Enhancement of the deposition processes of Cu(In,Ga)Se₂ and Cds thin films via in-situ and ex-situ measurements for solar cell application

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Enhancement of the Deposition Processes of Cu(In,Ga)Se₂ and CdS Thin Films via In-situ and Ex-situ Measurements for Solar Cell Application

by

Vikash Ranjan

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Doctor of Philosophy Degree in Physics

Dr. Sylvain X. Marsillac, Committee Chair

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College of Graduate Studies

The University of Toledo

May 2011
An Abstract of

Enhancement of the Deposition Processes of Cu(In,Ga)Se$_2$ and CdS Thin Films via In-situ and Ex-situ Measurements for Solar Cell Application

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Thin films of Cu(In,Ga)Se$_2$ deposited by 1-stage, 2-stage and 3-stage co-evaporation processes result into the highest efficiency solar cells. Controlling the rate and sequences of individual sources during these co-evaporation processes are important for better quality Cu(In,Ga)Se$_2$ absorber layers. At the same time, spectroscopic ellipsometry due to its ex-situ as well as in-situ application is considered as a very powerful tool to understand the material properties as well as to monitor the process. Nevertheless, spectroscopic ellipsometry was not properly utilized until now to characterize Cu(In,Ga)Se$_2$ thin films. In this study, one of our goal is to understand the optical and electrical properties of Cu(In,Ga)Se$_2$ as a function of process and composition.

In the first part of this study, we implemented ex-situ spectroscopic ellipsometry
(SE) along with other characterization techniques like Secondary ion mass spectroscopy (SIMS), Scanning electron microscopy (SEM), Auger electron spectroscopy (AES), x-ray diffraction (XRD), atomic force microscopy (AFM) etc. to compare Cu(In,Ga)Se₂ thin films deposited by the above mentioned three co-evaporation processes. During this study, we were able to use SE to find the thickness, roughness, band gap, Ga grading of the Cu(In,Ga)Se₂ deposited by 2-stage and 3-stage process. Finding of SE were correlated by SIMS, AES, SEM etc. In the case of Cu(In,Ga)Se₂ deposited by 1-stage process, due to the high surface roughness, we are not able to implement the ex-situ spectroscopic ellipsometry.

In the second and third part of this study, real time spectroscopic ellipsometry is implemented to study the material properties of Cu(In,Ga)Se₂ thin films as a function of Cu and Ga concentration. Effectively, in a 3-stage co-evaporation process, the composition of the film changes during the process. To monitor and control the composition of Cu(In,Ga)Se₂ during the 3-stage process by in-situ ellipsometry, it was necessary to understand the optical properties of Cu(In,Ga)Se₂ as a function of Cu atomic percentage (at.%) as well as Ga at.%. Along with this, the inability to implement ex-situ SE for Cu(In,Ga)Se₂ thin film motivated us to implement the spectroscopic ellipsometry in real time i.e. during the growth of the film. This in-situ real time application of SE helped us in understanding the microstructural evolution and dependence of the band gap with the Cu atomic percentage (at.%) as well as the Ga at.%. We also used this opportunity to understand the shift in the critical points as a function of temperature for CuInSe₂ alloys. Characterization like AES, XRD, AFM etc were performed after the growth at room temperature to corroborate the RTSE findings.
In the fourth and last part of this study, the growth of CdS on a Cu(In,Ga)Se₂ surface as a function of time was studied using SE as well as AFM. We also used this opportunity to compare the growth of CdS on another substrate (SiO₂). Spectroscopic ellipsometry and AFM revealed a quantum confinement effect in the case of CdS on SiO₂ whereas no such effect was observed for CdS on Cu(In,Ga)Se₂ surface due to the growth of compact CdS layers.
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Chapter One

Introduction to Photovoltaic Technology

1.1 Motivation

With the increasing population along with the growth of human activities all around the world the consumption of energy has increased, even though one-third of the world’s population is still deprived of energy supplies. To fulfill the energy demand of this population which is deprived of energy along with the increased demand due to fast industrialization, roughly 30TW of energy is required by the end of 2050. All these demands of energy are mostly dependent on fossil fuels and nuclear resources. Even if the available reserve of raw material is sufficient to meet this future demand, increased level of energy production from these sources will threaten human existence due to harmful side effects like pollution and climate change. In order to fulfill these future energy requirements, we need to have sufficient reserve, and a production that is environmentally friendly, therefore leading to a strong need of development and deployment of renewable sources of energy such as solar energy. Solar, wind, hydropower and geothermal are a few among many available renewable energy resources. U.N. studies indicate that with around 120,000 TW of solar power is absorbed by Earth's surface every year which is 10,000 times the existing annual demand of
energy. Thus solar cells with average conversion efficiency of 10% will require less than 0.6% of earth's emerged land to fulfill our energy needs [Philibert, 2005]. Even with all these advantages of solar cells on other sources of energy, there are many obstacles to the widespread use of solar energy. House hold electricity based on conventional sources cost around 4 cents/kWh whereas electricity based on solar cells costs around 15-30 cents/kWh in the US. Lowering the manufacturing cost and the material dimension as well as increasing the efficiency by improving the material quality will help in reducing the energy cost from solar cells.

1.2 Fundamentals of Solar Cell Operation

A solar cell is a device which converts light energy into electrical energy by generating current and voltage. This process of current and voltage generation consists of: (a) absorption of photons by a semiconductor with band gap lower than the absorbed photon and generation of electron-hole (e-h) pairs, (b) separation of these e–h pairs by some internal mechanism and (iii) collection of e–h pairs by external circuit. One of the widely used mechanisms for separating an e-h pair is based on the p–n junction.

1.2.1 p-n Junction

Doped semiconductors have large concentration of either holes or electrons and are called p-type or n-type respectively. When these two types of semiconductors are brought in contact to each other, the p-n junction is established. At this instant, electrons from the n-type semiconductor diffuse towards the p-type semiconductor due to the concentration gradient of electrons. Similarly, the holes from the p-type semiconductor diffuse towards the n-type semiconductor due to the concentration gradient of holes. This
diffusion of electrons leaves behind immobile positively charged ions in the n-type semiconductor, and diffusion of holes leaves behind immobile negatively charged ions in the p-type semiconductor. The region depleted of mobile charged carriers in either side of the junction is called the space charge region (SCR) or depletion region. The build up of positive charges on one side and negative charges on another side creates electrostatic potential difference and so an electric field from the n-type to the p-type semiconductor.

![Diagram of p-type and n-type semiconductors](image)

**Figure 1-1**  (a) Separate p-type and n-type semiconductor, (b) band bending of the p-n junction at the thermal equilibrium, (c) space charge distribution of p-n junction, (d) electric field distribution and (e) electrostatic potential distribution of the p-n junction. The $x_n$ and $x_p$ in the figure is the boundary of the space charge region in n-type and p-type respectively.

With more diffusion of electrons and holes, this electrostatics force increases. At the same time due to the electrostatic force from the n-type semiconductor to the p-type semiconductor, the electrons in the p-type semiconductor (minority carriers) are subject to an attraction force and swept away towards the n-type semiconductor where they
become majority carrier. Similarly, the holes are swept away towards the p-type semiconductor. The current due to the diffusion of charged carrier is called diffusion current and the current due to the electric field is called the drift current. Once the drift current due to the electrons and the holes becomes equal to the diffusion current, the Fermi level of the p-type and n-type semiconductors are aligned and the p-n junction is called under equilibrium. Under thermal equilibrium, the electrostatic potential developed is called build in potential ($V_{bi}$) which is the difference between the initial Fermi levels of the p-type and n-type semiconductor.

1.2.2 A p-n junction under illumination

Let’s assume that a p-n junction is illuminated under the solar spectrum. The photons with energy greater than the band gap of the p-type semiconductor are absorbed by the p-type semiconductor. Before being illuminated under the solar spectrum, the p-n junction behaves as a diode and the current through the p-n junction follows the ideal diode equation:

$$I = I_0 \left( e^{\frac{qV}{kT}} - 1 \right)$$  \hspace{1cm} (1.1)

where $I_0$ is the reverse saturation current, $V$ is the applied bias voltage, $k$ is the boltzman’s constant, and $T$ is the absolute temperature. Under illumination, there is also a photocurrent which is in the opposite direction of the dark current and the current equation is written as [Sze, 1981]:

$$I = I_0 \left( e^{\frac{qV}{kT}} - 1 \right) - I_L$$  \hspace{1cm} (1.2)

where $I_L$ is the light generated current. The circuit diagram of an ideal solar cell and the I-V curve of the p-n junction in the dark and under illumination are plotted in Figure 1-2. As shown in Figure 1-2, under illumination the I-V curve shifts in the fourth quadrant. In
Figure 1-2, $I_{SC}$ is the short circuit (i.e. at zero load) and is the maximum current extracted from the solar cell. Similarly, $V_{OC}$ is the open circuit voltage (i.e. voltage at infinite load) and is the maximum voltage extracted from the cell. But the function of the solar cell is to generate energy and at these two extreme values there is not any energy extracted from the solar cell. The maximum power is extracted at a finite load and is the area of the maximum power within the I-V curve. In Figure 1-2, the point corresponding to the maximum power is denoted by $P_{mp}$. The other important parameter to check the solar cell performance is called the fill factor of the solar cell. The fill factor of the solar cell determines the squareness of the I-V curve [Gray, 2003]:

$$FF = \frac{P_{mp}}{I_{SC}V_{OC}}$$  \hfill (1.3)

![Figure 1-2](image)

**Figure 1-2** (a) Equivalent circuit of an ideal solar cell under illumination, (b) I-V curve of the ideal solar cell under dark and illumination [Sze, 1982].

The most important parameter is called the conversion efficiency which is the ratio of the power extracted from solar cell to the input power:

$$\eta = \frac{P_{mp}}{P_{in}} = \frac{FFV_{OC}I_{SC}}{P_{in}}$$  \hfill (1.4)
where $P_{in}$ is the input power of the sunlight at AM 1.5 condition. The AM (air mass intensity) is used to denote the ratio of the thickness of the atmosphere that the Sun light must pass through to the normal path before striking the Earth surface in the cloudless day (PVCDROM):

$$AM = \frac{1}{\cos(\theta)} \quad (1.5)$$

where $\theta$ is the angle of the path Sun light travels with respect to the vertical. If this angle is $48.19^0$ then AM condition is called AM 1.5 ($AM = \frac{1}{\cos(48.19)} = 1.5$). Thus the AM 1.5 is equivalent to the sunlight passing through 1.5 times the air mass of vertical illumination (AM 1).

### 1.3 Photovoltaic (PV) Technology Development

As explained in the previous section, photovoltaic is the process of converting light energy to electrical energy by generating current and voltage and the device used to perform this action is called a Solar cell. Edmund Becquerel was first to reported such action when he observed the production of current and voltage by illuminating a silver chloride electrode immersed in an electrolytic solution in 1839 [DOE, 2005]. After that, it took nearly 100 years to fabricate a real solar cell when a solar cell based on a p-n junction was produced at the Bell labs in 1953 [Chapin et al., 1954]. The efficiency of that cell was around 6% and the semiconductor used to manufacture this solar cell was single crystal Si. Since that day, many different semiconductors and different techniques are used to make solar cells and classified as First, Second and Third generation of photovoltaic (PV) technology.
The First generation of PV is based on the crystalline silicon (c–Si) semiconductor and these solar cells have not only high efficiency (efficiency 25%) [Green et al., 2010] but also high cost. Crystalline Si is an indirect band gap (≈ 1.17 eV) semiconductor, which means they absorb the sun light poorly and require thickness of the order of hundred micro-meters (μm) to absorb most of the incident photons. The c-Si based solar cells either use monocrystalline (single crystal) Si produced by slicing wafers of around 250 thick from a high-purity single crystal ingot or multicrystalline silicon produced by sawing a cast block of silicon.

The Second generation PV also called thin film photovoltaic is based on direct band gap semiconductors like polycrystalline copper indium gallium diselenide (Cu(In,Ga)Se2), cadmium telluride (CdTe) and amorphous silicon (a–Si). Direct band gap semiconductors have a high absorption coefficient, which means most of the light is absorbed by few μm thick material; the absorber layer of these devices can therefore be only a fraction of that of thick crystalline silicon cells. Also these thin films can be deposited on many different substrates like glass, stainless steel etc. by any other thin deposition techniques already developed for other applications. These advantages can help in faster manufacturing, with less material and energy usage, which reduces the cost of manufacturing and production of the solar cells. Despite all these advantages, the actual market share of thin film technology is still far less than c-Si based solar cells due to notably to a lower efficiency compared to c-Si and a more recent implantation on the market.

Even though the thermodynamic limit of sunlight conversion is 67%-87% [Würfel, 2002], the theoretical upper limit of efficiency of the solar cells based on both
the first generation and second generation PV technology are 33% only [Kazmerski, 2006]. The two most important power-loss mechanisms which limit the cell efficiency are: the inability to absorb photons with energy lower than the band gap and the photogenerated carriers created by high energetic photon (called hot carriers), which produce heat via phonon emission when they relaxed back. These two losses can potentially be addressed by developing cell structures with several absorber band gap (multi-junction solar cell), quantum dots solar cells, organic solar cells etc.: these technologies are called third generation PV technology. In multi-junction solar cells, p-n junctions made up of different semiconductors are stacked on top of each other so that the photon with energy lower than the band gap transmitted through one layer can be absorbed by another layer. The hot electron issue is addressed by either removing highly energetic carries before they cool or using the energy of these hot carriers to produce another electron-hole pair [Kolodinski et al., 1982; Queisser et al, 1993]. Multi-junction [Crisp et al., 2004], Quantum dots [Tisdale et al., 2010] and dye-sensitized solar cell [Tennakone et al., 2001] are some examples of third generation PV technology.

1.4 Thesis Objectives and Organization

The main objective of this research is to enhance the deposition process for the fabrication of high efficiency Cu(In,Ga)Se2 thin film solar cell. The Cu(In,Ga)Se2 thin film solar cell is until now the most efficient solar cell among all thin film solar cells. Many different methods to deposit Cu(In,Ga)Se2 thin film have been tried until now but Cu(In,Ga)Se2 thin films prepared by co-evaporation of elemental sources are the most successful due to the control over the sequence of evaporation of individual material
[Shafarman et. al, 2003]. However, controlling the sequence and duration of each element during evaporation is difficult at large scale and this difficulty is the hindrance in the scale up of Cu(In,Ga)Se₂ at industrial level. Also due to being an alloy of four different materials, small variation of atomic percent of individual material changes the Cu(In,Ga)Se₂ properties. The precise control over deposition process is possible only if the changes in the material properties during deposition process are monitored. There are different methods to monitor the deposition process as well as in-situ monitoring of the product [Repins et al., 2005]. Most of these in-situ product monitor can fulfill the minimum requirement of monitoring the composition and thickness [Repins et al., 2005] but to achieve higher efficiency, in-situ monitoring of electrical and optical properties are necessary. Real time spectroscopic ellipsometry (RTSE) has already shown its potential as in-situ sensor for Si [Collins, 1990; Collins et al., 2001; Lee et al., 1998; Kim et al., 1995]. Once the optical properties of Cu(In,Ga)Se₂ as a function of the composition, temperature and other deposition conditions are known, RTSE (in combination with one of the process sensor) can become one of the most suitable in-situ sensor to monitor the thickness, roughness, optical and electrical properties, and growth temperature. Thus, the understanding of the optical and electrical properties as a function of composition during Cu(In,Ga)Se₂ growth is the main goal of this thesis.

Several critical parameters and problems have to be kept in mind before being able to achieve this goal:

- High efficiency Cu(In,Ga)Se₂ devices are fabricated from slightly Cu-poor Cu(In,Ga)Se₂ thin films with around 1.15 eV band gap;
- The efficiency of the device decreases if the Cu at.% in the Cu(In,Ga)Se₂ thin film is too low;
- Cu-rich Cu(In,Ga)Se₂ thin films result into shunted devices;
- The device quality Cu(In,Ga)Se₂ thin films are deposited by 2-stage and 3-stage co-evaporation process which involves Cu-rich to Cu-poor transitions;
- During the 3-stage process, Ga at.% changes as Cu(In,Ga)Se₂ thin film goes from Cu-poor to Cu-rich transition due to the inter-diffusion of Cu and In.

Thus for in-situ monitoring of device quality Cu(In,Ga)Se₂ thin film, understanding of the optical properties of Cu(In,Ga)Se₂ thin films as a function of Cu at.% as well as of the Ga at.% is necessary. Another vital constituent of the Cu(In,Ga)Se₂ based device is the thin CdS films which forms the p-n junction as well as acts as the window layer. Optical properties and thickness of the CdS film limit the efficiency of the device.

This is the reason why in this work, the material properties of Cu(In,Ga)Se₂ thin films deposited by different co-evaporation processes, changes in these properties with Cu at.% and Ga at.% as well as the properties of the CdS thin film are studied.

In chapter 2, the basic properties of Cu(In,Ga)Se₂ thin films and the different measurement techniques used to understand the Cu(In,Ga)Se₂ film are discussed.

In chapters 3, the properties of Cu(In,Ga)Se₂ thin films deposited by 1-stage, 2-stage and 3-stage processes and devices fabricated from these films are studied.

In chapter 4 and chapter 5, comprehensive and corroborative studies of Cu(In,Ga)Se₂ thin films as a function of Cu at.% and Ga at.% are presented. In-situ ellipsometry was used to study the properties of the films as a function of Cu at.% and
Ga at.% and these results were corroborated with *ex-situ* measurement techniques such as atomic force microscope (AFM), X-ray diffraction (XRD), scanning electron microscope (SEM), scanning tunneling electron microscope (STEM).

In chapter 6, a comparative study of the growth process of the chemical bath deposited CdS on SiO$_2$ surface and Cu(In,Ga)Se$_2$ surface is presented. In this chapter, ellipsometry was used as the primary tool to understand the growth of CdS on the two different substrates. The evolution of the optical properties with dipping time on these two different substrates was studied and ellipsometry results were corroborated with AFM measurements.

At the end, summary and conclusion of this work along with the future direction of research due to this work are presented.
2.1 Cu(In,Ga)Se₂ thin film properties

2.1.1 Structural properties

The Cu(In,Ga)Se₂ alloy is a semiconductor belonging to the I-III-VI₂ family where I, III and VI represents the group of elements in the periodic table from the column IA, IIIB and VIB respectively. "I" can often be either Cu, Ag or Au, "III" be Al, Ga, or In and "VI" be O, S, Se, or Te. According to Grimm-Sommerfeld rule, if the average number of valence electrons per atom is four in an atomic structure then that structure will be a tetragonal structure [Grimm et al., 1926; Böhm et al.,1985]. For the I-III-VI₂ compounds, the average number of valence electrons per atom is \((1*1+1*3+2*6)/4 = 4\) and they crystallized in the tetragonal chalcopyrite (CuFeS₂) structure [Jaffe et al., 1983]. Due to this Grimm-Sommerfeld rule, it is possible to partially replace In by Ga without losing the chalcopyrite lattice configuration. The scheme of formation of Cu(In,Ga)Se₂ structure from Si using Grimm-Sommerfeld rule is shown in Figure 2-1a and the corresponding evolution of the lattice structure from the Si lattice structure is shown in Figure 2-1b to Figure 2-1d. As shown in Figure 2-1d, the anion position in the Cu(In,Ga)Se₂ lattice structure remains the same as in the Zincblende structure whereas
the cation of the ZnS structure is replaced by Cu and (In,Ga), so that each Se (anion) is bond to two Cu atoms and two (In or Ga) atoms, and each Cu atom and (In or Ga) atom is tetrahedrally bonded to four Se atoms. In the simple case, one Se atom is bonded to 2 Cu atoms and 2 In atoms and, due to the different electronic property of the Cu and the In atom, the Se atom at equilibrium must be either near the Cu atoms or the In atom.

Figure 2-1  

a) Formation of different group compound starting from Si using Grimm-Sommerfeld rule, b) fcc structure of Si crystal with two identical atoms basis, c) Zincblende structure derived from Si structure by replacing identical atoms basis by two different atoms, d) Chalcopyrite structure derived from the zincblende structure by doubling the zincblende structure and replacing the cations by two different cations [Kasap, 2005; Jaffe et al., 1983].

Due to this unequal bond length between the Cu-Se and the In-Se, the tetragonal ratio \( \eta = c/2a \) of Figure 2-1d) is not equal to 1 as well as the anion displacement \( u \) is not equal to 1/4 and is given by [Jaffe et al., 1984]:

\[
u - \frac{1}{4} = \frac{R_{Cu-Se}^2 - R_{In-Se}^2}{a}
\]  \( (2.1) \)
where $R_{Cu-Se}$ is the bond length of the Cu-Se and $R_{In-Se}$ is the bond length of the In-Se.

2.1.2 Compositional properties

$Cu(In,Ga)Se_2$ can be a p-type or a n-type semiconductor due to the intrinsic defects. If $Cu(In,Ga)Se_2$ is grown under Cu rich flux with low Se pressure environment, Cu can either occupy interstitial sites or promote Se vacancies which leads to the n-type conductivity [Noufi et al., 1984] and in this case $V_{Se}$ is the dominant donor. If $Cu(In,Ga)Se_2$ is grown under Cu poor flux and high Se vapor pressure, Cu vacancy ($V_{Cu}$) leads to the p-type conductivity. In this case $V_{Cu}$ is the dominant acceptor and $V_{Se}$ is the compensating donor [Schock, 2004]. This p-type $Cu(In,Ga)Se_2$ is used as an absorber layer in solar cell application. The carrier concentration in this device quality p-type $Cu(In,Ga)Se_2$ is around $10^{16}$-$10^{17}$ cm$^{-3}$. The minority carrier (electron) life time in p-type slightly Cu poor film is around 1-9 ns and the diffusion length is around 1$\mu$m [Rau, 2001]. Due to the Cu-poor nature of quality devices, there is the possibility of high defect density. To qualify for high quality absorber layer, this defect density should be reasonably low and defects should be electronically inactive [Schock, 2004]. In Cu-poor films, the formation of $2V_{Cu}^{-}$ is compensated by $In_{Cu}^{2+}$ i.e. the defect pair $2V_{Cu}+In_{Cu}$ is electrically neutral and has no energy level within the band gap [Schock, 2004].

In the Pseudo-binary $In_2Se_3-Cu_2Se$ phase diagram of Figure 2-2, four different phases of CuInSe$_2$ as a function of Cu at.% are shown. The $\alpha$-phase is the chalcopyrite CuInSe$_2$ phase and exists in the narrow range of 24.0 to 24.5 at.% of Cu at room temperature. This range is maximum around 600 °C, vanishes above 800 °C and so the best suited growth temperature is around 600 °C. At the Cu-poor boundary, the $\alpha$-phase coexists with another phase called $\beta$-phase, which represents a number of compounds like
CuIn₃Se₅, CuIn₅Se₈ etc. Since the building blocks of these compounds are Vₐ₈ and Inₐ₈, these compounds are called ordered defect compounds (ODC). Fractional replacement of Ga and small addition of Na, hinders the ordering of defects [Schock, 2004] and so widens the α-phase towards the Cu poor boundary. This addition of Ga and Na thus gives more freedom on deposition conditions.

