03 cm/sec. The efficiencies of the cell prepared on the film processed at 475°C for 80 minutes reached values above 8% with corresponding $V_{oc}$ of 440 mV.

Table 11 presents the chemical composition of the film prepared with a higher amount of CuGa. The increase in the atomic concentration of Cu reduces the formation of In$_{Cu}$ compensating donor.

Table 11: EPMA of film and features, the film (43D) was grown at 475°C for 80 minutes

<table>
<thead>
<tr>
<th></th>
<th>Cu (at %)</th>
<th>In (at %)</th>
<th>Ga (at %)</th>
<th>Se (at %)</th>
<th>Cu/(In+Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10kV (film)</td>
<td>23.11</td>
<td>27.51</td>
<td>1.03</td>
<td>49.01</td>
<td>0.80</td>
</tr>
<tr>
<td>20kV (film)</td>
<td>22.92</td>
<td>26.61</td>
<td>2.32</td>
<td>49.74</td>
<td>0.79</td>
</tr>
<tr>
<td>10kV (feature)</td>
<td>22.18</td>
<td>28.24</td>
<td>1.15</td>
<td>47.53</td>
<td>0.75</td>
</tr>
<tr>
<td>20kV (feature)</td>
<td>22.11</td>
<td>27.93</td>
<td>2.43</td>
<td>49.9</td>
<td>0.73</td>
</tr>
</tbody>
</table>
Purpose: To study the effect of sodium quantity added in the form of NaF thickness on the morphology of the film and hence the performance of the cell

The following optical micrographs were selected from various experiments to demonstrate the effect of the amount of sodium added in the form of NaF on the features observed on the surface of the film. All the experiments were carried out at 500°C with fixed amounts of diluted DESe and metallic precursors. The metallic precursors were deposited in multiple layer sequence with layers of indium sandwiched between layers of CuGa. The amount of each precursor was controlled by moving the substrate over the CuGa target at a collective speed of 0.058 cm/sec while that during indium deposition was 0.03 cm/sec. Figure 50 shows the representative micrograph of the film prepared without NaF layer. The metallic precursors were deposited in multiple layers. The micrograph was recorded on a completed cell. Here, the white line appearing in the micrograph corresponds to the top contact finger. Since ZnO is transparent and the thickness of CdS is 50 nm, the features appearing on the surface of the absorber layer were visible. Very tiny features were visible. These features were randomly distributed over the entire surface of the absorber. The typical efficiency of the cells prepared on such absorbers was less than 5%. Figure 51 represents the film that had 4 nm thickness of NaF. The features observed on the absorber surface were agglomerations of many tiny features. EPMA at 10 kV showed a Cu/(In+Ga) ratio of 0.73 for the film while it was 0.71 for the features. Therefore with the addition of NaF the widespread segregation of indium-rich features was limited to specific spots making the film more uniform.
Features

Figure 50: Micrograph of completed cell on the film selenized with no layer of NaF. Numbers of tiny features were seen on the absorber layer. (Sample 41E, mag: 100X)

Figure 51: Micrograph of the absorber surface prepared from the film having 4 nm of NaF. (Sample 43B, mag: 50X)

The efficiency of the cells prepared on such absorbers was 6 to 6.9%. The number of features in this reduced when the amount of NaF was increased to 8 nm. Moreover, the features
Figure 52: Micrograph of the absorber surface prepared from the film having 8 nm of NaF. (sample 42C, mag: 50X)

appearing on the film surface appeared better organized and larger as shown in Figure 52. The reduction of features made the film more uniform and also helped in maintaining the indium amount in the film. The XEDS data collected at 20 kV revealed a Cu/(In+Ga) ratio of 0.83 in the film while that on the feature was 0.74. A PV conversion efficiency > 8% was obtained from the cells prepared on such films.

From the set of experiment carried out for optimizing NaF and amount of metallic precursors, it was inferred that 8 nm of NaF and Cu/(In+Ga) > 0.8 yields better efficiencies. The next selenization was carried out at 500°C for 60 minutes. The metallic precursor CuGa was deposited in 5 layers with each layer deposited by moving the substrate over the CuGa target at 0.052 x 5 = 0.26 cm/sec and over the indium target at 0.03 cm/sec. The NaF layer of 8 nm was deposited on the Mo layer prior to deposition of metallic precursors. The film was selenized in
Figure 53: Micrograph of the regularly spaced features on the film processed at 500°C for 60 minute. The film had 8 nm of NaF deposited on Mo layer. Magnification a- 50 X, b- 100 X, c- 500 X

Table 12: EPMA of the film and the features on the film processed at 500°C for 60 minute

<table>
<thead>
<tr>
<th></th>
<th>Cu (at %)</th>
<th>In (at %)</th>
<th>Ga (at %)</th>
<th>Se (at %)</th>
<th>Cu/(In+Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10kV (film)</td>
<td>23.42</td>
<td>26.5</td>
<td>1.04</td>
<td>49.01</td>
<td>0.85</td>
</tr>
<tr>
<td>20kV (film)</td>
<td>22.8</td>
<td>25.03</td>
<td>2.3</td>
<td>49.74</td>
<td>0.83</td>
</tr>
<tr>
<td>10kV (feature)</td>
<td>22.45</td>
<td>28.54</td>
<td>1.45</td>
<td>47.53</td>
<td>0.74</td>
</tr>
<tr>
<td>20kV (feature)</td>
<td>22.15</td>
<td>26.03</td>
<td>2.23</td>
<td>49.9</td>
<td>0.78</td>
</tr>
</tbody>
</table>
diluted DESe. Figure 53 shows the optical micrograph of the film taken at 50X, 100X and 500 X. Regularly spaced small indium-rich features (would be useful for quantum dot structures) were observed on the film. The chemical composition of the film suggests the formation of the $\alpha$-phase of CIGS. The features were found to be excessively indium rich as compared to the film (Table 12). The film as seen in the SEM image (Figure 54) is well faceted and the grain size is $> 1 \mu m$. The cross-sectional view of the film (Figure 55) shows large grains extending from the back contact to the surface. The thickness of the film was 2.6 $\mu m$.

Figure 54: SEM micrograph of the film having 8 nm layer of NaF and selenized at 500$^o$C for 60 minutes. The grains are well faceted and $> 1 \mu m$. 

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Figure 55: Cross-sectional view of the film having 8 nm layer of NaF and selenized at 500°C for 60 minutes. The large grains extend from the back contact to the surface.

The cells were completed by depositing CdS (~ 50 nm) followed by i:ZnO (70 nm), ZnO:Al (600 nm) and finally a Cr/Ag front contact. The cells have efficiencies greater than 9%. When the same cell was measured at the National Renewable Energy Laboratory, the official confirmed total-area efficiency was 12.33%. The other electrical parameters of the cell were; $V_{oc} = 495$ mV, $J_{sc} = 39.15$ mA/cm$^2$ and FF = 63.53%. The series resistance for the above cell was measured to be 14 $\Omega$/cm$^2$ and the shunt resistance was more than 2.5 k $\Omega$/cm$^2$. 
Figure 56: Current–voltage characteristics (I-V) of the cell having 8 nm layer of NaF and selenized at 500°C for 60 minutes.
Figure 57: Quantum efficiency measurement of the cell having 8 nm layer of NaF and selenized at 500°C for 60 minutes.
The I-V (Figure 56) and QE curve (Figure 57) provides valuable information about the cell and potential areas of improvement. The $J_{sc}$ value of 39.15 mA/cm$^2$ is near the maximum possible value for CIS with minimum recombination and interface losses. This indicates that the bulk of the material is well selenized with minimum defects. The $V_{oc}$ value of 495 mV is low and suggests a potential area of improvement at the p-n junction. $V_{oc}$ can be further improved by three possible ways; 1) fine tuning the amount of CuGa so as to achieve Cu/(In+Ga) ratio of between 0.88 and 0.92 and thereby reducing the In$_{Cu}$ compensating donors. 2) Increasing the thickness of i:ZnO to prevent shortening and leakage current paths. 3) Optimizing the post-sulfurization parameters to effectively reduce the recombination centers in the space charge region and also passivate the surface. In order to improve the FF the series should be as small as possible while the shunt resistance should be higher. The shunt resistance value was acceptable however, the series resistance needs to be further reduced by optimizing the thickness of ZnO:Al. The FF can be further improved by using Nickel/Aluminum as contact fingers instead of chromium/silver as nickel has better lattice matching with ZnO.

In the next experiment a post-sulfurization was carried out as well as thicker layer of i:ZnO was deposited to further increase $V_{oc}$. At the end of selenization the reactive gases were exhausted and diluted H$_2$S gas was filled. Selenization was carried out at 515$^\circ$C for 50 minutes and sulfurization was carried out at same temperature in diluted H$_2$S gas. The film had 8 nm layer of NaF and was selenized in dilute DESe. The cell were prepared by depositing CdS (~60 nm), i:ZnO (90 nm), ZnO:Al (600 nm) and finally the Cr/Ag front contact fingers. The $V_{oc}$ improved from 495 mV to 540 mV. The major improvement in photovoltaic property was from reduction in selenium vacancy due to incorporation of sulfur at the surface as seen in AES depth profile (Figure 58). AES profile shows the incorporation of sulfur at the surface and also near
back contact. Sulfur diffuses faster through grain boundaries therefore large quantity of sulfur was seen near back contact due to large number of grain boundaries owing to smaller grains. Reduction in the selenium vacancies in space charge region reduces recombination loss and thereby increases $V_{oc}$ as was evident from the results.