Figure 2-2 Pseudo-binary In₂Se₃-Cu₂Se equilibrium phase diagram for compositions around the α-phase of CuInSe₂ [Shafarman et al., 2003 and references therein].

2.1.2 Optical properties

For CuInSe₂, it has been demonstrated that the absorption coefficient can be written as [Neumann, 1985]:

\[
\alpha(h\nu) = \frac{A}{h\nu} (h\nu - E_g)^{1/2}
\]  

(2.2)
where $\alpha$ is the absorption coefficient at photon energy of $h\nu$, $A$ is a constant and $E_g$ is the band gap. Equation 2.2 shows that in the semiconductor CuInSe$_2$ the band gap is due to the direct allowed transition between parabolic bands [Neumann, 1985]. Thus CuInSe$_2$ and its other derivable compounds are direct band gap semiconductors and the band gap is tunable, depending on the Ga substitution [Albin et al., 1991]:

$$E_g = (1-x)E_g(CIS) + xE_g(CGS) - bx(1-x)$$

(2.3)

where $x$ is the Ga to In+Ga ratio, $E_g(CIS)$ is the band gap of CuInSe$_2$, $E_g(CGS)$ is the band gap of CuGaSe$_2$ and $b$ is the bowing parameter. Generally the bowing parameter lies between 0.15-0.24 eV [Wei et al., 1998]. The band gap of CuInSe$_2$ varies between 0.81 eV and 1.01 eV for single crystals [Neumann, 1985] whereas for thin film this value is very narrow i.e. $E_g$ of the thin film CuInSe$_2$ is 1.02 ± 0.02 [Shafrman et al., 2003]. Due to its direct band gap, the absorption in the Cu(In,Ga)Se$_2$ is very high and most of the photon are absorbed by a few $\mu$m thick Cu(In,Ga)Se$_2$. The high absorption coefficient, for example $10^5$ cm$^{-1}$ at 1.4 eV of photon energy [Kazmerski, 1983], makes Cu(In,Ga)Se$_2$ a suitable absorber layer for solar cell application. The variation of the band gap with Ga content has been used to make band gap graded Cu(In,Ga)Se$_2$ thin films for high efficient solar cells.

2.2 Material Characterizations

2.2.1 Energy dispersive X–ray spectroscopy (EDS)

Energy dispersive X–ray spectroscopy (EDS) is used to find the elemental composition of a material. This technique relies on the emission of X-rays as a result of interaction of the material with the high energy radiation at atomic level. Due to the
bombardment of high energetic beam from the electron source, an electron from the lower energy state is ejected and the atom goes to an excited state. An electron from a higher energy state falls back to the vacant state and in this process some energy is released in the form of X-rays. Since the atomic structure of an element distinguishes it from another element, this emitted X-ray is characteristic of the element. If a sample has many constituting elements, then the emitted radiation has a spectrum of X-rays corresponding to each individual element. By analyzing the spectrum, the composition of each element can be calculated using mathematical algorithm. A standard spectrum of the EDS measurement on a Cu(In,Ga)Se₂ thin film is shown in Figure 2-3. The EDS analysis can be used to find element with atomic number as low as 4 i.e. beryllium [Geiss, 1992].

![EDS spectrum](image)

**Figure 2-3** EDS spectrum of a 2 μm thick Cu(In,Ga)Se₂ thin film on Mo substrate.

2.2.2 Auger Electron Spectroscopy (AES)

Auger Electron Spectroscopy (AES) is a surface composition analysis (2-10 atomic layer) technique [Vickerman, 1997] and can be used for depth profile of composite
material in combination with a sputtering gun, where sputtering is used to remove the outer layers. The AES technique is based on the excitation of Auger electron. As explained in the previous section, due to the interaction of an atom with high energy electrons, electrons in lower energy states can be excited. To fill the empty position, electrons from higher states fall back to the lower states, while some energy which can knockout an electron from the atom is released. This process of production of doubly ionized charge is called the Auger process. The finally emitted electron has a kinetic energy characteristic of the parent atom [Schroder, 2006]:

\[ E_{Kin} = E_A(Z) - E_B(Z) - E_C(Z + \Delta) - q\phi \]  

(2.4)

where \( E_{Kin} \) is the kinetic energy of the finally ejected electron, \( E_{i=A,B,C} \) is the binding energy of electron in \( i^{th} \) orbit, \( Z \) is the atomic number of ionized state and \( \Delta \) is the factor that take into account the binding energy of the C orbit due to the ionized atom. The A is the inner most orbit and C is the outer most orbit of the Auger process. The kinetic energy of the emitted electrons is measured and the signal is proportional to the number of atoms sampled.

2.2.3 X-ray diffraction (XRD)

X-ray diffraction is used to probe the crystalline phases and to measure structural properties, parameters, the size and orientation of crystallites. For Cu(In,Ga)Se2 compounds, since the lattice parameters for different Ga/(In+Ga) are already known, XRD can also used to find the Ga/(In+Ga) value in the film. When a collimated beam of X-ray of wavelength between 0.5Å to 2 Å (of the order of the interatomic distance) interacts with a crystal, it is diffracted from the crystalline phase according to the Bragg's law \( (\lambda = 2d \sin \theta) \). The intensity of the diffracted X-ray received by the detector (as counts) is then plotted versus an angle, usually \( 2\theta \). Peaks appear when Bragg's law is satisfied. Comparing the peaks with already available
XRD data on the powdered sample gives the phase, crystal orientation, lattice constants among other information. The crystallites size can be predicted from XRD data using Scherrer formula:

$$D = \frac{K_s \lambda}{\beta \cos \theta}$$  \hspace{1cm} (2.5)

where D is grain size, $K_s$ is Scherrer constant, $\beta$ is the full width at half maximum of the peak in radians, $\lambda$ is the wavelength of the X-ray beam and $2\theta$ is the peak position [Suryanarayana et al., 1998]. For this work, $\lambda$ is 1.54 Å corresponding to the Cu Kα1 due to the use of a Cu source for the X-ray beam.

### 2.2.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is used to get topographical (surface feature) and morphological (shape and size of grains in thin film) information. In SEM, a beam of electrons is bombarded on the sample under investigation. The electrons of the incident beam can notably excite an electron, who leaves the sample if it has sufficient energy (called secondary electron), or be back-scattered (called back scattered electron). Either of these electrons is detected by their respective detectors and then sent through electronic amplifiers to modulate the brightness of the cathode ray tube. Secondary electrons are generally originating from near the surface (if they originate from deeper inside, they will lose their energy and will not come out of the sample); depending on the orientation of the surface, the number of electrons detected changes. Due to the variation in the number of detected electrons, the brightness on the CRT monitor changes which results in clear 3-dimensional images. On the other hand, back scattered electrons have different energy depending on whether they scattered from heavier or lighter nucleus.
Electrons scattered from heavier nucleus have higher energy than the one scattered from lighter electron and so image of heavier nucleus element appears brighter [Leamy, 1982].

2.2.5 Scanning Transmission Electron Microscopy (STEM)

In scanning transmission electron microscopy (STEM), high energetic electrons (100 eV – 400 eV) tunnel through the sample and so carries the information about the internal structure of the sample. The sample under investigation in STEM must be very thin (≈ 200 nm) so that the electrons can transmit through the sample. Like SEM, in STEM high energetic electrons also produce secondary and back scattered electrons [Schroder, 2006]. Also the basic principle of electron beam production, focusing and detection are similar. The very fine electron beam (≈ 0.1 nm) is used to scan across the sample and the transmitted electrons from all across the sample are collected by the objective lens and focused on the fluorescent screen. Since in STEM the electrons travel through the sample, this technique gives in-depth information about the sample.

2.2.6 Atomic Force Microscopy (AFM)

As a surface profiler, one of the most important uses of the AFM is to provide three dimensional images of the surface and is therefore very useful in measuring the surface roughness. In the AFM, a cantilever with a sharp tip (few hundred nanometers) made up of Si or SiO₂ is used. The tip is then kept in continuous or intermittent contact with the sample and the cantilever is translated over the sample using a piezocontroller. Due to the topographical variation, the cantilever deflects which can be measured using a laser beam continuously reflecting from the cantilever. During the movement of the cantilever as the tip height changes, the magnitude of the deflection (in Volts) is plotted against the position of the tip on the surface which creates a topographic map of the
surface [Eaton *et al.*, 2010]. Depending on the interaction of the surface and the tip, there are three main different modes of imaging. In contact mode, the tip is always kept in contact with the surface whereas in non-contact mode, the tip never touches the sample. In non-contact force, the change in the repulsive Van der Waals force due to the hill-valley of the sample is used to find the topographic image. The contact mode damages soft surfaces whereas the non-contact mode has bad resolution. The third mode is called tapping mode where the cantilever is oscillating at its resonance frequency via the piezoelectric crystal attached to the tip holder. During the oscillation, the tip keeps moving towards the surface till it taps the surface. As soon as there is contact between the tip and the surface, there is loss in the oscillation amplitude which is used to find the topographic changes. This technique has high resolution and is good for soft surfaces [Schroder, 2006].

2.2.7 Secondary Ion Mass Spectroscopy (SIMS)

Secondary Ion Mass Spectroscopy (SIMS) is used to find the composition of a sample. SIMS has the ability to detect elements present down to the parts per billion (ppb) and this high sensitivity is advantageous in tracing impurities or presence of small quantity of elements. In this work, SIMS was used to find elemental impurities as well as the composition of the films. When a high energetic ion beam (called primary ions) is incident on the sample, the surface atoms (within few monolayer of thickness for beams around 10-20 keV) are ejected out (sputtered) of the sample [Schroder, 2006]. In these ejected atoms, there are both ions (called secondary ions) as well as neutral atoms. In SIMS analysis, only these secondary ions are of importance and are analyzed by a
mass/charge analyzer using the atomic mass values. The counts of the secondary ions of different atomic mass give the sample's composition.

Different type of primary ions (such as $O_2^+$ and $Cs^+$) are used to sputter out a sufficient quantity of various secondary ions: $O_2^+$ facilitates the sputtering of positive ions whereas $Cs^+$ facilitates the sputtering of negatively charged ions. Also SIMS can be used as a depth profiler if the primary ions are bombarded at higher rate and [Vickerman, 1997] the intensity of the peak corresponding to a particular mass is recorded as a function of time (called dynamic SIMS) [Schroder, 2006]. For this study, to find the impurities in the solar cell stack as well as to find the composition of the absorber layer, a dynamic SIMS analysis was used.

2.2.8 Transmission and Reflection measurements

Optical transmission and reflection measurements help in finding the absorption coefficient and the band gap of a semiconductor. In the case of Cu(In,Ga)Se$_2$ thin film, transmission and reflection measurements help also in finding the presence of the semimetallic Cu$_{2-x}$Se phase.

The absorption coefficient can be calculated from the transmission and reflection measurements using $\alpha = \frac{2\ln(1-R) - \ln(T)}{d}$ where $d$ is thickness of the thin film, $R$ is the reflection, $T$ is the transmission and $\alpha$ is the absorption coefficient. Once the absorption coefficient $\alpha$ is calculated, then the band gap of any direct band gap semiconductor can be extracted by plotting $(\alpha h\nu)^2$ vs. $h\nu$ and by extrapolating the linear portion of the curve to the $h\nu$ axis. The intersection of this linear extrapolation with the $h\nu$ axis gives the band gap.
2.2.9 Ellipsometry measurement

The theory of the Ellipsometry is explained in Chapter 4.

2.2.10 Current-Voltage (J-V) measurement

The Current-Voltage (J-V) measurement helps not only in finding efficiency, fill factor, $J_{SC}$, $V_{OC}$ but also helps in finding the shunt resistance, series resistance and the voltage dependent current collection. The current density in a real solar cell is written as

$$J = J_0 \exp \left[ \frac{q}{AKT} (V - R_s J) \right] - J_0 + \frac{V - R_s J}{R_{sh}} - J_L$$

(2.6)

where $A$ is the ideality factor, $R_s$ is the series resistance and $R_{sh}$ is the shunt resistance of the solar cell. Equation 2.6 represents the equivalent circuit of Figure 2-4 below.

Figure 2-4 An equivalent circuit of a real solar cell.

As observed from Equation 2.6, a real solar cell has non-zero series and finite shunt resistance. The series resistance $R_s$ of a solar cell is not only due to the bulk resistance of the individual semiconductors of the solar cell stack but also due to the bulk resistance of the contact and resistance of the semiconductor-metal contacts. The series resistance can be calculated from Equation 2.6 by plotting [Hegedus et al, 2004]
\[
\{ \frac{dV}{dJ} = R_s + \frac{AkT}{q} (J + J_L)^{-1} \} \text{ vs. } (J + J_L)^{-1} \] under the condition that \( R_{sh} \) is infinitely high. This plot is a straight line with interception \( R_s \) on the \( dV/dJ \) axis. The effect of increase in the \( R_s \) is reflected by the decrease in the steepness of the I-V curve as illustrated in Figure 2-5. Small increase in the \( R_s \) from zero does not affect \( V_{OC} \) and \( I_{SC} \) and only decreases the FF of the solar cell. Since \( P_{mp} \) and efficiency of a solar cell is dependent on the fill factor, increase in the \( R_s \) also has adversely effect on these two quantities. Large increase in the \( R_s \) first affects the \( I_{SC} \) and then \( V_{OC} \).

**Figure 2-5** Thick lines in left and right figures are current-voltage curve with non zero series and finite shunt resistance respectively. In both figures, thin line is the J-V curve for ideal solar cell with ideality factor 1.

For an ideal solar cell, the shunt resistance \( R_{sh} \) is infinitely high but for a real solar cell \( R_{sh} \) has a finite value. The \( R_{sh} \) is lowered for a solar cell due to the leakage path near the junction as well as due to the presence of defects like pinhole in the absorber layer. \( R_{sh} \) can be calculated by reciprocal of the \( dJ/dV \) in the reverse biased region near \( J_{SC} \). Graphically, the presence of infinite value of \( R_{sh} \) can be observed in the increase in the
steepness of the slope of I-V curve around JSC. Again, the decrease in the Rsh has adverse effect on the fill factor.

Due to small minority carrier lifetimes, charged carriers can recombine before being swept across the junction by the in build electric field. If a reverse biased voltage is then applied across the terminal, the magnitude of the electric field increases, allowing electrons with small diffusion length to be collected. This increase in the current due to bias voltage is called voltage-dependent current collection JL (V). On the light I-V curve, the presence of voltage-dependent current is observed as an increase in the slope in the reversed bias region. Thus the observation of the light I-V curve can be confusing because the decrease in Rsh affects the I-V curve similarly. But Rsh also affects the dark I-V curve as it affects the light I-V curve. Thus if the dark I-V curve is well behaved but there is a slope in the light I-V curve, the voltage-dependent current collection can also be extracted from the I-V measurement.

The I-V curve also helps in finding the ideality factor of a solar cell. The slope of the line obtained by plotting \( \frac{dV}{dJ} = R_s + \frac{A k T}{q} (J + J_L)^{-1} \) vs. \( (J + J_L)^{-1} \) gives the value of AkT/q from which A can be calculated.

2.2.11 Quantum efficiency (QE) measurement

Quantum efficiency (QE) helps in measuring the maximum current from a solar cell as well as to identify the different electrical and optical losses responsible for reduced ISC from the optimal achievable current [Hegedus et al., 2004]. Quantum efficiency (QE) is defined as the ratio of the number of collected carriers to the number of incident photons on the solar cell at each energy [Hegedus et al., 2004]:

25
\[ QE(hv) = \frac{\text{# of electron-hole pair collected}}{\text{# of incident photons}} \]  \hfill (2.7)

The total current from the QE measurement is calculated by integrating over the entire wavelengths range the product of the measured external QE with the illumination spectrum (typically AM1.5 condition); this current should match the \( J_{SC} \) found from J-V measurement. Thus the relation between \( J_{SC} \) from J-V measurement and the total current from QE measurement is:

\[ J_{SC} = q \int_{\lambda} F(\lambda)QE(\lambda) d\lambda \]  \hfill (2.8)

where \( F(\lambda) \) is the flux density per unit wavelength (units of \([#/cm^2nm\] s\)). In an ideal solar cell, each photon incident on the solar cell produces one electron-hole pair to

\[ \text{Figure 2-6} \quad \text{Different losses in CIGS measured by QE [Hegedus et al., 2004].} \]
contribute in the photocurrent and so the QE is 100% above the band gap, and zero below the band gap energy. But this is not the case in the real solar cell where there are many optical and electrical losses. First and foremost loss is due to the reflection from the front surface; the QE after taking care of the reflection loss is called the internal QE. Different losses in the QE are shown in Figure 2-6 and are explained in Chapter 3 while evaluating the losses in efficiencies in different solar cells.

QE at negative bias voltage helps in separating the electronic losses from the optical losses because negative bias voltage helps in electrons collection with low minority carrier life time. If the QE measurement is performed under light bias, due to the redistribution of the electric field in the n-type photoconductive CdS, current collection increases [Hegedus et al., 2004].
Chapter Three

Studies of Cu(In,Ga)Se₂ Solar Cells: Deposition by 1-stage process, 2-stage process and 3-stage process

3.1 Introduction

Among all the photovoltaic materials, Cu(In,Ga)Se₂ is the most promising material as an absorber layer for the future of thin-film photovoltaic (TFPV) but also has some of the greatest problems. Potentially, solar cells based on Cu(In,Ga)Se₂ could lead to higher efficiency surpassing the crystalline Silicon but with all the advantages of a thin-film material: high efficiency to mass ratio, flexibility and lower manufacturing cost. Along with all these advantages, Cu(In,Ga)Se₂ has the disadvantages of a material whose characteristics are not yet properly understood. Thus it is clear that solar cells based on Cu(In,Ga)Se₂ will be the in the forefront of the photovoltaic race only if the material characteristics of the Cu(In,Ga)Se₂ thin film itself are totally understood.

Cu(In,Ga)Se₂ thin films are grown by many different techniques. Depending on the deposition process, the material properties of Cu(In,Ga)Se₂ thin films are different. On a laboratory scale, the highest efficiency (20.3 %) [ZSW, 2010] Cu(In,Ga)Se₂ solar cells are grown by thermal evaporation of individual sources. The process of thermal evaporation is a complex technique and, depending on the individual sources and substrate temperature, the films are grown with different characteristics. Different
research groups across the world have done studies on Cu(In,Ga)Se₂ thin films deposited by thermal evaporation, but the characteristics are still not fully understood. The characteristics of the thin film Cu(In,Ga)Se₂ changes with the change in the atomic percentage (at.%) of Cu, In, Ga and Se which depends on the evaporation conditions. Among different co-evaporation techniques to grow Cu(In,Ga)Se₂, 1-stage, 2-stage and 3-stage are the most successful processes. As will be explained in the later sections of this Chapter, there are changes in the Cu, Ga and In at.% during 2-stage and 3-stage processes. Irrespective of the process, the Cu at.% in high efficiency Cu(In,Ga)Se₂ based devices falls within the narrow range of 22% to 24% [Shafarman et al., 2003]. Among all the deposition processes, the 3-stage process resulted in growing the Cu(In,Ga)Se₂ thin films for the most efficient solar cells. As will be explained later in this Chapter, due to the sequence of the Cu, In and Ga fluxes the Cu(In,Ga)Se₂ film at the end of the deposition has different Ga concentration along the thickness of the film. To achieve the required Cu and Ga at.% at the end of the 2-stage and 3-stage processes, it requires a precise control over the sequence, time of each sequence and concentration of individual elements. Due to this complexity, and to study the material properties of Cu(In,Ga)Se₂ as a function of Cu at.% and Ga at.%, the first step in our research was to establish a baseline for solar cells fabricated with 1-stage, 2-stage and 3-stage processes.

In this Chapter, the experimental procedures for each of these three deposition processes, the problems encountered and troubleshooting in achieving the baseline efficiencies, the maximum efficiencies (baseline) achieved by growing the Cu(In,Ga)Se₂ thin film by each of these three processes and the material properties of these Cu(In,Ga)Se₂ thin films are presented.
3.2 Experimental Procedure

In this section, the deposition of Cu(In,Ga)Se$_2$ thin films by different thermal evaporation processes and the fabrication process of a complete solar cell device are explained.

3.2.1 Deposition process of the back contact

Solar cells reported in this chapter are fabricated with Molybdenum (Mo) as the metal back contact on soda lime glass (SLG). There are many advantages of using Mo as a back contact, such as the diffusion of Na into the Cu(In,Ga)Se$_2$ [Scofield et al., 1994; Al-Thani et al., 2002] or the formation of MoSe$_2$ at the interface of the Mo and Cu(In,Ga)Se$_2$, which reduces the recombination at the back contact [Wada et al., 2001]. Mo films are generally deposited on SLG by direct current (dc) sputtering. Mo thin films deposited at lower Argon (Ar) pressure (i.e. below 2 mTorr) have good conductivity but poor adhesion to the SLG [Scofield et al., 1995]. On the other hand if Mo is deposited at high Ar pressure (above 10 mTorr), it has a better adhesion but a higher resistivity. For all the solar cells reported here, this problem is addressed by depositing a bi-layer of Mo on SLG by dc sputtering: 100 nm is first deposited at 10 mTorr, followed by a thicker layer (400 nm) deposited at 1 mTorr.

3.2.2 Deposition of Cu(In,Ga)Se$_2$ thin film

As mentioned earlier, for this study, all Cu(In,Ga)Se$_2$ thin films were grown by a thermal evaporation process. Depending on the individual source and substrate temperature, Cu(In,Ga)Se$_2$ films used in this study were deposited by three different processes:
i) 1-stage co-evaporation process: This evaporation process is the simplest among all the thermal evaporation processes mentioned here. During this process, 2 μm of Cu(In,Ga)Se$_2$ films are grown by evaporating Cu, In, Ga and Se together for 60 min. The rate of each of the individual elements is kept constant by keeping the temperature of the source constant. Cu(In,Ga)Se$_2$ films grown by this process have constant atomic percent of each of the elements all across the film, which can be confirmed notably by Auger electron spectroscopy.

ii) 2-stage co-evaporation process: This process is the modified version of the original two stage process called Boeing process [Chen et al., 1980]. During this process, Cu(In,Ga)Se$_2$ is deposited with higher Cu rate at first so that the film becomes Cu-rich and then In and Ga rate are increased to get a Cu-poor film at the end of the deposition. A modified version of this process is shown in Figure 3-1. During the first stage, Cu-rich Cu(In,Ga)Se$_2$ is deposited. If the Cu(In,Ga)Se$_2$ is Cu-rich, a semi-metallic Cu$_{2-x}$Se phase exists along with the Cu(In,Ga)Se$_2$ phase [Kessler et al., 2001]. During the second stage, In and Ga at the same rate as the first stage are deposited without any Cu. The extra Cu from Cu$_{2-x}$Se is consumed in growing Cu(In,Ga)Se$_2$ during this stage and deposition of the film is stopped as soon as all the Cu from the Cu$_{2-x}$Se is consumed, which means when the film becomes Cu-poor. The End Point Detection (EPD) method is used to identify the Cu-poor phase during the process. In EPD [Scholdstrom et al., 2005], change in the substrate output power is used to track the Cu-rich to Cu-poor phase.