![AES plot](image1.png)

Figure 58: AES plot to verify the elemental concentration along the thickness of the film

![SEM image](image2.png)

Figure 59: SEM image of the film selenized and sulfurized at 515°C
From the SEM image shown in Figure 59 and Figure 60 the grains are highly faceted and has dimension greater than 1µm and extending from back contact to surface. I-V and QE characteristic are shown in Figure 61 and Figure 62 respectively. The dip in the center of QE curve of earlier cell (Figure 57) was not observed in this case as sulfur passivated the recombination centers. The curve was flat in the center region; however noticeable free carrier absorption was still evident. To the best of our knowledge the efficiency of 13.73% is the world record on small area cells prepared by selenization/sulfurization in conventional furnace.
Figure 61: Current–voltage characteristics (I-V) of the cell having 8 nm layer of NaF and selenized/sulfurized at 515°C
Figure 62: Quantum efficiency measurement of the cell having 8 nm layer of NaF and selenized/sulfurized at 515°C
Purpose: To investigate the morphology and chemical composition of the features

In this film, processed at higher temperature (515°C), the features had a deep ring surrounding them. The depth of the ring was less than 0.5 µm while the height of the feature was 3 µm (Figure 64). A similar feature was observed on the films prepared at 500°C. The exact growth behavior is not known, however it is postulated that a liquid-like indium-rich phase with a Cu:In:Ga:Se ratio of approximately 22.4:28.5:1.45:47.5 helps obtaining better morphology of the growing film. Figure 64 shows the profile of the feature depicted in Figure 63. The profile was created by converting the mechanical movement of the stylus as it moves over the feature.
Figure 64: Profile of features seen on the film selenized at 515°C for 60.

into an electronic signal that was used to plot the curve. The height of the feature varied in the range of 3 to 5 μm. The features were regularly distributed on the film. The remainder of the film apart from the features was homogeneous. From SEM image as shown in Figure 65 the group of features had a crater in the center. The tip of the stylus was not fine enough to discern the exact profile of the very small diameter feature, ~2 μm. The chemical composition at the center and outer base of the feature was the same and also the grain size was very small (Table 13). The group of features that forms the wall of the crater had comparatively larger grains that were very Cu-poor. The remaining film was homogeneous and slightly copper poor. Thus the effective indium content in the grains was increased from film surface to top of the feature.
Figure 65: SEM image of well developed feature. Showing a crater surrounded by the indium-rich wall

Figure 66 shows the interface between the base of the feature and the film on which it grows. Grains observed on the left region of the micrograph are the base of the feature while the larger grains represent the film morphology. Since the base of the feature forms a deep ring and the morphology of the grains is rough. The grains are very small as compared to the grains in the remaining film. The grain size again increases as well as the grains appear disintegrated towards the top of the features.
Figure 66: The base of the feature seen in Figure 65, the features starts towards the left while the homogeneous film is on right

Table 13: XEDS analysis at 8 kV of feature and film

<table>
<thead>
<tr>
<th></th>
<th>Cu (at%)</th>
<th>In (at%)</th>
<th>Se (at%)</th>
<th>S (at%)</th>
<th>Cu/In</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top of feature</td>
<td>18</td>
<td>30.1</td>
<td>45.4</td>
<td>6.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Middle of feature</td>
<td>20.35</td>
<td>30.6</td>
<td>43.6</td>
<td>5.4</td>
<td>0.66</td>
</tr>
<tr>
<td>Outer base</td>
<td>21.62</td>
<td>31.9</td>
<td>44.2</td>
<td>2.2</td>
<td>0.67</td>
</tr>
<tr>
<td>Film</td>
<td>20.4</td>
<td>28.2</td>
<td>45.6</td>
<td>5.7</td>
<td>0.72</td>
</tr>
</tbody>
</table>
The deposition and the process parameters for depositing a Mo back contact and the CIGSS absorber were optimized. Mo layer should be deposited with two layers having tensile stress sandwiched between three layers in compressive stress. The optimized Mo film had good adhesion with the substrate. It was also found to be compact and therefore less reactive with the selenium and sulfur gases. Device quality absorbers were prepared in the temperature range of 475°C to 515°C and soaking time in the range of 30 to 80 minutes. The addition to a small amount of sodium in the form of NaF layer was beneficial in improving the morphology of the film which showed large and well faceted compactly packed CIGSS grains. The metallic precursors with a Cu/(In+Ga) ratio of ~ 0.85 and NaF layer of 8 nm thickness, when selenized in DESe, produced CIGS thin-film solar cell of efficiency 12.33%. The corresponding device parameters were $V_{oc} = 495$ mV, $J_{sc} = 39.15$ mA/cm$^2$ and FF- 63.97%. Further, $V_{oc}$ was increased to 540 mV by depositing 90 nm thick layer of i:ZnO and incorporation of sulfur in the surface layer of the absorber. PV conversion efficiency of 13.73% was achieved with this modification. To the best of our knowledge this is the world record efficiency on small area cell prepared by sputtering and selenization approach in conventional furnace. This research demonstrated the potential of lower toxicity, easily stored and less safety stringent ‘diethylselenide’ to be used as a selenium precursor for preparing CIGSS/CdS thin-film solar cells by easily scalable sputtering technique.
LIST OF REFERENCES


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