During the deposition, the substrate temperature is set at 570 °C. Due to the presence of the semi-metallic Cu$_{2-x}$Se phase, the emissivity of the Cu-rich Cu(In,Ga)Se$_2$ film is higher than the Cu-poor film. When the film becomes Cu-poor, the emissivity of
the film decreases and so, to maintain the substrate temperature at 570 °C, the heater has to supply less power. By monitoring the substrate output power of the heater, Cu-rich to Cu-poor phase transitions can be tracked. This detection of Cu-rich to Cu-poor phase transition is called EPD and is shown in Figure 3-1 below.

![Figure 3-1](image)

**Figure 3-1**  Substrate OP% and temperature of individual sources as well as of the substrate as a function of time. Around 40 min, the Cu source is turned off. The Sub OP% starts decreasing as soon as the Cu flux is off. In and Ga rates did not change during the deposition.

iii) 3-stage co-evaporation process [Gabor et al., 1994]: As the name suggests, this process is divided into three stages. A schematic of this process is shown in Figure 3-2. During the first stage, In, Ga and Se are deposited at a substrate temperature of 400 °C. During the second stage of this process, in the absence of In and Ga flux, Cu and Se are
deposited and the substrate temperature is raised to 570 °C. Once the film becomes Cu-rich, the second stage is terminated. Then, in the absence of Cu flux, In and Ga along with Se are deposited at a substrate temperature of 570 °C until the film becomes Cu-poor. Again like for the 2-stage process, the change in the substrate output power is used to monitor the Cu-poor to Cu-rich and Cu-rich to Cu-poor transition. The duration of the first stage is chosen so that the amount of In and Ga in the third stage should be around 10% of the total In and Ga deposited in the first and third stage [Gabor et al., 1996]. As shown in Figure 3.2 below, the Cu source is switched off after 66 minutes, as soon as the substrate output power starts to increase due to the formation of the semi-metallic Cu_{2-x}Se phase. The same Figure shows that at 77 min the film becomes Cu-poor and that the In, Ga and substrate temperature are switched off.
Figure 3-2  Top figure is the rate of individual element during the 3-stage process. Bottom figure is the corresponding temperature of the individual sources as well as of the substrate.
3.2.3 Deposition of CdS, i-ZnO, ITO and Grids

To complete the p-n junction for each solar cell, n-type CdS layers were deposited for 10 minutes by chemical bath deposition (CBD). The complete method of CdS deposition by CBD method is explained in Chapter 6.

50 nm thick highly resistive intrinsic zinc oxide (i–ZnO) and 120 nm thick Indium tin oxide layer were deposited by RF magnetron sputtering in pure argon ambient without any intentional heating of the substrates. To deposit ITO, an ITO target with 90 wt. % In₂O₃–10 wt. % SnO₂ was used. The pressure and power during the deposition was kept at optimized value under which the resistivity was around $8 \times 10^{-4} \Omega \text{-cm}$ and the sub–band gap transmission above 85%. Furthermore, to enhance current collection, the devices were completed by thermal evaporation of Ni/Al/Ni metal grids of thicknesses $\sim$50 nm/$\sim$2 μm/$\sim$50 nm, respectively. A cell area of 0.5 cm² was defined by mechanical scribing.

3.3 Enhancement of the co-evaporation process:

As explained earlier, device quality Cu(In,Ga)Se₂ thin films need to be slightly Cu-poor. Also during the 3-stage process, Ga and In fluxes are switched off and switched on during the process. Thus monitoring and controlling the individual elements' flux is necessary to achieve the desired composition. A crystal monitor and the temperature of the individual sources are generally used to monitor and to control the rate of individual elements.

The disadvantage of using a crystal monitor is that once all the elements are evaporating, it can not distinguish between the different elements. At the same time, the evaporation temperatures of the metals are high enough to influence the temperature of
other sources. Minor increase in the crucible temperature can result in major increase in
the metal rate. Due to the limitations of a crystal monitor, the deviation in the rates can
not be detected and so can not be controlled. Also the evaporation rate is not reproducible
due to the dependence of the sources on factors like temperature of adjacent sources,
ramping rate etc. Thus monitoring and precise control of the individual fluxes are
necessary to achieve device quality Cu(In,Ga)Se₂ thin films.

3.3.1 Process control using Labview

At the start of the work reported in this thesis, the initial challenges were to:
- Implement techniques to monitor and to control the individual elemental rates
- Implement the 2-stage and the 3-stage processes
- Develop baseline efficiency for each of the process.

The first step in this direction was to develop a program for proportional–integral–
derivative (PID) controller to monitor and to control the change in the temperature of the
sources. A new program based on the Labview software was developed to monitor and to
control the temperature of each source, based on the feed-back of the individual
thermocouples connected to each source and to the substrate. This allowed better control
over the elemental rates at least during the 1-stage and 2-stage processes. The
development of the Labview based program also enabled us to read the temperature of
the substrate as well as the percentage of the substrate output power (Sub OP%). The
monitoring of the sub OP% helped in monitoring the End Point Detection and therefore
in the implementation of the 2-stage process and the partial implementation of the 3-stage
process. The Labview program also helped in the controlled ramping of the sources
temperature and of the substrate during deposition. This capability also helped in
advancing towards the implementation of the 3-stage process which requires increase in the substrate temperature as well as ramp up/down of the sources temperature. During the 2\textsuperscript{nd} stage of the 3-stage process, within the 5 minutes, it is desired to ramp the Cu rate to the required deposition rate. Similarly during the 3\textsuperscript{rd} stage of the 3-stage process, it is desired to quickly ramp up the Ga and In rate as well as to quickly ramp down the Cu rate. As mentioned earlier, ramping a rate to a particular temperature influences the elemental rate at that temperature. As the ramp up/down of Cu, In and Ga are done under Se environment, it is nearly impossible to have the precise knowledge of the metal rates using the crystal monitor during these stages and so this monitoring of and control on temperature to achieve the desired rates was intricate and undependable to achieve the desired composition every time.

This Labview program was used to interface the PID controller with the elemental sources to monitor and control the 1-stage, 2-stage and 3-stage processes. These Cu(In,Ga)Se\textsubscript{2} thin films were further characterized for the composition and structural properties and then processed for solar cells. The current-voltage (J-V) characteristics were preformed on these solar cells to find the efficiencies of these devices. A maximum efficiency of 10\% was achieved at the time for solar cells grown by 3-stage process, with even lower efficiencies for the other processes. Based on the J-V and QE measurements, a thorough device analysis was done on each of these devices to understand the reason behind the inability to overcome the barrier of 10\% efficiency. All these analysis were indicating that, even if 2 \(\mu\)m thick Cu(In,Ga)Se\textsubscript{2} was grown for each device, the actual active area was much thinner. Our analysis pointed out that this reduction in the active
area of the absorber layer was due to the presence of impurities. To confirm this theory, Secondary Ion Mass Spectroscopy (SIMS) analysis were performed on these samples.

3.3.2 Effect of impurities during the film growth

As explained in Chapter 2, SIMS is able to detect element with concentration of parts per billion (ppb). In SIMS, a primary ion impinges on the material and depending on the primary ion's charge, positively or negatively charged atoms are ejected out of the material. To find any type of impurities in the devices, devices were analyzed by positive secondary mode and negative secondary mode. SIMS analysis on the complete devices processed from the Cu(In,Ga)Se2 films, grown by each of the above mentioned three co-evaporation processes, confirms the presence of impurities like oxygen, hydrocarbon and boron as shown in Figure 3-3 and Figure 3-4. As shown in Figure 3-3 and Figure 3-4, boron is present all along the thickness of the Cu(In,Ga)Se2 absorber layer deposited by 1-stage process, along the first 3/4 of the thickness of the Cu(In,Ga)Se2 layer deposited by 2-stage process and in the middle of the Cu(In,Ga)Se2 layer deposited by 3-stage process. This corresponds precisely to the temperature profile of the Cu source. It has to be noted that the Cu source is the only one above 1100 °C. At the time, Boron Nitride crucibles were used as evaporation containers for Cu, In, Ga and Se, but the SIMS profile confirmed that only at temperatures above 1100 °C do these crucibles deteriorate. The crucibles were therefore replaced by new ones, which could withstand this temperature. SIMS depth profile on films grown after replacing the Boron Nitride crucible did not contain any boron peak. Also, after replacing those Boron Nitride crucibles, we were able to fabricate devices with efficiencies up to 15.9%.
Figure 3-3  SIMS depth profile in positive secondary mode (top) and negative secondary mode (bottom) of a device fabricated with Cu(In,Ga)Se₂ film deposited by 1-stage process.
Figure 3-4  SIMS depth profile of devices fabricated with Cu(In,Ga)Se$_2$ film deposited by 2 stage (top) and 3-stage (bottom) processes. The dotted line shows the Cu temperature during the deposition.

As observed in Figure 3-3 and Figure 3-4, a significant amount of hydrocarbon and oxygen are present not only in the Cu(In,Ga)Se$_2$ layer but also in the Mo, CdS, i-ZnO and
ITO layers. These impurities incorporate into the different layer during deposition as well as during transportation from one deposition chamber to another deposition chamber. Cleaner deposition chamber and the use of a load lock system will be helpful in the future to improve the efficiency of the devices.

3.3.3 Implementation of the Electron Impact Emission Spectroscopy (EIES)

As explained earlier in this Section, monitoring and controlling the deposition process using crystal monitor and various temperatures is not sufficient and the process has doubtful reproducibility. To make the process more robust, it was necessary to control the rate by monitoring the rate itself. This is possible only if the flux of each of the evaporating elements is monitored separately during deposition at high temperature. One way to distinguish between different elements is to use the atomic emission spectra, which is unique for each element. As explained in the literature [Lu et al., 2008], electron impact emission spectroscopy is based on measuring the emission of photons from different elements. The EIES sensor consists of a filament which emits electron beam when a voltage of magnitude 180V is applied across it. When this sensor is placed at a position so that the vapor flux passes through the sensor and interact with the electron beam, due to the excitation and de-excitation of outer electrons, photons are emitted. These emitted photons are characteristics of the element itself. These photons are detected by a photomultiplier tube, which measures the magnitude of the detected photons and convert them to an electric signal. If the vapor flux consists of many elements then several optical filters are used to separate the photons of different wavelengths. These different energy photons are transported by separate optical fiber cables to separate photomultiplier tubes. The electrical signal from each of these
photomultiplier tubes is then calibrated to give the deposition rate of each element. These electrical signals are then feedback into the PID controller to control the temperature of the sources. Thus, if the rate of any of the elements changes during the deposition, the PID controller receives different signal and adjust the output signal accordingly to bring back the rate to the set point.

To implement EIES, the deposition chamber was redesigned to keep the EIES sensor as close as possible to the substrate to increase the signal to noise ratio. At the same time, the sensor needs to be out of sight of the Se flux to reduce the background effects due to the broadband emission from Se. Due to this criterion of keeping the Se flux out of sight of the sensor, EIES can not be used to monitor the Se flux. Once the EIES started to work, the Cu, In and Ga rates were being controlled by the EIES system while the crystal monitor was still used to check the Se rate.

3.4 Characterization of Cu(In,Ga)Se₂ films and devices grown by 1-stage, 2-stage and 3-stage co-evaporation processes:

3.4.1 Energy Dispersive X-ray Spectroscopy (EDS)

Compositions of each film deposited by 1-stage, 2-stage and 3-stage processes were determined by energy dispersive X-ray spectroscopy (EDS). As explained in the previous Chapter, EDS gives an average composition of the bulk. For device quality Cu(In,Ga)Se₂ films, Cu at.% around but less than 25, (In+Ga) at.% around 25 and Se at.% around 50 are required. Two critical parameters extracted from these at.% are y=Cu/(In+Ga) and x=Ga/(In+Ga). The x value determines the band gap of the Cu(In,Ga)Se₂ films whereas the y value establishes the phase of the Cu(In,Ga)Se₂ as well
as the microstructure of the films. Thus knowledge of the \( y \) parameter helps us in finding whether the grown film is of device quality or not. In Table 3.1 below, results of EDS measurements done on \( \text{Cu(In,Ga)}\text{Se}_2 \) thin films deposited by 1-stage, 2-stage and 3-stage processes are reported.

**Table 3.1** Results of EDS measurements on 3 different \( \text{Cu(In,Ga)}\text{Se}_2 \) thin films deposited by 1-stage, 2-stage and 3-stage processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Cu at.%</th>
<th>In at%</th>
<th>Ga at.%</th>
<th>Se at.%</th>
<th>( y = \frac{\text{Cu}}{\text{In+Ga}} )</th>
<th>( x = \frac{\text{Ga}}{\text{In+Ga}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-stage</td>
<td>22.8</td>
<td>18.7</td>
<td>8.1</td>
<td>50.4</td>
<td>0.85</td>
<td>0.30</td>
</tr>
<tr>
<td>2-stage</td>
<td>22.8</td>
<td>18.9</td>
<td>7.5</td>
<td>50.9</td>
<td>0.87</td>
<td>0.28</td>
</tr>
<tr>
<td>3-stage</td>
<td>22.9</td>
<td>18.5</td>
<td>8.0</td>
<td>50.5</td>
<td>0.87</td>
<td>0.30</td>
</tr>
</tbody>
</table>

3.4.2 Auger electron spectroscopy (AES)

The composition of each film was also extracted from a depth profile using AES technique. In contrast to the EDS measurement, AES gives the composition as a function of depth along the film thickness. Some of the AES depth profiles reported in this Chapter were done at UIUC by Prof. Angus Rockett’s group. The others were done at UT. AES depth profiles for \( \text{Cu(In,Ga)}\text{Se}_2 \) films grown by 1-stage and 3-stage processes are shown in Figure 3-5 and 3-6 respectively. Note that the AES profile for the 2-stage process is similar to the one for the 1-stage process. The results of EDS measurements for \( \text{Cu(In,Ga)}\text{Se}_2 \) films grown by 1-stage and 2-stage processes were in good agreement with the one found by AES. For the films grown by 3-stage process, AES measurement gives more information about the composition of the film compared to EDS measurements.
Figure 3-5  AES depth profile of Cu(In,Ga)Se₂ film grown by 1-stage process. EDS measurement for the same film is reported in Table 3.1.

Figure 3-6  AES depth profile of Cu(In,Ga)Se₂ film grown by 3-stage process. EDS measurement for the same film is reported in Table 3.1.

As shown in Figure 3-5, AES profile for 1-stage and 2-stage processes confirms that the atomic percentage of each element remains constant along the thickness of the film. On
the other hand, AES depth profile of the 3-stage process (Figure 3-6) shows that the atomic concentration of In and Ga changes along the thickness of the film and gives a graded Ga/(In+Ga), i.e. x value. This profile is in agreement with the 3-stage deposition process itself, where the rate of each element is changed intentionally during the deposition to get a gradient of band gap along the bulk thickness. As explained earlier, in the second stage of the 3-stage process there was no In and Ga deposited. During this stage due to the higher out diffusion of In compared to Ga and higher in diffusion of Cu [Gabor et al., 1996], the Ga concentration decreases with increasing thickness. During the third stage of the 3-stage process, due to the same reason, the Ga concentration increases with increasing thickness (reverse of the trend developed in the second stage) and so results into the grading shown in Figure 3-6. The effect of this intentional band gap grading is explained later in Section 3.4.7 of this Chapter.

3.4.3 X-Ray Diffraction (XRD)

As mentioned previously, the X-ray diffraction technique is used to find the crystallographic structure of the films, the different phases present in the film, the crystallites orientation as well as the Ga/(In+Ga) ratio in the films. X-ray diffraction in scanning mode of $\theta/2\theta$ was used for each of the Cu(In,Ga)Se$_2$ films deposited by 1-stage, 2-stage and 3-stage processes, while the grazing incidence angle mode was used on the Cu(In,Ga)Se$_2$ films deposited by 3-stage process to find the variation in Ga/(In+Ga) along the film's thickness.

Results of the $\theta/2\theta$ scanning mode are presented in Figure 3-7 and the results of the grazing incidence angle mode are reported in Figure 3-8. Results of the $\theta/2\theta$ scan
show that there is not any other phase of Cu(In,Ga)Se$_2$ present except the $\alpha$-phase of Cu(In,Ga)Se$_2$ which has a tetragonal crystal structure.

![X-ray diffraction spectra](image)

**Figure 3-7** X-ray diffraction spectra, done in $\theta/2\theta$ mode, of Cu(In,Ga)Se$_2$ deposited on Mo. Lowest spectra is of the film deposited by 1-stage process, middle one is the one deposited by 2-stage process and top is the one deposited by 3-stage process.

The lattice parameters $a$, $c$ and their ratio $c/a$ for tetragonal CuIn$_{1-x}$Ga$_x$Se$_2$ film changes with $x=$Ga/(In+Ga) values and follows the Vegard's rule:

$$a(x) = (1-x)a(0) + xa(0) \quad (3.1a)$$

$$c(x) = (1-x)c(0) + xc(0) \quad (3.1b)$$

where $a$, $c$ and $c/a$ changes from 5.782 Å to 5.612 Å, 11.619 Å to 11.03 Å and 2.009 Å to 1.965 Å respectively as $x$ changes from 0 to 1. Due to these changes in $a$ and $c$, the lattice spacing $d$ also changes with Ga concentration. For a given $x$ and $(h,k,l)$ values, we can find $a(x)$, $c(x)$ and $d(x)$. Experimental value of the lattice spacing for a particular peak can be found by looking into the Joint Council for Powder diffraction Studies
(JCPDS) cards. Thus matching the d values found from calculation for a given x to one found by matching the JCPDS card, we can correlate the x value to the XRD spectrum. It was also observed that the degree of preferred orientation along the (112) direction for the Cu(In,Ga)Se₂ films deposited by 1-stage, 2-stage and 3-stage processes was 0.66, 0.36 and 0.32 respectively. These values show that these films have a slight (112) orientation when grown by the 1-stage process and a slight (220)/(204) orientation when grown by the 2-stage or 3-stage processes.

In Figure 3-8, the grazing incidence X-ray diffraction spectra of Cu(In,Ga)Se₂ film deposited by 3-stage process are reported. As shown in Figure 3-8, the peak position corresponding to the (112) direction shifts as the grazing angle of incidence changes from 0.5 degree to 4 degrees. The (112) peak position for different grazing angles did not match the same x value, and the results are summarized in Table 3.2. The GIXRD results correlate well with the Auger electron spectroscopy results, which show that the Ga concentration decreases with depth from the film surface.
Figure 3-8  GIXRD on Cu(In,Ga)Se₂ deposited by 3-stage process.

Table 3.2  Incidence angle for GIXRD measurements and the corresponding x value found using Vegard’s law.

<table>
<thead>
<tr>
<th>Incidence angle (degree)</th>
<th>x=Ga/(In+Ga)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.35</td>
</tr>
<tr>
<td>1.0</td>
<td>0.33</td>
</tr>
<tr>
<td>1.5</td>
<td>0.32</td>
</tr>
<tr>
<td>2.0</td>
<td>0.30</td>
</tr>
<tr>
<td>3.0</td>
<td>0.30</td>
</tr>
<tr>
<td>4.0</td>
<td>0.30</td>
</tr>
</tbody>
</table>
3.4.4 Scanning Electron Microscopy (SEM) and Scanning Transmission electron microscopy measurements (STEM)

Scanning electron microscopy (SEM) and Scanning transmission electron microscopy (STEM) can be used to find grain size, grain boundaries and the thickness of the different layers in the full device. Figure 3-9 below shows SEM images of Cu(In,Ga)Se₂ films grown by 1-stage, 2-stage and 3-stage processes. As shown in Figure 3-9, Cu(In,Ga)Se₂ films grown by 1-stage process have smaller grain than the ones grown by 2-stage and 3-stage processes. On the other hand, films grown by 2-stage and 3-stage processes have columnar and large grains. The reason for that is that these films go through a Cu-rich to Cu-poor transition. During the Cu-rich phase, the formation of semi-liquid Cu₂-xSe phase enhances the intermixing of Cu, In and Ga, which results in larger grains. Surface view of these films as shown in Figure 3-10 also confirms that films grown by 1-stage process have very small grains compared with films grown by 2-stage and 3-stage processes.
Cross sectional and surface SEM images of Cu(In,Ga)Se$_2$ films grown by 2-stage and 3-stage processes (Figures 3-9 and 3-10) also show that there are crevices between the grains. During the Cu-rich phase of deposition of the 2-stage and 3-stage processes, Cu$_{2-x}$Se forms between the grains as well as on the surface. The formation of crevices is likely to be due to the consumption of this Cu$_{2-x}$Se during the Cu-poor phase [Barreau et al., 2009].

Formation of large grains during the 3-stage process is also confirmed by the scanning tunneling electron microscopy (STEM) image of Figure 3-11(a). The STEM image of Figure 3-11 (a) and cross sectional SEM image of Figure 3-11 (b) also show all the layers of the full device. The Cross sectional STEM and cross sectional SEM image
of Figure 3-11 confirm that the thickness of the Mo layer is nearly 0.5μm, Cu(In,Ga)Se₂ layer is nearly 2 μm, CdS layer is nearly 50 nm, i-ZnO is nearly 50 nm and the ITO layer is nearly 200 nm.

Figure 3-11 (a) Cross sectional Scanning tunneling electron microscopy (STEM) image of a solar cell made from Cu(In,Ga)Se₂ thin film deposited by 3-stage process. (b) Cross sectional SEM view of the same device.

3.4.5 Secondary Ion Mass Spectroscopy (SIMS)

Secondary Ion Mass Spectroscopy (SIMS) was used to confirm Auger spectroscopy measurements as well as to find the impurities in the various layers. As shown in Figure 3-3 (top) and Figure 3-4 (top), SIMS depth profile in positive secondary mode was able to confirm AES measurements that the atomic concentration of Cu, In, Ga and Se atoms are constant along the Cu(In,Ga)Se₂ thickness for films deposited by 1-stage and 2-stage processes. On the other hand, as observed in Figure 3-4 (bottom) SIMS depth profile was able to confirm that the Ga and In concentration changes along the thickness of the film. As discussed earlier in the AES result section, this variation in In and Ga concentration is due to the intentional variation of In, Ga and Cu rate during the deposition. As shown in Figure 3-3 (top), SIMS measurements were also able to confirm
the presence of sodium (Na) in the Cu(In,Ga)Se₂. It should be noted here that not any Na was deposited on top of Mo intentionally. Thus SIMS confirms that the Na diffuses from the soda lime glass, through the 2 μm of Mo, into the Cu(In,Ga)Se₂ layer. Figure 3-3 (top) also shows that the Na concentration is higher at the back and at the front surfaces of Cu(In,Ga)Se₂ film than in the middle of the film. As earlier studied by other groups, the presence of Na in the Cu(In,Ga)Se₂ layer is beneficial for device quality [Rockett, 2005]. We found the same result for the Cu(In,Ga)Se₂ films deposited by 2-stage and 3-stage processes.

3.4.6 Spectroscopic Ellipsometry (SE) measurement

As a non-destructive optical characterization technique, spectroscopic ellipsometry has already been used to characterize the optical properties of thin film materials and devices [Collins et al., 1998]. In this chapter, SE is used to find the band gap, thickness and the roughness of Cu(In,Ga)Se₂ thin films as well as to correlate the variation of Ga along the thickness of the Cu(In,Ga)Se₂ deposited by the 3-stage process. The theory of ellipsometry, required for understanding this work, will be discussed in Chapter 4. A variable angle spectroscopic ellipsometer (VASE) was used (ex-situ) to acquire data at three angles of incidence, 65°, 70°, and 75° in the energy range of 0.74 eV to 6.5 eV.

As explained in the literature [Paulson et al., 2003; Hermann et al., 2001], high surface roughness of the Cu(In,Ga)Se₂ thin film makes it difficult to analyze and uniquely determine the optical function from the ellipsometry data measured on the rougher side of the film. In previous work [Paulson et al., 2003], ellipsometry data was measured and
analyzed by peeling off the Cu(In,Ga)Se$_2$ from Mo surface and then taking measurement on that Cu(In,Ga)Se$_2$/Mo interface side of the Cu(In,Ga)Se$_2$ film.

The loss of signal due to high surface roughness is also observed in Figure 3-12, which shows that the specular reflectivity from the Cu(In,Ga)Se$_2$ films deposited by 1-stage, 2-stage and 3-stage processes is low towards the UV region of the electromagnetic spectrum. At the same time, as shown in Figure 3-13, the pseudo $\varepsilon_2$ of the films deposited by 2-stage and 3-stage processes has much of the electronic band structure encoded in the specular SE beam whereas the Cu(In,Ga)Se$_2$ film deposited by the 1-stage process loses this information as we go further into the UV. Due to these losses, it is difficult to analyze and uniquely determine the optical constants for the Cu(In,Ga)Se$_2$ film prepared by 1-stage process. To overcome this difficulty of analyzing the ellipsometry data on Cu(In,Ga)Se$_2$ film grown by 1-stage process, real time spectroscopic ellipsometry (RTSE) was used to find the optical constants of Cu(In,Ga)Se$_2$ films deposited by the 1-stage process. In Chapter 4 and Chapter 5, the process and results of RTSE on the Cu(In,Ga)Se$_2$ thin films deposited by 1-stage co evaporation process are discussed.
The optical constants of the Cu(In,Ga)Se$_2$ films deposited by 2-stage and 3-stage processes were determined by using appropriate models as explained in the next few paragraphs. During the analysis of the ex-situ ellipsometry data, exact inversion along with the artifact-minimization and semiconductor criterion are used. In the exact inversion, experimental errors such as incorrect thickness transfer to the dielectric function [Collins et al., 2005]. To remove these errors in the artifact minimization procedure, the bulk and surface roughness layer thicknesses $d_b$ and $d_s$, are chosen by trial and error to ensure that no interference-fringe-related artifacts appear in the dielectric function. On the other hand, in semiconductor criterion, since $\varepsilon_2$ is zero below some spectral range for the semiconductors, the bulk layer thickness and surface roughness are varied until $\varepsilon_2$ becomes zero below the desired energy.

The optical model to find the dielectric function of a Cu(In,Ga)Se$_2$ film deposited by 2-stage process consists of: 0) soda lime glass (SLG), 1) bulk Cu(In,Ga)Se$_2$ and 2) surface roughness (EMA layer consisting of 50% void/50% bulk Cu(In,Ga)Se$_2$). The dielectric constants ($\varepsilon_1$ and $\varepsilon_2$) obtained using this optical model is plotted in Figure 3-13.
The bulk layer thickness \((d_b)\) and surface roughness thickness \((d_r)\) obtained from this model are 2240 \pm 6 nm and 40 \pm 3 nm respectively. The band gap of this Cu(In,Ga)Se\(_2\) film was obtained by fitting the second derivative of the dielectric function with critical point parabolic oscillator (CPPB):

\[
\varepsilon(\omega) = C - Ae^{i\phi} (\omega - E + i\gamma)^n
\]

where \(A\) is the amplitude, \(\gamma\) is the broadening is the phase and \(n=\text{-1,-1/2,0 and 1/2 for excitonic, 1D,2D and 3D critical points respectively.}\) A band gap of 1.17 \pm 0.08 eV was obtained by fitting the CPPB oscillators corresponding to the excitonic transitions of the first two transitions. The \(x\) value i.e. \((\text{Ga/In}+\text{Ga})\) ratio corresponding to the band gap of 1.17 eV is around 0.31 which confirms the EDS measurement of Section 3.4.1.
For Cu(In,Ga)Se$_2$ film grown by 3-stage process, SE data was used to extract the bulk layer thickness and surface roughness as well as to correlate the Ga grading (or the band gap grading) explained in Section 3.4.2 (Auger electron spectroscopy (AES)). In this case, the optical model is similar to the one explained for 2-stage process except that the Cu(In,Ga)Se$_2$ layer was divided into 36 sub-layers of equal thickness. The optical functions of each sub-layer were parameterized by K-K consistent oscillators. To find the band gap of each sub-layer, the oscillator parameters describing the fundamental band gap were allowed to be free during the fitting procedure. The standard technique of exact inversion and artifact minimization/semiconductor criterion was employed for the data analysis. Such analysis led to a bulk layer thickness ($d_b$) and a surface roughness thickness ($d_s$) of 2212.6±0.50 nm, and $= 23.17±0.70$ nm, respectively. During this analysis, the band gap energy as a function of thickness of the Cu(In,Ga)Se$_2$ was also extracted. To extract the Ga profile along the thickness of Cu(In,Ga)Se$_2$, it was necessary to have a set of reference dielectric functions (of Cu(In,Ga)Se$_2$) as a function of [Ga]/[In] ratio. Also, the composition of each of these reference films had to be uniform along the thickness of the film. This helped in extracting [Ga]/[In] ratio as a function of the band gap. Now to find the compositional profile, it was assumed that the film had 23 at.% of Cu and 51 at% of Se all along the depth of the film.
3.4.7 Current Density-Voltage (J-V) measurement

The current density-voltage measurement allows to extract the efficiency of the completed device. This measurement is simulated as the real environment condition of AM 1.5, 100 mW/cm². Results of the J-V measurements on devices fabricated from Cu(In,Ga)Se₂ thin films deposited by 1-stage, 2-stage and 3-stage processes are plotted in Figure 3-15, and Figure 3-16 respectively. Table 3.3 gives the summarized results for each of these three devices. It shows that the $V_{OC}$ for the device with Cu(In,Ga)Se₂ deposited by a 1-stage process is the lowest. The low $V_{OC}$ for devices with Cu(In,Ga)Se₂ deposited by 1-stage process may be attributed to large grain boundaries (GB) per unit volume [Lundberg et al., 2003] as well as lower junction quality.
Figure 3-15  J-V measurement of device fabricated from Cu(In,Ga)Se$_2$ thin film deposited by (left) 1-stage process with efficiency 12.0 %, and (right) 2-stage process with efficiency 13.4 %. Both devices are without any MgF$_2$ anti-reflecting coating. J-V measurement.

Figure 3-16  J-V measurement of device fabricated from Cu(In,Ga)Se$_2$ thin film deposited by 3-stage process (a) The efficiency of this device is 14.2 % without any MgF$_2$ anti-reflecting coating, and (b)15.9 % with 100 nm of MgF$_2$ coating.

Table 3.3  Summarized results of the solar cells fabricated from Cu(In,Ga)Se$_2$ thin films deposited by 1, 2 and 3-stage processes.

<table>
<thead>
<tr>
<th>Device specification</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>Fill Factor (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-stage</td>
<td>0.56</td>
<td>30.5</td>
<td>69.8</td>
<td>12.0</td>
</tr>
<tr>
<td>2-stage</td>
<td>0.60</td>
<td>29.9</td>
<td>74.5</td>
<td>13.4</td>
</tr>
<tr>
<td>3-stage</td>
<td>0.63</td>
<td>30.2</td>
<td>73.3</td>
<td>14.2</td>
</tr>
<tr>
<td>3-stage with MgF$_2$</td>
<td>0.64</td>
<td>33.6</td>
<td>73.5</td>
<td>15.9</td>
</tr>
</tbody>
</table>
On the other hand, the solar cell fabricated from Cu(In,Ga)Se$_2$ deposited by 3-stage process has the best $V_{OC}$. As explained in the AES and SIMS characterization section above, during the 3-stage process, Ga and so Ga/(In+Ga) grading is achieved by varying the deposition time of Cu, In and Ga fluxes. Ga/(In+Ga) affects the band gap by the following equation [Shafarman et al., 2003]:

$$E_g = 1.01 + 0.626x - 0.167x(1-x)$$

(3.3)

where $x$ is Ga/(In+Ga). Thus as shown in Figure 3-2 (Auger depth profile), the Cu(In,Ga)Se$_2$ has a wider band gap at the back and front interfaces. This increase in the band gap towards the back of the Cu(In,Ga)Se$_2$ layer (at CIGS and Mo interface) is due to the up lift of the conduction band minima while the valence band maxima remains nearly unchanged [Wei et al., 1998]. Due to this increase in the band gap, there is an increase in the force due to the extra electric field $q(dE_g/dx)$ which pushes the electrons towards the p-n junction of the device and so reduces the recombination at the back contact and enhance the current collection [Contreras et al., 1996].

The voltage at which the forward bias diffusion current is equal to the short circuit current is called open circuit voltage ($V_{OC}$) [PVCDROM]. $V_{OC}$ and the short circuit current are related by the following equation [Rau et al., 2001]:

$$V_{OC} = \frac{E_g}{q} - \frac{AK}{q} \ln \left( \frac{J_{00}}{J_{SC}} \right)$$

(3.4)

where $J_{SC}$ is the short circuit current density and $J_{00}$ is the prefactor used to define the diode saturation current density. In the literature, it is claimed the $V_{OC}$ is correlated to the band gap in the SCR [Dullweber et al., 2001] (and so $E_g$ in Equation 3.4 is in the space charge region) and so an increase in the band gap near the junction is expected to helps in
increasing the $V_{oc}$ but can also reduce the current due to the reduced absorption. In this work, no loss in the current due to the increase in the band gap is observed. Similar results were observed by simulation studies on Cu(In,Ga)Se$_2$ [Song et al., 2004]. It has also been claimed that the $J_{sc}$ in the graded band gap is more correlated to the minimum band gap [Dullweber et al., 2001]. In general, the band gap grading of Figure 3-4 is not always only beneficial for device performance due to the trade off between gain in voltage and loss in current. It can depend on the magnitude of the grading, the distance of the minima inside the space charge region and the carrier density [Gabor et al., 1996]. To understand the material properties of C(In,Ga)Se$_2$ with different band gap, a detailed study has been done in Chapter 5. In our case, the current obtained by 3-stage process is similar to the ones obtained by 1- and 2-stage process, and no detrimental effect appears here.

3.4.8 Quantum Efficiency (QE) measurements

Quantum efficiency measurements were done under 100 mW/cm$^2$ white light bias. If the measurement is done under real conditions, i.e. zero biased voltage and illumination corresponds to AM1.5, then the short circuit current can be calculated from the QE measurements by using [Hegedus et al., 2004]:

$$J_{sc} = q \int \Phi_{AM1.5}(\lambda)QE(\lambda)d\lambda$$

(3.5)

where $\Phi_{AM1.5}$ is the photon flux at AM1.5 condition and QE is the ratio of the number of electrons collected to the number of photons incident. The current density we find from QE measurements are always lower that the one we get from equation 3 under ideal condition. The losses in the current are due to the optical properties of the different layers as well as to the electrical defects in the absorber Cu(In,Ga)Se$_2$ layer. Current losses in the current can be divided into three main categories [Hegedus et al., 2004]:
a) Optical losses due to the reflection and the absorption in the grids, ITO, i-ZnO, CdS and at different interfaces. Lower losses due to absorption in ITO, i-ZnO and CdS can be achieved by reducing the thickness of each of the layers. But there are some downsides of reducing the thickness. If the thickness is reduced too much then there are chances of bad junction between CdS and CIGS, shunting through i-ZnO layer and reduction in current collection due to increase in sheet resistance in the ITO layer. So there must be a balance between the optical losses and the electrical losses due to these layers. Losses due to reflection can be reduced by depositing a thin layer of anti-reflecting coating. As shown in the QE curve of Figure 3-12, QE of the Cu(In,Ga)Se₂ device deposited by 3-stage process is maximized by coating 100 nm of anti-reflecting MgF₂ layer. As shown in Figure 3-11, the gain in the current due to anti-reflecting coating is also found by comparing the J-V measurement before and after the coating. The current found from QE measurement was in good agreement to the one found from J-V measurement.

b) Optical loss in Cu(In,Ga)Se₂ layer is due to incomplete absorption near the band gap of the Cu(In,Ga)Se₂. Long wavelength photons have to penetrate deep into the Cu(In,Ga)Se₂ film before being absorbed. By making high absorbing materials or increasing the thickness, this loss can be addressed. As shown in Figure 3-12 below, due to this loss near and above 1000 nm of wavelength, we have less current and therefore a lower efficiency.

c) The third loss is the electrical loss in the Cu(In,Ga)Se₂ layer due to incomplete collection of the charge carrier. This loss is the result of recombination due to traps or due to a low diffusion length. This loss can be visualized by measuring the QE
under negative biased voltage. In our study, we did QE measurement on the device having lower $J_{SC}$ and efficiency. The QE measurement on that device is plotted in Figure 3-18.

![QE Measurement Graph](image)

**Figure 3-17**  QE of the devices reported in Table 3.3.

Negative biased voltage increases the electric field and so the force on the electrons generated deep into the absorber Cu(In,Ga)Se$_2$ layer. Due to this force, electrons generated farther from the junction also drift across the junction. As shown in Figure 3-18, the QE efficiency, and therefore the generated current, increases as the negative biased voltage increases from 0V to -1V for devices of lower quality. This confirms that for the particular device, there is incomplete collection of the photogenerated electrons.
Figure 3-18  QE of device under 0V, -0.5V and -1V of biased voltage. Increase of the QE towards high wavelength with increasing biased voltage shows that the photo-generated electrons recombine before reaching the junction.

3.5  Conclusions

In this chapter, three different co-evaporation processes were used to grow Cu(In,Ga)Se$_2$ thin films. At the start of this work, initial challenges were to implement these deposition processes to grow device quality Cu(In,Ga)Se$_2$ thin films for this work and then to establish the base line efficiency for devices processed from thin film Cu(In,Ga)Se$_2$ grown by all these three co-evaporation processes. To implement these three processes, a Labview based program was developed to monitor and control different process parameters. Once the Labview based program was in place, it was used to implement 1-stage, 2-stage and 3-stage processes. Evaluation of the materials and devices were performed by J-V and SIMS measurements which indicated that impurities like boron
had incorporated into the films. By replacing the containers, this problem of boron incorporation into the film was solved. During the same period, we tried to have better control on the deposition process by implementing EIES in the deposition chamber.

After enhancing the deposition process, baseline efficiencies (for this work) of 12.0%, 13.4% and 15.9% were achieved for Cu(In,Ga)Se2 films grown by 1-stage, 2-stage and 3-stage processes. Different characterization were done on these Cu(In,Ga)Se2 films to understand the electrical and optical properties. XRD measurements confirmed that the grains are randomly orientated irrespective of the deposition process. XRD measurements also confirmed that no other phase except the α-Cu(In,Ga)Se2 phase was present. XRD measurements were also able to predict the [Ga]/[In+Ga] content in the Cu(In,Ga)Se2 deposited by 1-stage and 2-stage process as well as gave indication that the Cu(In,Ga)Se2 film deposited by 3-stage process was graded with respect to the [Ga]/[In+Ga] ratio. AES measurements were done to confirm the composition along the thickness of the film. As expected for the Cu(In,Ga)Se2 film grown by 1-stage and 2-stage process, these films had uniform composition whereas the Cu(In,Ga)Se2 film grown by 3-stage process had [Ga]/[In+Ga] grading along the thickness of the film.

Ellipsometry was used here to extract the band gap, thickness and roughness of these Cu(In,Ga)Se2 films. Due to the loss of the signal, it was not possible to analyze the SE data for Cu(In,Ga)Se2 deposited by 1-stage process. But for Cu(In,Ga)Se2 deposited by 2-stage and 3-stage process, SE data were analyzed and allowed us to extract the band gap, thickness and roughness. The graded nature of the Cu(In,Ga)Se2 deposited by 3-stage process was also confirmed. Comparison of the SEM images of the Cu(In,Ga)Se2 deposited by these three processes revealed that the grains were smallest and largest for
films grown by 1-stage and 3-stage process respectively. These measurements pointed out that due to better material quality, the highest baseline efficiency was achieved for the solar cell processed from a 3-stage process.

To cross the barrier of 15.9% efficiency (in our laboratory) and 20.3% (World record), it is necessary to have a better understanding of the Cu(In,Ga)Se$_2$ material properties. To achieve that, more research to understand the material properties of Cu(In,Ga)Se$_2$ film as a function of Cu and Ga contents were done and reported in the next two Chapters.
Chapter Four

Studies of Cu(In,Ga)Se$_2$ thin films and Solar Cells as a function of Cu content

4.1 Introduction

As explained in the previous chapter, the Cu(In,Ga)Se$_2$ films for high efficiency solar cells are grown at high temperature and the Cu content in the film is slightly less than stoichiometry (25 at.%). Device quality Cu-poor Cu(In,Ga)Se$_2$ films can be grown at high temperature either by a 1-stage, 2-stage or 3-stage process. During the 1-stage process, the film is always Cu-poor whereas during the 2-stage and 3-stage processes, the film becomes Cu-poor only at the end of the deposition. Cu-poor Cu(In,Ga)Se$_2$ absorber layers grown by 2-stage and 3-stage processes are best suited for high efficiency solar cells. During these processes, there are compositional changes during the film growth as well as Cu-rich to Cu-poor transitions. Due to these changes, the electrical and optical properties of the films also change during the growth. To grow better quality Cu(In,Ga)Se$_2$ films and to improve the device efficiency, it is necessary to understand these evolution of material properties Cu(In,Ga)Se$_2$ as function of their Cu content [Marsillac et al., 2010]. Since the properties of Cu(In,Ga)Se$_2$ evolve during growth i.e. at temperature of around 570 °C, it is also of interest to study the changes in the properties
at deposition temperature and then correlate these properties after the growth with other measurements.

In this chapter, we will investigate the variation of properties of Cu(In,Ga)Se₂ thin films as a function of their Cu content during the deposition as well as post-deposition. Real time spectroscopic ellipsometry was used to study the material properties during growth. In this chapter, a brief overview of spectroscopic ellipsometry (SE), of the experimental set–up for data acquisition and of RTSE data analysis methodologies along with the RTSE results obtained on Cu(In,Ga)Se₂ films as a function of Cu content are presented. At the same time, these RTSE results are correlated with ex-situ measurements. One particular goal of this Chapter is to identify the Cu-poor and Cu-rich phases as well as to monitor and control the film growth during the deposition process.

4.2 Characteristics of Real Time Spectroscopic Ellipsometry (RTSE)

Ellipsometry is an optical measurement technique that measures the changes in the state of polarization of the light upon interaction (reflection or transmission) with the material [Collins et al., 2001; Fujiwara 2007]. The Polarization of the light represents the orientation and phase of the field vectors of the corresponding light wave. These field vectors are described in equation 4.1 below. A change in thickness as small as a monolayer changes the polarization of the interacting light wave. Thanks to modern computing, this change in polarization due to a small change in thickness can now be recorded. Thus data for a wide spectral range can be collected for time periods corresponding to monolayer growth; this technique of data collection during film's
growth is called real time spectroscopic ellipsometry [Collins and Yang, 1989; Collins, 1990]. Thus by analyzing the collected data, film's thickness and other properties can be extracted.

4.2.1 Mathematical relations

To understand the extraction of material properties by ellipsometry, it is necessary to apprehend some mathematical relationship of polarized state of light. A light wave propagating through vacuum or a solid medium is completely represented by the following four Maxwell’s equations in SI units:

\[ \nabla \cdot \vec{D} = \rho \quad (4.1a) \]
\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (4.1b) \]
\[ \nabla \cdot \vec{B} = 0 \quad (4.1c) \]
\[ \nabla \times \vec{H} = \vec{J} + \left( \frac{\partial \vec{D}}{\partial t} \right) \quad (4.1d) \]

where \( \vec{E}, \vec{B}, \vec{D} \) and \( \vec{H} \) are the electric field, the magnetic field, the displacement field and the magnetic field strength respectively [Jackson, 1999]. \( \rho \) and \( J \) are the free charge density and the free current respectively in the free space. In the case of the interaction of light with a Linear, Homogeneous, Isotropic and non-Dispersive (LHIND) medium, the above described four vectors are related to each other by the following two equations:

\[ \vec{D} = \varepsilon_0 \varepsilon_r \vec{E} \quad (4.2a), \quad \vec{B} = \mu_0 \mu_r \vec{H} \quad (4.2b) \]

where \( \varepsilon_0, \mu_0, \varepsilon_r, \mu_r \) are the permittivity in free space, the permeability in free space, the relative permittivity and the relative permeability of the dielectric medium respectively. In the case of a non-LHIND media, \( \varepsilon_r \) and \( \mu_r \) become tensor. The relative permittivity and the relative permeability represent the optical response of the material to the interacting light and are called the optical functions of the material [Wooten, 1972].
Using some vector algebra on equation 4.1 above and assuming a LHIND, non magnetic material with no external current or charges, the wave equation can be written as [Collins et. al., 2005]

$$\nabla^2 \vec{E} = \frac{\varepsilon_r}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} + \frac{4\pi\sigma}{c^2} \frac{\partial \vec{E}}{\partial t}$$

(4.3)

where $\sigma$ is the real optical conductivity. The plane wave solutions of the above equation can be written as [Collins and Ferlauto, 2001]:

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \exp \left[ i \left( \frac{\vec{q} \cdot \vec{r}}{c} - \omega t \right) \right]$$

(4.4)

where $\omega$ is the angular frequency of the wave, $\vec{q}$ is the complex wave vector along the propagation direction, and $\vec{E}_0$ is the complex electric field vector perpendicular to $\vec{q}$, which defines the amplitude and polarization state of the wave. The complex wave vector $\vec{q}$ is defined as:

$$q^2 = \left( \frac{\omega}{c} \right)^2 \left[ \varepsilon_r + i \left( \frac{4\pi\sigma}{\omega} \right) \right]$$

(4.5)

The right hand side of equation 4.5 can be equated to the complex index of refraction $N$ by:

$$N^2 = \left[ \varepsilon_r + i \left( \frac{4\pi\sigma}{\omega} \right) \right]$$

(4.6)

The complex index of refraction can also be written as $N \equiv n + ik$. Thus equation 4.4 can be rewritten as [Wooten, 1972]:

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \exp \left[ -\frac{\vec{k} \cdot \vec{r}}{c} \right] \exp \left[ i \left( \frac{\vec{n} \cdot \vec{r}}{c} - \omega t \right) \right]$$

(4.7)
The exponential factor containing k describes the amount of photons absorbed in the material as light propagates through it and k is called the extinction coefficient. The other term which describes the absorption of photons is called the absorption coefficient (α) and is related to the extinction coefficient by:

\[ \alpha = \frac{2\omega k}{c} = \frac{4\pi k}{\lambda} \]  

(4.8)

The second exponential factor of equation 4.5 represents the traveling wave with phase velocity c/n, where n is called the refractive index of the material. The right hand side of equation 4.6 is called the complex dielectric function (ε). Like N, the complex dielectric function ε is also used to define the optical properties of a material. Rewriting equation 4.6 in terms of n and k yields:

\[ (n + ik)^2 = \left(n^2 - k^2\right) + i(2nk) = \varepsilon_1 + i\left(\frac{4\pi\sigma}{\omega}\right) = \varepsilon_1 + i\varepsilon_2 \]  

(4.9)

Where the imaginary part of the dielectric function (ε_2) is \(\frac{4\pi\sigma}{\omega}\). Equating real and imaginary parts separately gives the following relationship for the real refractive index, the absorption coefficient, and the real and imaginary parts of the dielectric function:

\[ \varepsilon_1 = n^2 - k^2 \]  

(4.10a)

\[ \varepsilon_2 = 2nk \]  

(4.10b)

\[ n = \left[ \frac{1}{2} \left( \varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} + \varepsilon_1 \right]^{1/2} \]  

(4.11a)

\[ k = \left[ \frac{1}{2} \left( \varepsilon_1^2 + \varepsilon_2^2 \right)^{1/2} - \varepsilon_1 \right]^{1/2} \]  

(4.11b)
4.2.2 *Measured quantities and their relationship with the dielectric constant*

If $\vec{q}$, the complex wave vector, is along the $z$ axis then the complex electric field vector $
E_0$ of equation 4.4 can be written as:

$$E_0 = E_{0x} \exp(i\delta_x) \hat{x} + E_{0y} \exp(i\delta_y) \hat{y}$$

(4.12)

where $\delta_x, \delta_y$ represents the absolute phase of $E_x, E_y$ at $z = 0$ and $t = 0$. To describe the state of polarization, only the phase difference $\delta_x - \delta_y$ (or $\delta_y - \delta_x$) is required and not the absolute values of the initial phases. Figure 4-1 below describes the various phase differences and the corresponding polarization states.

In ellipsometry experiments, instead of using orthogonal x-y axis, a coordinate system based on the plane of incidence of the obliquely reflecting light is used. In this coordinate system, the electric field is resolved into components parallel (p) and perpendicular (s) to the plane of incidence. The p and s components of the electric field of the reflected wave are connected to the p and s components of the incident wave through reflection coefficients called the Fresnel coefficients [Guenter, 1990]:

$$r_p = \left| r_p \right| \exp(i\delta_p) = \frac{E'_p}{E^i_p}$$

(4.13a)

$$r_s = \left| r_s \right| \exp(i\delta_s) = \frac{E'_s}{E^i_s}$$

(4.13b)

where the superscripts "i" and "r" are used to indicate the incident wave and reflected wave respectively. If the linearly polarized light is reflected from a surface, the p-and s-polarizations undergo different changes in amplitude and phase. Ellipsometry measures the amplitude ratio and phase difference between the p- and s-polarizations, respectively. These two quantities are represented by $\psi$ and $\Delta$, respectively.
Figure 4-1  Representation of the variation of the polarization state with the phase difference a) $\delta_x - \delta_y = 0$ represents the linearly polarized light and the orientation of the resultant vector of $E_x$ and $E_y$ is always oriented at $45^\circ$ in the x-y plane, b) $\delta_x - \delta_y = \pi/2$ represents the circularly polarized light and the resultant vector of $E_x$ and $E_y$ rotates in the x-y plane as light propagates, c) $\delta_x - \delta_y = \pi/4$ represents the elliptically polarized light and the resultant vector rotates in the x-y plane. As shown in the figure, if the direction of rotation is clockwise for light traveling along the positive z axis, the polarization is called right circular/elliptical polarization. For each of the figure, $E_x = E_y$. [Fujiwara, 2007].

Mathematically, these two quantities are written as:

$$\rho_r \equiv \tan \psi \exp(i\Delta) = \left| \frac{r_p}{r_s} \right| \exp\left[i(\delta_p - \delta_s) \right]$$

(4.14)

Thus the angle $\psi$ and $\Delta$ are defined as:

$$\tan \psi = \left| \frac{r_p}{r_s} \right|$$

(4.15a)

$$\Delta = \delta_p - \delta_s$$

(4.15b)

Since $\psi$ represents the angle determined from the absolute value of the amplitude ratio, $\psi$ is confined between 0 and $90^\circ$. On the other hand $\Delta$ is the phase difference and so it ranges from $0^\circ$ to $360^\circ$. In the simplest case when the sample structure is simple, $\psi$ is characterized by the refractive index $n$ and $\Delta$ by the extinction coefficient $k$. 72
4.3 Experimental Set-Up

Figure 4-3 shows a schematic of the co-evaporation chamber along with the ellipsometer used in this work. The ellipsometer used here is a rotating compensator ellipsometer capable of collecting 706 wavelengths over a spectral range of 190–1700 nm. Deuterium (D₂) and Quartz–Tungsten–Halogen (QTH) lamps are used in this ellipsometer as broad wavelength light source. The light from these sources is linearly polarized after passing through the fixed polarizer with its transmission axis (TA) set at 45° with respect to the plane of incidence. A rotating compensator which is an anisotropic optical element with two axes, fast and slow, generates the phase difference (called retardence) between the p– and s–components of the electric field. This phase shift depends on the angle of the fast axis with respect to the plane of incidence. Since the compensator rotates at constant frequency $\omega_c$ (this is not the frequency of the light wave), the net result is the time–dependent or modulated polarization state of the photons incident on the sample. Due to the reflection from the sample, there is a change in the nature of the polarization state modulation. This reflected light passes through the fixed analyzer which is another linear polarizer. After passing through the analyzer, the light is collected by the irradiance detector. The irradiance detector consists of an InGaAs photodiode array and a Si charge coupled device (CCD). The low energy (0.75–1.25 eV) light is collected by the InGaAs photodiode array and the high energy light (1.25–6.5 eV) is collected by the CCD detector. The light is split into 706 wavelength channels and can be collected in a time as short as 50 ms.
Figure 4-2  Diagram of the co-evaporation chamber and RTSE system components used in this study. Stress free fused silica windows are mounted in both the incident and reflection ports of the vacuum chamber, with the goal of eliminating birefringence due to uneven application of stresses and developed strain.

A 1-stage process, as described in Chapter 3, was used to deposit multiple Cu(In,Ga)Se₂ films at 570 °C. The temperature of the sources was chosen so that the Ga/(In+Ga) ratio, x, was constant at 0.3 so that the band gap due to these two elements remains constant. The copper content in the films, and the ratio Cu/(In+Ga), was varied from 22.5 at.% to 27.5 at.%.

The substrate holder for this evaporation chamber is designed to hold 4 substrates. Due to this advantage, during each deposition at least one Si thermal oxide, one Mo and one soda lime glass (SLG) substrates were used. RTSE data were acquired in situ during the film growth at an angle of incidence of 70±0.011°. Pairs of (Ψ,Δ) spectra were collected with an acquisition time of 6 seconds. Analyses of the spectra involved numerical inversions and least-squares regression algorithms.
4.4 Data Analysis

As described in the previous section, the ellipsometry measurement provides \((\psi, \Delta)\) spectra, which represents the changes in the polarization state of the light beam upon reflection from the sample. Ellipsometry does not directly give information about the sample; however, \(\psi\) and \(\Delta\) are functions of the material properties like thickness and dielectric function. To extract these characteristics, analyses of these \(\psi, \Delta\) data are required. A general schematic of the analysis procedure for data taken by real time spectroscopic ellipsometry is presented in Figure 4-3. The starting point for the data analysis is to develop an appropriate optical model for the sample. If the component materials of the sample structure and their dielectric functions are known, the first step in building an optical model is by placing the right sequence of different layers, including each layer’s thickness and optical properties as shown in Figure 4.4 for the simplest sample. If the dielectric functions of the composite material are not known then different dielectric function models are used [Fujiwara, 2007]. Complexity can be added to the model, such as intermix layers and voids fraction, to improve the fitting and can be correlated with other theoretical and experimental techniques.
Figure 4-3  Simplified algorithm for data analysis from data acquired during RTSE measurement.

Figure 4-4  Simplest optical model for a sample.

Once the optical model is built, \((\psi, \Delta)\) are generated by assigning “first guess” values to the various energy–independent unknown parameters such as bulk layer thickness, surface roughness. These generated \((\psi, \Delta)\) are then fitted to the experimental data. A
numerical algorithm, called least square regression algorithm, is used to minimize the differences between the generated spectra and the experimental data by adjusting the variable parameters in the model. Similarly to any numerical fitting procedure, a figure of merit is used to accept the fitted data from a set of many fitted data. One of the two choices used as a figure of merit for ellipsometry data analysis is called unbiased estimator or the mean square error (MSE), and is written as:

$$\text{MSE} = \sqrt{\frac{1}{2N - M} \sum_{i=1}^{N} \left[ \left( \frac{\psi_{i}^{\text{mod}} - \psi_{i}^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 + \left( \frac{\Delta_{i}^{\text{mod}} - \Delta_{i}^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^2 \right]}$$  \hspace{1cm} (4.16)

where “gen.” denotes a generated value and “exp.” denotes an experimentally measured value. N is the number of ($\psi$, $\Delta$) pairs, M is the variable parameters in the model and $\sigma$ is the standard deviation of the experimental data. The process of fitting is stopped as soon as MSE is minimized. The procedure of finding the lowest MSE is called least square regression.

As explained in the previous paragraph, the dielectric function modeling is used to extract the dielectric function if the dielectric function is unknown. Due to the complex nature of the layers, a complete modeling of the dielectric function over a wide wavelength range is sometimes tedious. To prevent that, the data analysis can be done on a short range of wavelength, where the dielectric function is calculated with a reasonable fitting in that region for a specific value of the thickness. This thickness is then fixed and the measured ($\psi$, $\Delta$) of the layer is then converted into optical functions. For example, consider the optical model of thin film on semi-infinite substrate as "air($N_{\text{air}}$)/film($N_{\text{film}}$)/Substrate($N_s$)". The measured ($\psi$, $\Delta$) are defined as:

$$\tan \psi^{\text{exp}}(i\Delta) = \rho(N_{\text{air}}^{\text{film}}, N_{\text{film}}^{\text{air}}, N_{\text{substrate}}, d_i, \theta)$$  \hspace{1cm} (4.17)
where \( N_i \) denotes the complex refractive index of \( i^{\text{th}} \) layer (i.e., if \( i^{\text{th}} \) layer is air, \( N_i \) becomes \( N_{\text{air}} \)), \( d \) is the film's thickness and \( \theta \) is the angle of incidence at the air/film interface. Let's assume that \( N_{\text{air}}, N_s \), and \( \theta \) are known and that \( N_{\text{film}} \) along with \( d \) is unknown. If the dielectric function of the film is expressed by Cauchy model parameters in a small range of wavelength and a good fitting is obtained, using a specific \( d_s \), then the only unknown parameter will be \( N_{\text{film}} \) in the whole range of measured energy. Now if equation 4.17 is solved, the measured \((\psi, \Delta)\) will be converted into \( N_{\text{film}} \) [Collins and Ferlauto, 2001; Fujiwara, 2007]. This procedure is called mathematical inversion.

During ex-situ SE measurements, measurements can be performed at multiple angles of incidence and the resulting spectra can be analyzed together. Due to data acquisition at multiple angles, the number of unknown parameters is the same but the number of measured quantities is 1412 (706 values of \( \psi \), 706 values of \( \Delta \)) multiplied by the number of angles of incidence. In this case the total number of measured quantities is larger than the total number of unknown parameters and so more easily modeled by the least square regression analysis. In the case of RTSE, the angle of incidence is fixed and this approach is not readily applicable; a least square regression is therefore combined with mathematical inversion. If the film is being deposited on an already fully characterized substrate, then RTSE analysis can be performed, using an appropriate model, during the growth even if the dielectric function is unknown. To extract the dielectric function and analyze the growth of Cu(In,Ga)Se_2, an optical model similar to Figure 4-4 with a bulk layer made up of the Cu(In,Ga)Se_2 material and a surface roughness layer made up of 50% Cu(In,Ga)Se_2/ 50% Void was used. At a specific time of deposition, the thickness of the growing film can be estimated from the growth rate.
and so, by mathematical inversion trial, the dielectric functions \((\varepsilon_1, \varepsilon_2)\) can be obtained, as shown in Figure 4-5. Using these trial dielectric functions as a reference for the growing film, a least square regression analysis can now give a good estimation of the thickness. Examples of this approach can be found in various references [Collins et al., 1994; An et al., 1991; Fujiwara et al., 2000]. This method enables therefore one to determine, simultaneously, the dielectric functions and the structure of the sample.

**Figure 4-5** Algorithm for the RTSE data analysis.

### 4.5 Characterization of Cu(In,Ga)Se\(_2\) thin films as a function of Cu at.%

#### 4.5.1 Compositional analysis

As mentioned previously, a series of CIGS thin films were deposited by 1-stage process at 570 °C with a constant Ga/(In+Ga) ratio but various Cu atomic percentages. The Cu rate during each of the deposition was kept constant. The atomic percentage of Cu in the different films was changed by changing the Cu rate only and keeping the In, Ga and Se rates similar so that the Ga to In+Ga ratio remained constant. The composition of each film was determined by EDS analysis. Typical compositions of the films
deposited were: Se = 51 at.%, Ga/(In+Ga) of 0.3 and Cu at.% of 22.5, 23.5, 25.5 and 27.5 at.%. AES was used to check whether the composition was uniform all along the thickness of the film, and it was confirmed that no variation of composition occurred throughout the films. Since for Cu(In,Ga)Se₂ thin film, the tetragonal lattice parameters a and c varies with the Ga/(In+Ga) ratio, XRD measurements was also used to determine the x = Ga/(In+Ga) ratio in the film from the change in the lattice parameters. As observed in Figure 4-6, for all four films, the (112) peak is nearly at 26.95° which indicates that there is not any significant change in the lattice constant and that the Ga/(In+Ga) ratio is 0.30 for all these films. An asymmetry or splitting in the peak would indicate that the film is graded or has different phases. No asymmetry in any of the peaks plotted in Figure 4-6 is observed, which indicates that all these films are grading free which supports the finding of AES measurements. However, for films with more than 25 at.% of Cu, another low intensity peak at around 26.7° was observed which is not visible in Figure 4-6 due to the high intensity of the peak at 26.9°. Cross reference from Joint Council for Powder Diffraction Studies (JCPDS) data indicates that this peak is due to the presence of Cu₂₋ₓSe compound in the film.
Figure 4-6  (112) peak of the XRD spectra of Cu(In,Ga)Se₂ thin films on Si thermal oxide substrates grown by one stage process with various copper content.

4.5.2 Growth analysis

Real time spectroscopic ellipsometry was used to acquire, in real time and \textit{in situ}, pairs of ($\psi$, $\Delta$) on Cu(In,Ga)Se₂ thin films deposited on thermal oxide covered Si wafer substrate at 570 °C with various copper content. In the previous sub-section 4.5.1, the Cu content of these films were found using EDS and AES. The time evolution of the surface roughness $d_s$ and bulk layer thicknesses $d_b$ of these four Cu(In,Ga)Se₂ thin films were extracted using the same optical model that was used to extract the dielectric functions and is plotted in Figure 4-7. As seen in Figure 4-7, two distinct growth rate regimes are visible for each film. The first is associated with the thin film nucleation on the substrate
surface, where the surface roughness thickness describes the nuclei height above the substrate [Fujiwara et al., 2000]. The second regime starts with the formation of the first bulk monolayer due to coalescence, an indication of a Volmer-Weber growth process [Venables et al. 1984].

For each of the films, at time \( t = 0 \) in Figure 4-7, the Cu, In, Ga, and Se fluxes start to reach the bare substrate as soon as the shutter below the substrate holder is opened. Instantly Cu, In, Ga, and Se atoms nucleate together to form Cu(In,Ga)Se\(_2\) in the form of islands, a process evidenced by an abrupt increase in the surface roughness layer thickness [An et al., 1990]. The start of the coalescence of these islands is reflected in the abrupt decrease in the surface roughness thickness and increase in the bulk layer thickness. After complete coalescence, there is a further increase in the surface roughness thickness along with the bulk layer thickness. The thickness of each of the film at the end of deposition, as seen in Figure 4-7, is in good agreement with those obtained ex situ from profilometry measurements.

A closer comparison of all these four films during the nucleation region indicates that the nuclei height (surface roughness before growth of the bulk layer) is the largest for the film with the lowest Cu at.\%. This increase in the nuclei height with decreasing Cu at.\% may be attributed to the slower nucleation rate (i.e. lower islands density), leading to an increase growth time for the islands before contact and therefore larger clusters [Li, 2010]. Another potential explanation comes from the presence of a semi-liquid Cu\(_{2-x}\)Se phase along with the Cu(In,Ga)Se\(_2\) phase for the Cu-rich Cu(In,Ga)Se\(_2\) films (see section 4.5.4). Due to the high diffusivity of In and Ga in the Cu\(_{2-x}\)Se at 570 °C [Park et al., 2000], it is likely that the presence of this semi-liquid Cu\(_{2-x}\)Se helps in the fast
interdiffusion of the In and Ga with the Cu, accelerating the nucleation and coalescence, and therefore limiting the maximum height of the nuclei.

![Graph showing surface roughness and bulk layer thickness versus time for various Cu at.% in the film obtained by RTSE for four Cu(In,Ga)Se₂ films.](image)

**Figure 4-7** Surface roughness (solid line) and bulk layer (dash line) thicknesses versus time for various Cu at.% in the film obtained by RTSE for four Cu(In,Ga)Se₂ films.

The final surface roughness for each film, extracted from the (dₘ, dₛ) model of Figure 4-7 shows that the surface roughness thickness is higher for film with lower Cu at.%; this observation is corroborated by the SEM and AFM images of Figure 4-8.
Figure 4-8  Surface SEM image (top) and AFM images of surface topography (bottom) of Cu(In,Ga)Se$_2$ films with different Cu at.%. Top left and bottom left are for Cu at.% of 22.5 whereas right top and bottom are for Cu at.% of 27.5.

The surface roughness extracted from RTSE data were not same as the one measured by AFM but a linear correlation is observed which is plotted in Figure 4-9 and mathematically expressed by $d_s$ (SE)$\sim 1.6 \ d_{rms}$ (AFM)$ - 9.1$nm. This relationship is similar to one found in literature for a-Si:H thin films [Fujiwara, 2007] and for CdS films [Li, 2010]. The offset of 9.1 nm may be due to the limitations of RTSE which can not detect the component of the surface roughness of the order of the wavelength of the light, whereas it is detectable by the AFM [Li, 2010].
4.5.3 Analysis of the Dielectric Functions

The same pairs of \((\psi, \Delta)\) that allowed for the growth analysis of the CIGS thin films during their deposition at high temperature (570 °C) also allows for the extraction of the dielectric functions of the films. Some of the features observed in the dielectric functions of a semiconductor can be viewed as inter-band transition points in the electronic band structure of the semiconductor and are called critical points (CPs). The electronic band structure for \(\text{Cu(In,Ga)}\text{Se}_2\) is shown for a single crystal at room temperature in Figure 4-10a [Alonso et al., 2001] and the different critical points (CPs) are indicated by vertical arrows. In Figure 4-10b, the imaginary part of the dielectric function \((\varepsilon_2)\) of \(\text{Cu(In,Ga)}\text{Se}_2\) at 570 °C for Cu of 23.5 at. % is plotted as an example. Since the dielectric functions and the electronic band structure are linked together, the CPs shown by arrows in Figure 4-10a must be present in the dielectric functions of
Figure 4-10b. However, due to the polycrystalline nature of our films as well as the high temperature, the attribution of the CPs and analysis of the data is not necessarily straightforward.

One way to resolve this problem is to calculate the second derivative of the dielectric function, allowing for the CP features to become sharper, and isolated one from another (Figure 4-11). As observed in Figure 4-11, there are several minima and each of these minima corresponds to a specific CP of Figure 4-10a. To find the position of the critical points and related parameters, critical point parabolic oscillators were used, using the following equations:

$$
\varepsilon_j(\omega) = \begin{cases} 
C_j - A_j e^{i\phi} (\omega - E_j + i\Gamma_j)^n, & n = -1, -\frac{1}{2}, +\frac{1}{2} \\
C_j - A_j e^{i\phi} \ln(\omega - E_j + i\Gamma_j), & n = 0
\end{cases}
$$

(4.18)
Figure 4-11  Second derivative of the imaginary part of the spectra reported in Figure 4-10b. The data are depicted in the black circles and the fits based on equation 4.18 are depicted as line.

where $E$ is the energy, $A_j$, $\omega_j$, $E_j$ and $\Gamma_j$ are the amplitude, phase, energy and broadening of the $j^{th}$ oscillator, respectively [Alonso et al., 2001]. In equation 4.18, $n = -1, -1/2, 0, +1/2$ correspond to excitonic, 1D, 2D, and 3D critical points respectively (Alonso et al., 2001). If the dielectric function is expressed by equation 4.18 then the second derivative is also expressed by equation 4.18 with new value of $A_j$, $\omega_j$ and $n$ but with the same $E_j$ and $\Gamma_j$.

Table 4.1  CP Energies as well as broadening of CPs for Cu(In,Ga)Se$_2$ thin films at 570 $^\circ$C for Cu of 23.5 at.\% (Figure 4-10).

<table>
<thead>
<tr>
<th></th>
<th>$E_0$($A,B$)</th>
<th>$E_0$($C$)</th>
<th>$E_1$($A$)</th>
<th>$E$ ($\Gamma$)</th>
<th>$E_1$($B$)</th>
<th>$E$($X\Gamma$)</th>
<th>$E_2$($A$)</th>
<th>$E_3$</th>
<th>$E_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broadening (eV)</td>
<td>0.56</td>
<td>0.44</td>
<td>0.88</td>
<td>0.55</td>
<td>0.44</td>
<td>0.40</td>
<td>0.44</td>
<td>1.64</td>
<td>0.37</td>
</tr>
<tr>
<td>CP energies (eV)</td>
<td>1.06</td>
<td>1.36</td>
<td>2.62</td>
<td>3.11</td>
<td>3.71</td>
<td>4.07</td>
<td>4.52</td>
<td>5.14</td>
<td>5.42</td>
</tr>
</tbody>
</table>
The CP energies reported in Table 4.1 are obtained by the best fit of the oscillators given by equation 4.18. For the first three transitions, $E_0(A,B)$ and $E_0(C)$, the best fits were obtained with excitonic line shapes; for the rest of the transitions, 2D line shapes were used. In Table 4.1, two high energy transitions labeled $E_3$ and $E_4$ have been identified for the first time; however, assignments to specific electronic transitions in the band-structure are not yet possible. For these dielectric functions at 570 °C, the $E(\Delta X)$, $E_2(B)$, and $E_5$ transitions observed at room temperature were not resolvable due to broadening and were hence removed from the fit.

4.5.4 CPs and their broadening as a function of Cu at.%

Now that we have described the procedure to extract the dielectric functions for our CIGS thin films at high temperature, we will focus on their evolution as a function of copper content. The changes in materials properties during 2-stage and 3-stage processes, due to Cu-rich to Cu-poor and Cu-poor to Cu-rich transitions, provide interesting opportunities for the analysis of the dielectric functions of Cu(In,Ga)Se$_2$ with different Cu at.%. Previous ellipsometry studies [Han et al., 2005] showed for example that with large decrease in Cu content the CPs of the CuInSe$_2$ thin films shifted. To study the shift in the CP energies as well as the changes in broadening due to Cu at%, four typical Cu(In,Ga)Se$_2$ composition reported in section 4.5.2 of this chapter were used. The dielectric functions of the films with Cu percentage atomic concentration of 22.5, 23.5, 25.5 and 27.5 are plotted in Figure 4-12.
Figure 4-12  Dielectric functions of Cu(In,Ga)Se$_2$ thin films as a function of Cu at.%. The solid lines denote the real part of the dielectric functions ($\varepsilon_1$) and the dotted lines denote the imaginary part of the dielectric functions ($\varepsilon_2$).

As described in the previous section, the second derivative of each of the dielectric function spectra of Figure 4-12 was fitted with CPPB oscillators given by equation 4.18 to allow for the extraction of the CPs. The fitting procedure was similar to the one described in the previous section. As observed in Figure 4-13, there is not any significant shift in the $E_0$ position for Cu(In,Ga)Se$_2$ if Cu at.% in the film changes from 22.5 to 27.5. On the other hand, the broadening of the CP oscillator decreases as the atomic percent of Cu increases. This result will be discussed in the next section.
4.5.5 Grain growth as a function of Cu at.%

The broadening of the CP oscillator is generated by photons interacting with phonons and other scatterers. Thus, temperature and grain boundaries can cause such changes in the broadening term. Therefore, the grain size of Cu(In,Ga)Se$_2$ films with different Cu at.% can be compared by comparing the broadening of the peaks, as long as the temperature is kept constant which is the case here. A small grain implies a short time for an excited carrier to reach and to be scattered by its boundary. This causes a limitation of the excited-state lifetime and thus broadens the excited-state energy. In this case, the following equation relates the broadening and the grain size [Feng et al., 1989]:

$$\Gamma_n = \Gamma_{bn} + \frac{hV_{gn}}{R}$$

(4.19)

where $\Gamma_n$ is the broadening parameter for the $n^{th}$ CP; $\Gamma_{bn}$ is the corresponding parameter for the single crystal; $h$ is Planck’s constant; $V_{gn}$ is the group velocity of the excited electron associated with $n^{th}$ CP and $R$ is the grain size. Since the broadening is decreasing
with increasing Cu at.% (Figure 4-13), using equation 4.19 it can be shown that the grain size increases with increasing Cu at.%.

To further study the evolution of the grain size with Cu at.% \textit{ex-situ} measurements such as XRD and cross sectional STEM were used. Grain size can be extrapolated from XRD measurements by using Scherrer’s formula [Patterson, 1939]:

\[
D = \frac{K_\beta \lambda}{\beta \cos \theta}
\]

(4.20)

where \(D\), \(K_\beta\), \(\lambda\), and \(\beta\) are the grain size, the Scherrer’s constant, the full width at half maximum (FWHM) and the broadening of the diffraction peak, respectively. Thus the grain size is inversely proportional to the FWHM of the peak. The broadening in the diffraction peak is not only due to the particle size but also to inhomogeneous strain or instrumental effects. Due to these effects, the particle size can be larger than the one predicted from the Scherrer’s formula, which predicts only the lower limit of the particle size. The FWHM of the (112) peak (Figure 4-6) is 0.163\(^0\), 0.130\(^0\), 0.119\(^0\) and 0.075\(^0\) for Cu at.% 22.3, 23.4, 25.5 and 27.5 respectively. This decrease in the FWHM with increasing Cu at.%, indicating an increase in the grain size, supports the results obtained by RTSE.

This observation of increase in the grain size was also corroborated from surface scanning electron microscopy (SEM) as well as cross sectional scanning tunneling electron microscopy (STEM) measurements. The surface SEM images of Cu(In,Ga)Se\(_2\) films with two extreme Cu at.% are shown Figure 4-8. The STEM images of the Cu(In,Ga)Se\(_2\) thin film with Cu percentage atomic concentration of 22.5, 23.5, 25.5 and 27.5 are shown in Figure 4-14. As one can see in the cross sectional STEM images, the grains are the largest for the Cu(In,Ga)Se\(_2\) film with Cu at.% of 27.5 and the smallest for
the film with Cu at.% of 22.5. The growth of larger grains in the Cu-rich Cu(In,Ga)Se2 film will be explained in the next few paragraphs.

**Figure 4-14** STEM images of Cu(In,Ga)Se2 thin films with Cu at.% a) 22.5, b) 23.5 c) 25.5, and d) 27.5. In each of the film, the cross arrows show the grain boundaries. The lower two films have Cu_{2-x}Se on top of Cu(In,Ga)Se2 as indicated by the red arrow. On top of each film, there is a Platinum layer deposited during the ion beam thinning.

STEM images of Cu-rich films (Figures 4-14c and 4-14d) show that there is a thin layer on top of the Cu(In,Ga)Se2 grains whereas for Cu-poor films (Figures 4-14a and 4-14b), there is no additional layer. EDS spectra were taken on this thin layer (Figures 4-14c and 4-14d). Only Cu and Se peaks were present in the spectra, confirming the presence of a Cu_{2-x}Se film. Such a layer as been observed previously for Cu-rich films [Abushama et al., 2001]. EDS measurements were also done along the vertical axis (along the depth of the film). For each of the films, except the one with 27.5 at% of Cu, the Cu, In, Ga and Se signals were overall constant. For this specific film (Figure 4-14d),
the magnified view of the TEM cross section is shown in Figure 4-15. The vertical line through "2" in Figure 4.15a below is the grain boundary. EDS measurements at "2" shows much higher Cu and Se at.% than the one at "1" and "3". Similarly at "spectrum 1" and "spectrum 3" (Figure 4-15b), Cu and Se at.% are much higher than the one at "spectrum 2" and "spectrum 4". These observations confirm that the Cu$_{2-x}$Se phase exists between the grains as well as inside the grains [Yan et al., 2001].

![TEM image](image)

**Figure 4.15** Magnified view of the TEM image of Figure 4.14d. a) Point 2 is at the grain boundary and 1 and 2 are on each side of the grain boundaries. b) Spectrum 1, 2, 3 and 4 are fours points inside the grains where EDS measurements were done.

During Cu-rich to Cu-poor transition of the 2-stage and 3-stage processes, the Cu flux is switched off and these extra Cu$_{2-x}$Se spots are consumed by In and Ga, causing the formation of intragrain domain boundaries and of crevices between the grains [AbuShama et al., 2001; Park et al., 2000]. The presence of the semi-liquid Cu$_{2-x}$Se at 570 °C [Tuttle et al., 1993; Albin et al., (solar cells)1991; Gabor et al., 1994] in Cu-rich Cu(In,Ga)Se$_2$ has beneficiary effects on the growth of the Cu(In,Ga)Se$_2$ thin films. Due to the high mobility of In (and Ga) [Park et al., 2000] in the semi-liquid Cu$_{2-x}$Se, the presence of Cu$_{2-x}$Se does not only help in the better intermixing of Ga and In but also provides extra nucleation and growth site for Cu(In,Ga)Se$_2$. The Cu$_{2-x}$Se then provides...
the transportation medium for these grains towards the solid liquid interface which facilitates the epitaxial growth normal to the substrate [Tuttle et al., 1993; Gabor et al., 1994; AbuShama et al., 2001]. It is also possible that the presence of the semi-liquid Cu$_2$-xSe provides continuous supply of Cu and so helps in better bonding of In and Ga to form Cu(In,Ga)Se$_2$ compound. These beneficiary effects, associated with the presence of the semi-metallic Cu$_2$-xSe phase, helps in the growth of larger Cu(In,Ga)Se$_2$ grains normal to the substrate. The cross sectional STEM images of Figure 4-14 are clearly showing that, in the Cu-rich Cu(In,Ga)Se$_2$ films, the grains have columnar growth and that the size of the grains are almost equal to the thickness of the film. Due to the larger columnar grains, the grain boundary density is reduced, allowing therefore most of the carriers to not cross the grain boundaries [Shafarman et al., 2003]. If these Cu$_2$-xSe clusters are removed from the Cu(In,Ga)Se$_2$ layer after the growth of larger grains, the grain boundary recombination sites can be reduced in the absorber Cu(In,Ga)Se$_2$ layer. The lessening of the recombination sites may be helpful in increasing the $V_{OC}$ of the device [Tuttle et al., 1993; Rau et al., 1999]. The purpose of the 2-stage and 3-stage process is to remove these Cu$_2$-xSe at the end of the growth to grow thin film Cu(In,Ga)Se$_2$ with larger grains.

The presence of semi-metallic Cu$_2$-xSe compound was also confirmed by the appearance of a Drude oscillator in the imaginary part of the dielectric function (Figure 4-12). This appearance of a Drude oscillator can be observed below the band gap in the Cu-rich Cu(In,Ga)Se$_2$ film. The Drude oscillator is effectively used to describe the light absorption by free electrons in metals and free carriers in semiconductors [Fujiwara, 2007].
The presence of the semi-metallic phase was also confirmed by transmission measurements. Transmission measurements were done on Cu(In,Ga)Se$_2$ thin films deposited on the SLG placed beside the Si substrate during the deposition.

![Figure 4-16](image.png)

**Figure 4-16** Transmission spectra of Cu(In,Ga)Se$_2$ thin films deposited on soda lime glass (SLG). All these films have the same thickness.

Figure 4-18 shows that there is an important loss in the transmission through the film with high Cu at.%, which comes from the presence of the semi-metal Cu$_{2-x}$Se.

### 4.6 Fabrication and characterization of CIGS solar cells as a function of Cu content

#### 4.6.1 Fabricating the complete device

2 μm thick Cu(In,Ga)Se$_2$ thin films on Mo coated soda lime glass (SLG) were deposited under the same conditions as described in the previous section. The
composition of each of the films was confirmed by EDS measurements. These films were processed to complete solar cells as described in an earlier chapter. All the J-V measurement and QE measurements, reported here, were done before MgF₂ coating.

4.6.2 Current Density-Voltage (J-V) measurement

The results of the J-V measurements on devices fabricated from Cu(In,Ga)Se₂ thin films with different Cu at.% are plotted Figure 4-17 and summarized in Table 4.2. As observed in Figure 4-17, for the devices processed from Cu-poor Cu(In,Ga)Se₂ films, very well-behaved dark and light J–V curves have been obtained. If the dominant recombination mechanism is in the space charge region, the change in VOC with the change in acceptors’ concentration is given by [Ruckh et al. 1996]:

\[ \Delta V_{OC} = \frac{2kT}{q} \ln \sqrt{\frac{N_A}{N_{AO}}} \]  \hspace{1cm} (4.21)

where \( N_A \) is the increased in the acceptors’ concentration and \( N_{AO} \) is the base acceptors’ concentration. For Cu(In,Ga)Se₂ alloys with a Cu/(In+Ga) ratio below 1.0 (i.e. Cu at.% below 25), even though the p-type conductivity is mostly due to Cu vacancy, the majority carrier concentration increases with the Cu at.% if the Se concentration is kept constant [Noufi et al., 1984]. Thus increase in the \( V_{OC} \) as observed in Figure 4-17 is justified by equation 4.21 with the increase in the Cu at.%, while there is not any significant change in the \( J_{SC} \).
Figure 4-17  J-V measurements as a function of Cu at.%. 

Also it is evident from Table 4.2 that this increase in the $V_{OC}$ is also responsible for the increase in the efficiency of the device with increasing Cu at.% (for CIGS with less than 25% of Cu). Solar cells fabricated from Cu-rich Cu(In,Ga)Se$_2$ thin films are of low quality and all of them are mostly shunted. This shunting is attributed to the presence of the semi-metallic Cu$_{2-x}$Se on the surface and inside the films.

<table>
<thead>
<tr>
<th>Cu at.% in the absorber layer</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>Efficiency (%)</th>
<th>Fill Factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5</td>
<td>0.50</td>
<td>29.2</td>
<td>9.3</td>
<td>62.3</td>
</tr>
<tr>
<td>22.5</td>
<td>0.54</td>
<td>29.9</td>
<td>11.6</td>
<td>68.8</td>
</tr>
<tr>
<td>23.5</td>
<td>0.56</td>
<td>30.5</td>
<td>12.0</td>
<td>69.8</td>
</tr>
<tr>
<td>27.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

As explained in Chapter 2, a small increase in the sheet resistance ($R_s$) from zero does not affect $V_{OC}$ and $I_{SC}$ and only decreases the FF of the solar cell whereas large
increase in the $R_S$ affects $I_{SC}$ first and then the $V_{OC}$. Thus the decrease in the FF (as observed in Table 4.2) with the decrease in the Cu at.% in the absorber layer may be attributed to a small increase in the $R_S$. As shown in Figure 4-17, the slope in the reverse bias region of the light J-V curve increases with the decreasing Cu at.% in the absorber layer, while there is no increase in the slope of the dark J-V curve. This increase in the slope indicates that the material quality gets inferior or that the diffusion length of the minority carrier decreases as the Cu at.% decreases in the film. All these effects lead to the highest efficiency for a Cu at.% of 23.5.

4.6.3 Quantum-Efficiency (QE) measurement

QE measurements were done on all the devices reported in the section 4.6.2 under standard condition. The integrated photocurrent from the QE measurement for each of the devices (reported in Figure 4-18) correlates well with the J-V measurement values. As described by other authors [Hegedus et al., 2004], the QE curve should be of square shape but due to different optical and electrical losses, the shape changes. The optical loss due to the shading and reflection of light from collection grid as well as by air/ZnO/CdS/Cu(In,Ga)Se$_2$ interfaces reduces the QE of the device. This loss can be reduced by coating an antireflection MgF$_2$ layer on top of the device. At the longer wavelength, the zero quantum efficiency indicates the band gap of the absorbing semiconductor. Thus the band gap of the Cu(In,Ga)Se$_2$ absorber layer can be predicted by looking at the QE curves, which for Figure 4-18 indicates that all these three devices have absorber layer with the same band gap of around 1050 nm which agrees well with measurements like EDS and XRD. Whether the absorber Cu(In,Ga)Se$_2$ film is graded or not can be verified using the QE curve too. The QE curves of Figure 4-18 are relatively
steep at longer wavelength, indicating that all these Cu(In,Ga)Se₂ films have uniform composition.

![Figure 4-18 Quantum efficiency of devices fabricated from Cu(In,Ga)Se₂ thin films having Cu at.% 21.5, 22.5, and 23.5. These measurements were done at 0V of bias.]

Low energy photons generate more electron-hole pairs at the back of the Cu(In,Ga)Se₂ absorber. If these carriers are recombined before reaching the space charge region they can not contribute to the current; the recombination of these carriers is therefore reflected in the QE curve above 900 nm. In Figure 4-18, a drop in the QE around 900 nm is observed, which is probably due to the recombination of charge carriers within the bulk of the Cu(In,Ga)Se₂ [Turcu et al., 2006]. This recombination may be due to a short diffusion length of the minority carriers (electrons here) or to defects in the material itself.
Below 520 nm of wavelength, losses in QE are attributed to the optical losses due to the absorption in CdS and below the 400 nm of wavelength, losses are due to ZnO band gap. As observed in Figure 4-18, there are losses in the QE around and above 900 nm which can be attributed to the free carrier absorption in the ITO layer. As observed in Figure 4-18, the optical losses like absorption in CdS layer, free carrier absorption in TCO layer etc. are approximately the same for each of the solar cells. This indicates that the processing conditions for each of the layers of the solar cell stack are consistent for every device. At the same time, $J_{SC}$ is limited by the band gap of the absorber layer. This means that the band gap of the absorber layer of different devices can be compared if the optical losses due to the other layers are similar (as it is the case here). The J-V measurements indicate that $J_{SC}$ is the same for each of the devices, so it can be anticipated from the J-V measurements and corroborated by the QE measurements that the band gap of each of the absorber layers is the same.

4.7 Conclusions

Cu(In,Ga)Se$_2$ films with different Cu at.% prepared by one stage co evaporation process were studied by in-situ and ex-situ techniques. The composition of these films was confirmed by EDS as well as by AES measurements. Real time spectroscopic ellipsometry (RTSE) measurement were done on each of the samples to find the growth process, thickness, roughness as well as other material properties of these films. Data analysis of these in-situ measurements revealed that irrespective of the Cu at.% between 22.5 to 27.5, the Cu(In,Ga)Se$_2$ films follow a Volmer-Weber growth process. Ellipsometry data analysis also revealed that the roughness of the Cu(In,Ga)Se$_2$ film
decreases as the Cu at.% in the film increases. The analysis of the dielectric function extracted from the RTSE revealed that there is not any significant change in the critical points (CPs) if the Cu at.% in the Cu(In,Ga)Se2 film is changed from 22.5 through 27.5. The same analysis proved that the grain size increases with the increasing Cu content in the Cu(In,Ga)Se2 film. This trend in the increase in the grain size was corroborated with \textit{ex-situ} measurements like STEM and XRD. XRD measurement also confirmed the presence of the Cu$_{2-x}$Se compound in the Cu-rich Cu(In,Ga)Se$_2$ films. The semi-metallic nature of the Cu$_{2-x}$Se was confirmed by the appearance of a Drude oscillator for Cu-rich Cu(In,Ga)Se$_2$ films. Transmission measurement on these Cu(In,Ga)Se$_2$ indicated that the percentage of transmission through Cu-rich Cu(In,Ga)Se$_2$ films was lower than for the Cu-poor Cu(In,Ga)Se$_2$ films. The cross- sectional STEM images and EDS measurement during cross-sectional STEM imaging proved that the Cu$_{2-x}$Se compound mostly stays at the surface of the Cu(In,Ga)Se$_2$ film, but that some of the Cu$_{2-x}$Se can be found at the grains boundaries and in the grains. These measurements also confirmed that the Cu$_{2-x}$Se helps in the formation of larger Cu(In,Ga)Se$_2$ grains. In essence, the material properties of Cu(In,Ga)Se$_2$ thin film as a function of Cu content was investigated by \textit{in-situ} \textit{and ex-situ} measurements. Our findings will, in the future, help in the implementation of RTSE to identify the Cu-rich to Cu-poor or Cu-poor to Cu-rich transitions and therefore enhance further the control over the Cu(In,Ga)Se$_2$ deposition process.
Chapter Five

Studies of Cu(In,Ga)Se$_2$ thin film and Solar Cells as a function of the Ga content

5.1 Introduction

Since the first thin film solar cell based on CuInSe$_2$ was fabricated [Kazmerski et al., 1976] the efficiency of devices based on thin-film CuInSe$_2$ has been improved by the addition of Ga to form Cu(In,Ga)Se$_2$ absorber layers. The addition of Ga into CuInSe$_2$ enlarges the band gap following [Wei et al., 1995]:

$$E_g = (1 - x)E_g(CuInSe_2) + xE_g(CuGaSe_2) - bx(1 - x)$$

(5.1)

where $x$=Ga/(In+Ga) and $b$ is called the bowing parameter with value around 0.15-0.24 eV [Wei et al., 1995]. Incorporation of Ga into Cu(In,Ga)Se$_2$ changes the level of the conduction band minimum which in turn changes the band gap [Wei et al., 1998]. With the addition of Ga in CuInSe$_2$, the open circuit voltage ($V_{OC}$) increases whereas the short circuit current ($J_{SC}$) decreases. Due to this trade off between current and voltage, the efficiency initially increases with increasing $x$ but start decreasing for $x$ value above 0.2, unless manipulations like band gap grading are used. This is due in part because at higher Ga content, the increase in the $V_{OC}$ is not proportional to the band gap [Schock et al., 1994; Stewart et al., 1987]. Even though the efficiency falls, these tradeoffs between voltage and current are beneficial for some applications. Another benefit comes from the
fact that incorporating Ga into the CuInSe₂ film widens the α phase domain [Gödecke et al., 2000] necessary for high quality devices, while domains of the adjacent phases of ordered defect compound Cu(In,Ga)₃Se₅ become narrower.

Cu(In,Ga)Se₂ thin films as a function of Ga content have been studied by spectroscopic ellipsometry by other researchers [Paulson et al., 2003; Alonso et al., 2002; Kawashima et al., 1998; Alonso et al., 2001]. The Cu(In,Ga)Se₂ alloys studied were either single crystals, polycrystalline ingots or films at room temperature, which means after the complete growth. However, these studies did not address the possible effects of temperature and growth on the optical properties. Previous studies [Wei et al., 1998; Paulson et al., 2003; Alonso et al., 2002; Kawashima et al., 1998; Alonso et al., 2001] also showed that the variation of the Ga content in Cu(In,Ga)Se₂ thin films changes the band gap. In this Chapter, we will study the Cu(In,Ga)Se₂ thin films as a function of Ga/(In+Ga) content during deposition (temperature of 570 °C) using *in-situ* real time spectroscopic ellipsometry (RTSE) and will also correlate RTSE results with *ex-situ* measurements.

### 5.2 Experimental Set-Up

The set-up of the co-evaporation chamber along with the ellipsometer used to deposit the films and do data acquisition has been described in Chapter 4. The Cu(In,Ga)Se₂ films were deposited by 1-stage process. Each film was deposited at a substrate temperature of 570 °C and the temperature of the sources was kept constant so that the Cu, In, Ga and Se fluxes remain constant during each deposition. Cu was deposited at the same temperature to keep the ratio Cu/(In+Ga) ≈ 0.9 during all deposition but the Ga and In temperatures were changed from one deposition to another to change
the Ga/(In+Ga) ratio. RTSE data were acquired in situ during film growth and analyzed as described previously.

5.3 Characterization of Cu(In,Ga)Se$_2$ thin films as a function of $x$=Ga/(In+Ga)

5.3.1 Compositional analysis

The composition of each of the films was determined by EDS analysis as described earlier. AES measurements confirmed that the composition was uniform all along the thickness of the film. XRD measurements were also used to determine the $x$=Ga/(In+Ga) ratio in the films from the lattice parameters. For Cu(In,Ga)Se$_2$ thin films, the tetragonal lattice parameters $a$ and $c$ varies with the Ga/(In+Ga) ratio and are expressed by Vegard's law:

$$a(x) = (1-x)a(x=0) + xa(x=1)$$  \hspace{1cm} (5.2a)
$$c(x) = (1-x)c(x=0) + xc(x=1)$$  \hspace{1cm} (5.2b)

where $a(x=0)$ and $c(x=0)$ correspond to CuInSe$_2$, and $a(x=1)$ and $c(x=1)$ correspond to CuGaSe$_2$ [Suri et al., 1989]. Once $a(x)$ and $c(x)$ are known, then for any (hkl) the lattice spacing $d(x)$ and the diffraction angles can be obtained.

The results for the XRD measurements on films with $x$= Ga/(In+Ga) value of 0, 0.3, 0.43 and 0.55 (as measured by EDS) are reported in Figure 5-1, specifically for the (112) peak. This peak position was found to be at 26.64°, 26.94°, 27.10°, and 27.23° which corresponds very well to the value expected for these compositions. It is also noticeable that the diffraction peaks are highly symmetrical with no evidence of compositional broadening or splitting. The asymmetry or splitting in the peak generally
indicates that the film is graded or has different phases. Thus, the XRD results also confirm the AES measurements that each of the film has uniform Ga concentration.

Figure 5-1  (112) peak of the XRD spectra of the Cu(In,Ga)Se$_2$ thin films on Si thermal oxide substrates grown by one stage co evaporation process.

5.3.2 Growth analysis as a function of Ga/(In+Ga)

Figure 5.2 shows the time evolution of the surface roughness $d_s$ and bulk layer thicknesses $d_b$ for Cu(In,Ga)Se$_2$ thin films as a function of time, for various Ga/(In+Ga) ratio. Films were deposited on thermal oxide covered Si wafer substrate by 1-stage process. As seen in Figure 5-2, similarly to Figure 4-7, two distinct growth rate regimes are visible for each film. The first is associated with thin film nucleation on the substrate surface, where the surface roughness thickness describes the nuclei height above the
substrate [Fujiwara et al., 2000]. The second regime starts with the formation of the bulk monolayer due to coalescence, an indication of a Volmer-Weber growth process [Venables et al, 1984].

For each of the films, after complete coalescence, there is a further increase in the surface roughness thickness along with the bulk layer thickness.

![Image](image.png)

**Figure 5-2** Evolution of the surface roughness (solid line) and the bulk layer (dash line) thicknesses with time obtained by RTSE for four Cu(In,Ga)Se$_2$ films.

The film thickness obtained from the ($d_b$, $d_s$) model of Figure 5-2 is in good agreement with the one obtained ex situ from profilometry. The final surface roughness for each film, extracted from the ($d_b$, $d_s$) model of Figure 5-2 shows that the surface roughness barely changed as the $x$ value changed from 0.0 to 0.55. To investigate the surface
morphology, AFM and SEM measurements were done. Images from SEM and AFM measurements shown in Figure 5-3 for x = 0.0 and x = 0.55 show similar surface morphology. RMS roughness found from AFM, for different x, agrees well with the roughness extracted from RSTE with the relation \( d_s(\text{SE}) \approx 1.62 \ d_{\text{RMS(AFM)}} - 1.5 \) which is similar to the one found in Chapter 4. The reason for negative intercept is already explained in Chapter 4.

![SEM and AFM images](image)

**Figure 5-3** Surface SEM image (top) and AFM images of surface topography (bottom) of Cu(In,Ga)Se\(_2\) films with different x value. Top left and bottom left are for x = 0 whereas the right top and bottom are for x = 0.55.

### 5.3.3 Dielectric Function Evolution as a function of Ga/(In+Ga)

As explained in the previous Chapter (Section 4.5.2), the inter-band transition points can be extracted from the features observed in the dielectric function of a semiconductor.
Dielectric functions of Cu(In,Ga)Se$_2$ films with different Ga/(In+Ga) ratio at substrate temperature of 570 °C are plotted Figure 5-4. As observed in Figure 5-4, the fundamental absorption, observed at low energy, shifts towards higher energy as the x value increases. This is related to an increase in the band gap as x increases. However, to better analyze these dielectric functions, especially ones measured at high temperature like here (570 °C), it is necessary to calculate the second derivative of the dielectric functions to extract the position of the CPs.

![Dielectric function of Cu(In,Ga)Se$_2$ for three different values of x. Solid, dash and dotted lines are for x = 0.55, 0.3 and 0.0 respectively.](image)

**Figure 5-4** Dielectric function of Cu(In,Ga)Se$_2$ for three different values of x. Solid, dash and dotted lines are for x = 0.55, 0.3 and 0.0 respectively.

The second derivative of the imaginary part of the dielectric functions of Figure 5-4 are plotted in Figure 5-5 and these second derivatives are fitted with critical point parabolic (CPPB) oscillators, such as:
\[
\varepsilon_j(\omega) = \begin{cases} 
C_j - A_j e^{i\omega_j} (\omega - E_j + i\Gamma_j)^n, & n = -1, -\frac{1}{2}, +\frac{1}{2} \\
C_j - A_j e^{i\omega_j} \ln(\omega - E_j + i\Gamma_j), & n = 0 
\end{cases} 
\] 
(5.3)

**Figure 5-5** Second derivative of the imaginary part of the dielectric functions reported in Figure 5-4.

where \( A_j, \omega_j, E_j \) and \( \Gamma_j \) are the amplitude, phase, energy and broadening of the \( j^{th} \) oscillator [Alonso, 2001]. In equation 5.3, \( n = -1, -\frac{1}{2}, 0, +\frac{1}{2} \) are excitonic, 1D, 2D, and 3D critical points respectively [Alonso, 2001]. As explained in Chapter 4, if the dielectric function is expressed by equation 5.3 then the second derivative can also be expressed by equation 5.3 with new value of \( A_j, \omega_j \) and \( n \) but with similar \( E_j \) and \( \Gamma_j \).

The CP energies reported in Figure 5-6 are obtained by the best fit of the oscillators given by Equation 5.3. For the first two transitions, \( E_0(A,B) \) and \( E_0(C) \), the best fits were obtained with excitonic line shapes and for the rest of the transition 2D line shapes were used. In Figure 5-6, two high energy transitions labeled \( E_3 \) and \( E_4 \) have been identified for the first time; however, assignments to specific electronic transitions in the band-structure are not yet possible. For the dielectric function at 570 °C, the \( E(\Gamma X), E(\Delta X), E_2(B) \), and \( E_5 \) transitions were not resolvable due to the broadening and were hence
removed from the fit. In the Cu(In,Ga)Se₂ alloy, the valence band maximum (VBM) is mainly a hybridization of Cu-d and Se-p like states, and the conduction band minimum (CBM) contains mainly (In,Ga)-s and Se-sp like states. The Ga atom is smaller than the In atom and so the bond length between Ga-Se is less than the one for In-Se. Due to this lattice compression, the CBM minimum moves upward. At the same time, the shift in the valence band maximum (VBM) is negligibly small [Wei et al., 1995]. Thus the shift in the band gap observed in Figure 5-6 is due to the upward lift of the conduction band with increasing x. At the same time, Figure 5-6 (right) indicates that the addition of the Ga in the Cu(In,Ga)Se₂ alloy also shifts the higher order optical transition towards the higher energies. These results are consistent with the one found for Cu(In,Ga)Se₂ alloys at room temperature [Paulson et al., 2003].

The valance band maximum of the Cu(In,Ga)Se₂ at the BZ center is a triply degenerate state as shown in Figure 5-7 for two extreme case. This degeneracy is the result of the perturbation due to the tetragonal crystal filed. The crystal field splitting depends on the tetragonal lattice parameters a and c [Tell et al., 1975]:

**Figure 5-6** Position of the fundamental transitions (left) as well as higher energy transitions (right) for Cu(In,Ga)Se₂ thin films as a function of x at deposition temperature of 570 °C.
\[ \Delta_{ct} = -b \left(1 - \frac{c}{2a}\right) \]  

(5.4)

where \( b \), with a magnitude of around 1 eV, is called the deformation potential. Since \( c/2a = 1.004 \) for CuInSe\(_2\) and \( c/2a = 0.9825 \) for CuGaSe\(_2\), \( \Delta_{ct} \) changes from positive to negative [Paulson et al., 2003]. The further splitting is due to the spin-orbital interaction as shown in Figure 5-4. The crystal field splitting (\( \Delta_{cf} \)) and spin-orbital splitting (\( \Delta_{so} \)) can be calculated from the following equation:

\[ \Delta = \frac{E_1 + E_2}{2} \pm \left[ \frac{3}{2} \left( \frac{E_1 + E_2}{2} \right)^2 - \frac{1}{2} \left( \frac{E_1 + E_2}{2} \right)^2 \right]^{1/2} \]  

(5.4)

where \( \Delta_+ \) is \( \Delta_{so} \) and \( \Delta_- \) is \( \Delta_{cf} \). \( E_1 \) is the magnitude of the difference between \( E_0(B) \) and \( E_0(A) \); \( E_2 \) is the magnitude of the difference between \( E_0(C) \) and \( E_0(A) \) or \( E_0(B) \).

![Figure 5-7](image)

**Figure 5-7**  Energy band structure near the centre of the Brillouin zone showing how the crystal field and spin–orbit interaction leads to formation of non-degenerate energy levels for CuInSe\(_2\) alloy. In this diagram, \( \Delta_{cf} \) is positive. For the other extreme case i.e. CuGaSe\(_2\), \( \Delta_{cf} \) is negative [Kawashima et al., 1998; Paulson et al., 2003; Newman, 1986].

The variation in \( E_0(A,B) \) and \( E_0(C) \) with the \( x \) value is fitted with the second degree polynomial of equation 5.5 below:
Equation 5.5a shows that the bowing parameter for the fundamental band gap is 0.79 which is much larger than the one reported at room temperature of 0.29 [Wei et al., 1998]. The reason for the higher value of the bowing parameter may be attributed to the narrow fitting range from $x = 0$ to $x = 0.55$ rather than $x = 0$ to $x = 1$ as well as the fact that the ellipsometry data were acquired at high temperature ($570 ^\circ C$). This difference in the bowing parameter may also be because $E_0(A)$ and $E_0(B)$ are not resolved separately at $570 ^\circ C$ and so there is a cross-over between $E_0(A)$ and $E_0(B)$ as opposed to the one reported in the literature [Paulson et al., 2003]. The separation between the $E_0(A)$ and $E_0(B)$ is unresolved at higher temperature because of the negligible crystal field splitting [Paulson et al., 2003]. On the other hand, the bowing parameter corresponding to $E_0(C)$ transition is around the one reported in the literature at room temperature [Alonso et al., 2002; Paulson et al., 2003]. The spin-orbital splitting calculated from equation 5.4, using $E_0(A,B)$ and $E_0(C)$ of Figure 5-6, is plotted in Figure 5-8 below. The spin-orbital splitting plotted in Figure 5-8 follows upward bowing as a function of $x$ which is consistent with the result observed for Cu(In,Ga)Se$_2$ at room temperature [Alonso et al., 2002; Durante Rincon et al., 2001; Paulson et al., 2003].
To confirm the variation of the band gap with x, transmission (T) and reflection (R) measurements were done on each of the films on soda lime glass (SLG). The transmission data are plotted in Figure 5-9. There is a systematic decrease in the band gap wavelength (or increase in the band gap energy) around which the transmission starts to decrease, as the x value in the films increases. This confirms that the band gap (in the units of eV) increases with increase in x. These transmission spectra also confirm that each of the film has low sub-band gap absorption, which point out that all these films have minimum allowed impurity states in the band gap. Since Cu(In,Ga)Se$_2$ is a direct band gap semiconductor, the absorption coefficient, $\alpha$, is related to the energy by [Kazmerski et al., 1982; Durante Rincon et al., 2001]:

$$(ah\nu)^2 = A(h\nu - E_g)$$  \hspace{1cm} (5.6)$$

where A is a constant and $E_g$ is the band gap. Thus as explained in the literature [Kazmerski et al. 1982], a plot of $(h\nu\alpha)^2$ vs. $h\nu$ should be a straight line and the point of interception of this line with the energy axis will give the band gap. The absorption
coefficient can be calculated from the transmission and reflection coefficients via [Schroder, 2006]:

\[
\alpha = \frac{2 \ln(1 - R) - \ln(T)}{d}
\]  

(5.7)

where \(d\) is the thickness of the thin film. Linear extrapolation of the \((h\nu \alpha)^2\) vs. \(h\nu\) curve for different \(x\) of 0, 0.3, 0.43 and 0.53 gives band gap of 1.01, 1.16, 1.24 and 1.31 eV respectively. These band gap energies are higher than the one reported in Figure 5-6 for corresponding \(x\) values. The reason for this anomaly is the temperature difference of around 550 °C between the RTSE and the T&R measurements.

It is already reported [Kazmerski et al. 1982] for CuInSe\(_2\) that by increasing the temperature from 100 K to 300 K lowers the band gap from the band gap from 1.04 eV to 1.02 eV.

During this study we also confirmed this shift in the band gap with temperature by comparing the dielectric function extracted from spectroscopic ellipsometry (SE) data taken at 570 °C and at 20 °C for CuInSe\(_2\). The data at 20 °C was acquired from RTSE set
up after the sample was cooled down to room temperature. The dielectric function at 20 °C was extracted by using the final surface roughness thickness (d_s) and bulk layer thickness (d_b) obtained from the (d_b, d_s) model of Figure 5-2 assuming that the final values of d_s and d_b were not changed while cooling down. Then as described in the previous paragraphs, the second derivative of the dielectric functions was fitted with the CPPB oscillators given by Equation 5.3. The CP energies obtained by fitting the second derivative of the dielectric functions of Figure 5-10 with the CPPB oscillators are presented in Table 5.1. Table 5.1 confirms the difference between the fundamental band gap energy (E_0(A,B)) reported in Figure 5-6 and the one in Figure 5-9b for CuInSe₂.

![Dielectric functions of CuInSe₂ at two different temperatures: 570 °C (solid line) and 20 °C (dashed line).](image)

**Figure 5-10** Dielectric functions of CuInSe₂ at two different temperatures: 570 °C (solid line) and 20 °C (dashed line).

It is also observed in Table 5.1 that CPs shift towards lower energy as the temperature of the film increases. This finding is consistent with the earlier study done at temperature between 10K to 300K on the n-type CuInSe₂ crystal [Rincon et al., 1986].
Table 5.1   CP energies extracted by fitting the CPPB oscillators to the dielectric functions of CuInSe$_2$ at 570 $^\circ$C and 20 $^\circ$C.

<table>
<thead>
<tr>
<th></th>
<th>570 $^\circ$C</th>
<th>20 $^\circ$C</th>
</tr>
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<tbody>
<tr>
<td>$E_0$(A,B)</td>
<td>0.96</td>
<td>1.01</td>
</tr>
<tr>
<td>$E_0$(C)</td>
<td>1.15</td>
<td>1.23</td>
</tr>
<tr>
<td>$E(\Gamma X)$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$E_1$(A)</td>
<td>2.60</td>
<td>2.81</td>
</tr>
<tr>
<td>$E(X\Gamma)$</td>
<td>3.01</td>
<td>3.23</td>
</tr>
<tr>
<td>$E_1$(B)</td>
<td>3.64</td>
<td>3.65</td>
</tr>
<tr>
<td>$E(\Delta X)$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$E'(\Gamma X)$</td>
<td>4.04</td>
<td>4.16</td>
</tr>
<tr>
<td>$E_2$(A)</td>
<td>4.47</td>
<td>4.56</td>
</tr>
<tr>
<td>$E_2$(B)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$E_3$</td>
<td>5.04</td>
<td>5.11</td>
</tr>
<tr>
<td>$E_4$</td>
<td>5.36</td>
<td>5.41</td>
</tr>
</tbody>
</table>

5.3.4   Grain size as a function of Ga/(In+Ga)

As explained in the previous chapter, the broadening of the oscillator associated to the CP energy is directly proportional to the grain size if the broadening is generated by photons interacting with phonons and other scatterers at constant temperature. Thus the increase in the broadening indicates that the grain size is decreasing or vice versa. For the Cu(In,Ga)Se$_2$ thin films studied here, the broadening of the oscillator fitted at the fundamental energy $E_0$(A,B) first decreases and then increases as x changes from 0 to 0.55. The minimum value of the broadening is for the films with x = 0.3. This trend in the broadening indicates that there is small increase in the grain size as the x changes from 0.0 to 0.3 and then a small decrease in the grain size with the further increase in the x. The grain size can also be predicted by XRD measurement using the Scherrer formula. The full width at half maximum (FWHM) of the (112) peaks decreases from 0.0032 radians to 0.003 radians as x increases from 0.0 to 0.3 and then increases through 0.0033 radians to 0.0034 radians as x further increases through 0.43 to 0.55. Using these value of the FWHM, the grain sizes calculated are 54 nm, 58 nm, 52 nm and 51 nm respectively.
This XRD calculation shows that grain size is maximum for $x = 0.3$, but that there is not much difference. This is in good correlation with the results obtained by SEM (Figure 5-3) and by RTSE. All these three results indicates that the Ga/(In+Ga) ratio has very little effect on the grain size which is consistent with earlier studies done on Cu(In,Ga)Se$_2$ thin films [Shafarman et al., 1996].

![Graph showing $E_0(A,B)$ peak broadening from RTSE data analysis (left) and grain size calculated from XRD measurement (right).]

**Figure 5-11**  $E_0(A,B)$ peak broadening from RTSE data analysis (left) and grain size calculated from XRD measurement (right).

### 5.4 Fabrication and characterization of Cu(In,Ga)Se$_2$ based device as a function of Ga/(Ga+In)

In this section, J-V and QE results of the devices fabricated from 2 μm thick Cu(In,Ga)Se$_2$ thin films with $x = 0.3$, 0.43 and 0.55 will be discussed. All these 2 μm thick Cu(In,Ga)Se$_2$ thin films were deposited on Mo coated soda lime glass (SLG) under the same conditions as the ones described in the previous section. These films were processed to complete solar cells as described in an earlier Chapter.
5.4.1 Current Density-Voltage (J-V) measurement

Results of the J-V measurements on devices fabricated from the Cu(In,Ga)Se₂ thin films mentioned above are plotted Figure 5-12 and the results summarized in Table 5.2. As observed in the Table 5.2, the decrease in the current density of the device may be attributed to lower absorption of photons due to the increase in the band gap.

![Figure 5-12](image)

**Figure 5-12** J-V measurements as a function of Ga/(In+Ga). Solid, dash and dot lines represents data for x = 0.30, 0.43, 0.55 respectively.

**Table 5.2** Different cell parameters as a function of Ga/(In+Ga).

<table>
<thead>
<tr>
<th>Ga/(In+Ga)</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm²)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>0.56</td>
<td>30.5</td>
<td>69.8</td>
<td>12.0</td>
</tr>
<tr>
<td>0.43</td>
<td>0.62</td>
<td>27.9</td>
<td>59.5</td>
<td>10.4</td>
</tr>
<tr>
<td>0.55</td>
<td>0.67</td>
<td>22.4</td>
<td>49.8</td>
<td>9.1</td>
</tr>
</tbody>
</table>

As explained in the previous chapters, the small decrease in the shunt resistance (R<sub>sh</sub>) from infinitely high value is observed in the increase in the steepness of the slope of
the dark J-V around $J_{SC}$ whereas the increase in the slope of the light J-V curve alone in the reverse bias is due to the voltage-dependent current collection. As shown in Figure 5-12, the slope in the reverse bias region of the light J-V curve increases with the increasing Ga/(Ga+In) ratio which indicates that there is voltage-dependent current collection in the devices with Ga/(Ga+In) ratio of 0.43 and 0.55. The voltage-dependent current collection points out that the minority carrier collection, which depends on the space charge width, increases with increasing voltage bias. This may be attributed to the poor minority-carrier diffusion length or the material quality [Shafarman et al., 1996].

As reported in the literature [Rau et al., 2001; Rau et al., 2000], the dominant recombination mechanism in the Cu(In,Ga)Se$_2$ thin film based solar cell is recombination in the space charge region which limits the open circuit voltage of these devices. The limitation on the open circuit voltage is given by [Rau et al., 2001]:

$$V_{OC} = \frac{E_g}{q} - \frac{A}{q} \ln \left( \frac{J_{oo}}{J_{SC}} \right)$$  \hspace{1cm} (5.9)

where $E_g$ is the band gap, $q$ the electronic charge, $A$ the diode ideality factor, $kT/q$ the thermal voltage, $J_{oo}$ a prefactor which is proportional to the density of recombination centre. In terms of the density of recombination centre, the loss in the $V_{OC}$ (for $A=1$) can be written as:

$$\left[ \frac{E_g}{q} - V_{OC} \right] \alpha \left[ \text{constant} + \frac{kT}{q} \ln(N_{max}) \right]$$  \hspace{1cm} (5.10)

where $N_{max}$ is the maximum defect density. This equation explains that the loss in $V_{OC}$ is due to the increase in the defect density and that devices with the lowest loss in $V_{OC}$ (with respect to the respective band gap of the Cu(In,Ga)Se$_2$ layer) have the lowest $N_{max}$ [Rau et al., 2001]. For the devices reported in Figure 5-12, we observe a loss in $V_{OC}$ with
respect to the band gap. As observed in Table 5.3, the loss in $V_{OC}$ increases with increasing band gap which indicates that the addition of Ga not only increases the band gap but also the defect in the absorber layer. The same effect of Ga addition was observed by other researchers [Rau et al., 2001]. It has been reported [Rau et al., 1998] that the addition of small amount of S passivate the deep trap state. Thus one way to tackle this increase of defects is to add small amount of S in the Cu(In,Ga)Se$_2$ compound.

<table>
<thead>
<tr>
<th>$E_g$ (eV)</th>
<th>$V_{OC}$ (V)</th>
<th>$V_{OC} - \frac{E_g/q}{V_{OC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.16</td>
<td>0.56</td>
<td>0.60</td>
</tr>
<tr>
<td>1.23</td>
<td>0.62</td>
<td>0.61</td>
</tr>
<tr>
<td>1.31</td>
<td>0.67</td>
<td>0.64</td>
</tr>
</tbody>
</table>

One can also observe that there is an increase in the slope of the J-V curve around $V_{OC}$ with increasing Ga content. This indicated that either the $R_s$ or the ideality factor ($A$) increases with increasing in the Ga content. At the same time, increase in either of these factors as well as the voltage-dependent current are also responsible for the decrease in the FF of devices with increasing Ga content in the absorber layer.

5.4.2 Quantum-Efficiency (QE) measurement

QE measurements were done on all the devices reported in Section 5.4.2 under standard conditions as described in Chapter 3 and Chapter 4. Current calculated from the QE measurement for all the devices reported in Figure 5-13 (or Figure 5-12) agrees well together, as expected from quality measurements. It is also visible in Figure 5-13 that the position of the zero QE (QE =0) towards the long wavelength shifts to the lower wavelength (or larger energy) which indicates that the band gap of the Cu(In,Ga)Se$_2$ increases with increasing Ga content. The band gap predicted from the QE is around 1070 nm, 1010 nm and 950 nm for Ga/(In+Ga) ratio of 0.30, 0.43 and 0.55 respectively.
The identical QE curves below 600 nm for all devices indicate that the optical losses due to the other layers of the solar cell stack are similar for all these devices. Correlating the QE curve around 900 nm with the reverse biased (light) J-V curve indicates that there are losses in the QE efficiency due to lower carrier collection. As explained in Section 5.4.2, these losses may be due to a low minority carrier diffusion length.

Figure 5-13  Quantum efficiency of devices fabricated from Cu(In,Ga)Se$_2$ thin films having Ga/(In+Ga) ratio 0.3, 0.43 and 0.55. These measurements were done at 0V of bias.

5.5 Conclusions

Cu(In,Ga)Se$_2$ films with different Ga at.% prepared by one stage co-evaporation process were studied by real time spectroscopic ellipsometry (RTSE) at high temperature
(570 °C) and ex-situ measurements done at room temperature were used to correlate the RTSE results. Also, for the first time we are reporting dielectric functions as well as different optical transition points at 570 °C for thin film Cu(In,Ga)Se2.

Compositions of these films were confirmed by EDS as well as AES measurements. Ga/(In+Ga) ratio in these films were also confirmed by XRD measurements. Real time spectroscopic ellipsometry (RTSE) measurement were done on each of the samples to find the growth process, thickness, roughness as well as shift in the critical points as a function of Ga content at 570 °C. Data analysis of the RTSE measurements revealed that irrespective of the Ga at.%, growth of the Cu(In,Ga)Se2 film at 570 °C follows a Volmer-Weber growth process. The same analysis also revealed that the surface morphology does not significantly change with the change in the Ga content. SEM and AFM surface images of these films confirm the ellipsometry results. RTSE measurements were also helpful in finding different critical points (CPs) at 570 °C in the Cu(In,Ga)Se2 thin films. At the same time, the analysis of the second derivative of the dielectric function also revealed that CPs shift towards high energy if the Ga content in the film increases which is in agreement with studies done at room temperature. As opposed to room temperature results, we were not able to resolve the E₀(A) and E₀(B) transition due to the negligible crystal field splitting. At the same time, we were able to find the spin-orbital splitting as a function of the Ga content. Also, the effect of the Ga content on the different device parameters were discussed using J-V and QE measurements. Again, these results will help in the future implementation of RTSE for control over the thin film Cu(In,Ga)Se2 deposition process.
Chapter Six

Study of the deposition of cadmium sulfide by chemical bath deposition on various substrates

6.1 Introduction and Motivation

Cadmium sulfide (CdS), with a band gap of around 2.4 eV [Hernandez-calderon et al., 2002] at room temperature, is a II-VI compound semiconductor. Cd rich CdS exhibits n-type conductivity due to the sulfur vacancies [Murai et al., 2005]. Depending on the thermodynamic conditions, CdS may have either hexagonal greenockite (wurtize) or cubic hawleyte (zincblende) crystal structures. Thin films of cadmium sulfide (CdS) have received considerable attention because of their applications in photovoltaics [Shafarman et al., 2003; McCandless et al., 2003], optoelectronics [Cao et al., 2007] and photonics [Li et al., 2005]. In photovoltaic, CdS is used as the n-type heterojunction partner to p-type Cu(In,Ga)Se2 or p-type CdTe. Due to its high band gap, it allows a high number of photons to reach the absorber layer as well as helps in efficiently separating the charge carriers created due to these photons. In photonics and optoelectronics, it is used to make optical switches, photocells, LEDs etc.

Many different n-type semiconductors have been used as heterojunction partners for Cu(In,Ga)Se2 solar cell applications [Hariskos et al., 2005]. But CdS thin films
deposited by chemical bath deposition (CBD) (which will be explained later in this Chapter) yield the most efficient Cu(In,Ga)Se₂ thin film based devices. It has been demonstrated that chemical bath deposited CdS has beneficial effect as heterojunction partner to Cu(In,Ga)Se₂ because: 1) it provides optimal band alignment, 2) it increases the excess carrier life time and 3) it has minimal lattice mismatch [Li et al., 1996; Schmid et al., 1996; Jones et al., 1975]. There are a variety of reasons to deposit CdS by chemical bath deposition. Not only the CBD is conformal for very thin films (50-100 nm) even on rough Cu(In,Ga)Se₂ but also produces epitaxial quality film due to its growth process [Kaur et al., 1980]. Also the CBD process helps in cleaning the Cu(In,Ga)Se₂ layers and in intermixing the Cd by chemically driven ion-exchange mechanism [Kessler et al., 1993; Lincot et al., 1992]. Even with all these beneficial effects of CdS deposited by CBD on Cu(In,Ga)Se₂, it is important to notice that it can also deteriorate the solar cell quality as well as lower the efficiency. Effectively, due to the absorption in the CdS layer at and below ~520 nm (corresponding to the CdS band gap of 2.4 eV), there is a loss of current in the solar cell which can be viewed in the QE curve. This loss in QE below the wavelength of 520 nm is increased with the increase in the CdS thickness due to the fact that the electron–hole pairs generated in the CdS are not collected [Shafarman et al., 2003]. At the same time, thinner CdS results into shunting of the device or in bad interface which also leads to loss in voltage or current. So there is a trade-off between loss in current due to absorption by thicker CdS and bad electrical properties of junction due to thinner CdS. The actual effect of CdS thickness on the solar cell is shown in Figure 6-1. Also the chemical bath deposition process is self limiting in the sense that the solution tends to saturate when 50 nm to 200 nm of CdS film is deposited.
Due to the saturation and the depletion of reactants, small colloids start to form on the substrate (here Cu(In,Ga)Se₂) or in the solution which leads to porous films.

Many studies have been done to understand the optical and electrical properties as well as the growth process of CdS deposited by CBD but none of them, to our best knowledge, were done on Cu(In,Ga)Se₂ substrate. In this chapter, we will present for the first time, ellipsometry studies of CdS films deposited by CBD on Cu(In,Ga)Se₂ substrate and will compare them to the growth of CdS on SiO₂ substrate. We will use other characterization techniques to corroborate the ellipsometry results.
6.2 Brief Overview of the chemical bath deposition technique

Chemical bath deposition (CBD) is a technique where films are grown on a solid substrate from a chemical reaction occurring in an aqueous solution. For example, CdS forms in the aqueous solution made of Cd salt, thiourea, NH₄OH and water. In the solution, the rate of chemical reaction should be controlled so that the CdS will: 1) either directly form and grow on the substrate; 2) or CdS will form in the solution itself and then diffuse towards the substrate to stick to the substrate or to the growing film. If the rate of reaction is not controlled then the final compound instead of forming a film will aggregate into larger particles in solution and precipitate out [Hodes, 2002].

Using formation of CdS as an example, there are two mechanisms for the formation of CdS thin film by CBD method. One is the ionic reaction of Cd⁺ and S⁻ and another is the decomposition of Cd(OH)₂ by sulphide. The first is called Ion-by-Ion mechanism [Kaur et al., 1980] and the other is called hydroxide cluster mechanism [Kitaev et al., 1965]. For these two mechanisms, the following equations can be written [Voss et al., 2004]:

- Formation of Cd ion
  \[ \text{CdSO}_4 \rightarrow \text{Cd}^{2+} + \text{SO}_4^{2-} \]

- Equilibrium of ammonium hydroxide
  \[ \text{NH}_4^+ + \text{OH}^- \leftrightarrow \text{NH}_3 + \text{H}_2\text{O} \]

- Cd complex formation
  \[ \text{Cd}^{2+} + n\text{NH}_3 \leftrightarrow \text{Cd}(\text{NH}_3)_n^{2+} \]

- Hydrolysis of thiourea
  \[ \text{CS(NH}_2)_2 \rightarrow \text{H}_2\text{S} + \text{CN}_2\text{H}_2 \]

\[ \text{H}_2\text{S} + 2\text{OH}^- \leftrightarrow 2\text{H}_2\text{O} + \text{S}^{2-} \]

The reaction between free Cd ions and free S ions defines whether the mechanism is Ion-by-Ion mechanism or hydroxide cluster mechanism.
In the Ion-by-Ion mechanism, free Cd$^{2+}$ and S$^{2-}$ diffuse to the substrate. Since the energy required to form an interface between the embryos (here nuclei of CdS) and the surface is lower than the one required to form CdS particles in the solution, nucleation of Cd and S ions on the surface result in CdS nuclei which further grow as CdS crystal according to the following equation:

$$Cd^{2+} + S^{2-} \rightarrow CdS(s)$$

On the other hand, in the hydroxide cluster mechanism, free Cd$^{2+}$ reacts with the hydroxide (OH) to form solid Cd(OH)$_2$ compound in the solution, according to:

$$Cd^{2+} + 2OH^- \rightarrow Cd(OH)_2$$

which then reacts with the S$^{2-}$ ion to form CdS:

$$Cd(OH)_2 + S^{2-} \rightarrow CdS + 2OH^-$$

Once Cd(OH)$_2$ forms in the solution, it can either diffuse to the substrate (forming CdS on the surface) or remains in the solution (forming CdS in the solution, which leads to large clusters). In the later mechanism since colloids form in the solution and then stick to the substrate surface, there is a small probability of change in crystal size with thickness. On the other hand, in the Ion-by-Ion growth, since the nucleation occurs on the substrate like chemical vapor deposition, it is most probable that the crystal size will increase with increasing thickness [Hodes, 2002].

### 6.3 Experimental set up

We compare growth and properties of thin CdS films deposited on Cu(In,Ga)Se$_2$/SiO$_2$/Si substrate and on SiO$_2$/Si substrate. During each set of experiments, fourteen 1" by 1" slides of the same substrate were dipped inside the chemical bath made of 0.1M of cadmium acetate [Cd(CH$_3$COO)$_2$] which is the source of Cd$^{2+}$ ions, 0.0015 M
of thiourea \([\text{CS(NH}_2\text{)_2}]\) which is the source of \(\text{S}^2\) and 1M of ammonium hydroxide (NH\(_4\)OH) which acts as catalyst. During the deposition, the bath temperature was kept at 60 \(^\circ\)C. Every 30 seconds, one slide was taken out of the bath, cleaned with deionized (DI) water and dried under Ar stream. Once all 14 slides were taken out, different measurements such as spectroscopic ellipsometry and AFM were performed.

### 6.4 Experimental Study of CdS films on SiO\(_2\) and Cu(In,Ga)Se\(_2\) substrates

#### 6.4.1 Phase identification

X–ray diffraction (XRD) in the \(\theta/2\theta\) scanning mode is generally used to identify the compound deposited on the substrates as well as the phase and the structure of the films. In \(\theta/2\theta\) mode, the angle of the x-ray source as well as of the detector is continuously varied so that the incoming x-ray beam on the sample exits the sample at an angle of 2\(\theta\) with respect to the incoming beam. The penetration depth of the x-ray in CdS, depending on the angle of incidence, is 10 \(\mu\)m to 100 \(\mu\)m [Birkholz, 2006]. Due to high angles of incidence in the \(\theta/2\theta\) mode, for thin films, peaks arising from the substrate rather than from the film are predominant. If the angle of incidence of the x-ray is kept low so that the path of the x-ray will attenuate before penetrating too deep into the substrate, then peaks arising from the film rather than from the substrate are predominant. This technique is called grazing incidence x-ray diffraction (GIXRD). During the data acquisition in the GIXRD mode, the angle of incidence is kept constant and the angle of detection is varied. Figure 6-2 illustrates the GIXRD spectra of a CdS film deposited on Cu(In,Ga)Se\(_2\) substrate as well as on SiO\(_2\) substrate. These data were taken on the CdS removed from the bath at the end of the deposition. As shown in Figure 6-2, GIXRD spectra on CdS deposited on either of the substrates have diffraction peak around \(2\theta = \)
26.5° which, when compared to the JCPDS data, can be associated with the (111) reflection of the cubic CdS or with the (002) reflection of the hexagonal CdS. Another two prominent peaks for CdS on Cu(In,Ga)Se₂ substrate are around 2θ = 28.2° which can be assigned to the (101) of the hexagonal CdS. At the same time, apart from the (111) cubic/(002) hexagonal peak, another prominent peak for both substrates is around 52° which can be assigned to the (311) reflection of the cubic CdS or the (112) hexagonal reflection.

![GIXRD spectra of CdS deposited by CBD on: a) Cu(In,Ga)Se₂/SiO₂/Si substrate and, b) SiO₂/Si substrate.](image)

In Table 6.2 below, reflection peaks for the XRD spectrum of the CdS deposited on SiO₂ and on Cu(In,Ga)Se₂ are summarized. Thus the GIXRD indicates that CdS grown on Cu(In,Ga)Se₂ seems to have predominantly an hexagonal lattice structure, while the ones grown on the SiO₂ seems to have either a cubic or a mixed cubic/hexagonal structure. As the cubic lattice structure of CdS is metastable and the hexagonal phase is stable [Zeleya-Angel et al., 1997], it has been often stated that the hexagonal CdS is preferred for Cu(In,Ga)Se₂ based solar cells [Oladeji et al., 2000; Wada et. al., 1997].
Table 6.1 GIXRD diffraction data for CdS grown on SiO$_2$ and CdS grown on the Cu(In,Ga)Se$_2$ substrate by chemical bath deposition.

<table>
<thead>
<tr>
<th>CdS on CIGS</th>
<th>CdS on SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.5° (111) Cubic</td>
<td>26.5° (111) Cubic</td>
</tr>
<tr>
<td>(002) Hexagonal</td>
<td>(002) Hexagonal</td>
</tr>
<tr>
<td>28.2° (101) Hexagonal</td>
<td>52.1° (311) Cubic</td>
</tr>
<tr>
<td>51.9° (311) Cubic</td>
<td>(112) Hexagonal</td>
</tr>
<tr>
<td>(112) Hexagonal</td>
<td></td>
</tr>
</tbody>
</table>

6.4.2 Growth of CdS on SiO$_2$

As mentioned earlier, fourteen 1" by 1" SiO$_2$/Si substrates were dipped in the chemical bath together and then taken out of the chemical bath at equal intervals of 30 seconds each. Just after being taken out and dried under Ar flow, ellipsometry measurements ($\psi, \Delta$) were done on each of the sample using variable angle rotating compensator multichannel spectroscopic ellipsometer in the energy range of 0.75 to 6.5 eV at four angles of incidence ($\theta_i$)= 55°, 65°, 75° and 85°. Also all these substrates were measured with the same ellipsometer under the same conditions before being submerged into the chemical bath. Thus the optical properties of each of the SiO$_2$/Si substrate were already known before the start of the CdS growth.

To extract the growth and optical functions of CdS deposited on the SiO$_2$/Si substrate, we first used spectroscopic ellipsometry measurements independently without any other ex-situ measurements and then correlated these ellipsometry results with the other ex-situ results. Since we did not know the nature of the growth, we used a generalized model in which the bottom layer is the fully characterized substrate, with a bulk CdS layer and a Bruggeman EMA layer composite of bulk CdS and void on top [Collins et al., (TSF)1998; Fujiwara et al., 2007]. Using this model, the imaginary part of
the dielectric function for CdS grown on the SiO₂ substrate (for different dip time) is plotted in Figure 6-3.

![Figure 6-3](image)

**Figure 6-3** Imaginary part of the dielectric function of CdS grown on SiO₂/Si substrates. The shift in the dielectric functions in the direction of the arrow indicates the dielectric function of the CdS grown for longer times.

As observed in Figure 6-3, as the time of the substrate inside the bath increases, the maximum amplitude of the imaginary part of the dielectric functions increases, while the onset of the absorption shifts towards lower energy. The bulk layer thickness \( t (d_b) \) and surface roughness layer thickness \( (d_s) \) extracted during the data analysis corresponding to the same data analysis is plotted in Figure 6-4. The bulk layer thickness of CdS corresponding to each of the above mentioned (Figure 6-3) imaginary part of the dielectric functions \( (\varepsilon_2) \) remained zero and only the EMA layer thickness increases. This
increase of the EMA layer thickness without any bulk layer thickness is the indication of a Volmer-Weber growth process.

![Graph showing the evolution of thickness over time.](image)

**Figure 6-4**  Bulk layer thickness ($d_b$) and surface roughness layer thickness ($d_s$) evolution of the CdS on the SiO$_2$ surface.

To extract the band gap of the CdS film as a function of time and to find the broadening and amplitude of the corresponding oscillator, the dielectric functions were fitted with an analytical model where each of the critical points was represented as [Leng *et al.*, 1998]:

$$
\varepsilon(\omega) = \varepsilon_0 + A_0 \left[ e^{i\phi} (\omega - \omega - i\Gamma)^{\mu} + e^{-i\phi} (\omega + \omega + i\Gamma)^{\mu} \right]
$$

where $A_0$ is the amplitude, $\phi$ is the phase, $\Gamma$ is the broadening and $\omega_g$ is the critical point frequency. For CdS in an energy range up to 6 eV, three CPs, one for the fundamental band gap and two are for higher transition have been reported [Ninomiya *et al.*, 1995].
The CPs corresponding to the higher transitions are very close to each other and are spin-orbital coupled. At the same time, they are broadened due to the small grains. It was therefore not possible to resolve them and we focused on the fundamental transition \( E_0 \) CP only. As shown in Figure 6-5, the band gap energy decreases as a function of time (or effective thickness) and approaches the value for bulk CdS as the effective thickness of the CdS increases. The effective thickness reported in Figure 6-5 is only due to the EMA layer, which indicates that these CdS were grown in form of crystallite cluster in which electrons are still partially or fully confined within the cluster. In these clusters, electrons are not fully delocalized and so the electronic spectra of these clusters are different from the bulk material [Rossetti et al., 1983; Brus, 1986], even though these clusters retain the crystal structure of the bulk [Brus, 1986]. This property of small semiconductor clusters of atoms to have different electronic structure compared to the bulk semiconductor may be attributed to quantum confinement. In this case, increase in the band gap energy with the decreasing \( d_{\text{eff}} \) of CdS thin films on SiO\(_2\)/Si substrate can be explained with the well known model of the "particle in a box" and the following equation [Brus, 1986]:

\[
E_{\text{confined}} = E_{\text{Bulk}} + \frac{\pi^2 \hbar^2}{2 \mu R^2}
\]  

(6.2)

where \( E_{\text{confined}} \) is the energy of the confined cluster, \( E_{\text{Bulk}} \) is the energy of the bulk semiconductor and the last term is the quantum energy of localization, \( \mu \) is the effective mass of the electron and hole and \( R \) is the particle size. In Equation 6.2, the Coulomb interaction is neglected for CdS which is a wide band gap semiconductor. For small band gap semiconductors, there is an extra term in Equation 6.2 due to the coulomb interaction [Brus, 1986]. As noticed from Equation 6.2, the quantization energy decreases with the
increasing cluster size and is cancelled for large particles. Thus Equation 6.2 is in good agreement with the finding of Figure 6-5.

![Figure 6-5](image)

**Figure 6-5** Magnitude of the fundamental band gap of the CdS films grown on SiO$_2$/Si substrate as a function of effective thickness.

A charged particle can be confined within a space if the band gap of the adjacent surface is much higher than the energy of the charge particle. To understand the quantum confinement in CdS grown on SiO$_2$ substrate, consider the motion of charge carriers in the direction normal to the plane of SiO$_2$. On the substrate side, since CdS were grown on 25 nm thick SiO$_2$, charged carriers in the CdS can not overcome the barrier height due to the large band gap ($\approx 9$ eV) of the SiO$_2$ nor tunnel through the sufficiently thick SiO$_2$. On the other side of the cluster, the vacuum provides a natural potential barrier. Thus, as long
as the small clusters are not touching each other, there is quantum confinement of carriers in the CdS on SiO$_2$.

![Graphs showing amplitude and broadening](image)

**Figure 6-6** Amplitude and broadening of the oscillators fitted at the CPs of Figure 6-5.

As shown in Figure 6-6, the broadening of the oscillator corresponding to the fundamental band gap decreases with the increasing $d_{\text{eff}}$ which is the indication of increase in the average grain size with increasing $d_{\text{eff}}$. As shown in Figure 6-6, the amplitudes of the dielectric functions are very low. The exact value of the amplitudes of the oscillators fitted at CP corresponding to the fundamental band gap of CdS for various thicknesses are plotted in Figure 6-6. It indicates that the absorption in these CdS thin films is very low. This low absorption by CdS thin films is also confirmed from the transmission spectra taken on glass slides. These glass slides were kept back to back along with SiO$_2$/Si substrates in the bath. In Figure 6-7, transmission spectra farthest from the arrow head is for the thinnest film (least $d_{\text{eff}}$ for Figure 6-3) which shows significant transmission above the band gap energy. The transmission spectra nearest to the arrow head is for the thickest film (maximum $d_{\text{eff}}$ for Figure 6-3) which also shows transmission above the band gap energy, even if lower than for the thinner films.
Transmission spectra of CdS thin films on glass substrates. These substrates were immersed in the bath at the same time as SiO₂/Si substrates of this section. The decrease in the transmission along the direction of the arrow is due to the increase in the \( d_{\text{eff}} \) (effective thickness).

For direct band gap semiconductors, the band gap can be extracted from transmission and reflection spectra by extrapolating the plot of \((h\nu)²\) vs. \(h\nu\) at a zero value of \((h\nu)²\). But for these thinner films (or CdS clusters), the density of states in the valence and conduction bands might be quite different than for the bulk [Hodes, 2002] and this extrapolation does not work as accurately, proving here also the value of spectroscopic ellipsometry.

The CdS grown on the SiO₂/Si substrates were also characterized by atomic force microscopy (AFM) in non-contact tapping mode to check the growth of CdS after various dipping times. Figure 6-8 shows some of these AFM images and clearly indicates that the
CdS initially grows in small clusters, which then become larger and finally start touching each other. This is in excellent agreement with the SE results.

Figure 6-8  AFM images of CdS thin films deposited on SiO₂/Si substrate. Dipping time increases from a to d.

6.4.3 Growth of CdS on Cu(In,Ga)Se₂

Ellipsometry measurements were taken on Cu(In,Ga)Se₂/SiO₂/Si substrates as they were removed from the chemical bath as described previously. Ellipsometry measurements were also done on these Cu(In,Ga)Se₂/SiO₂/Si substrates before immersing them into the bath to know the material properties of these layers beforehand. An optical model, shown Figure 6-8, was used to extract the thickness, roughness and dielectric constants of the deposited CdS. Since the roughness of the Cu(In,Ga)Se₂ was of the order of 15 nm, an intermix layer of bulk CdS and bulk Cu(In,Ga)Se₂ was necessary here.
Using the model described in Figure 6-9, bulk layer thickness \( (d_b) \) and roughness layer thickness \( (d_s) \) were obtained for different immersion time. The intermixed layer (CIGS/CdS) thickness \( (d_i) \) was kept constant at 15 nm (roughness of the CIGS layer). The CdS fraction in the EMA layer of CIGS/CdS was varied. For sample with dip time up to 2 min, this void fraction was less than 0.5 and the surface roughness (EMA of CdS/Void) and bulk layer thickness of CdS remained zero. At 2 min, the CdS fraction in EMA of CIGS/CdS became 0.5 and the surface roughness thickness started to rise. The bulk (CdS) thickness \( (d_b) \) and surface roughness \( (d_s) \) calculated for each of these films by removing the substrate related artifacts in the dielectric function [Nguyen et al., 1993; Arwin et al., 1984] are reported in Figure 6-10. Figure 6-10 shows that a surface roughness of around 10 nm appears before the thickness of the bulk layer starts to increase, which is the indication of a Volmer-Weber growth process.

**Figure 6-9** Optical model to extract thickness, roughness and dielectric function of CdS on Cu(In,Ga)Se\(_2\)/SiO\(_2\)/Si substrate.
Figure 6-10  Bulk layer thickness ($d_b$) and surface roughness layer thickness ($d_s$) evolution of the CdS on the Cu(In,Ga)Se$_2$ surface.

Figure 6-11  Dielectric function of CdS on Cu(In,Ga)Se$_2$ for two different effective thicknesses (broken line: 24 nm; solid line: 50 nm).
At the same time as the different thicknesses were calculated, the complex
dielectric functions of CdS were extracted. The dielectric functions for CdS grown on
Cu(In,Ga)Se₂ substrate are reported in Figure 6-11 for two different times of immersion.
To extract the band gap of the CdS film as a function of time and to find the broadening
and amplitude of the corresponding oscillator, the dielectric functions (corresponding to
various dip time) were fitted with an analytical model represented by Equation 6.1. Apart
from the fundamental band gap, CdS has two additional critical points around 5 eV due to
spin-orbital interactions [Ninomiya et al., 1995]. However, these two CPs are close one
to another and broad due to the very small grains, so it was impossible to resolve them (as
observed in Figure 6-11). For this work, we therefore focused on the fundamental
transition (E₀) CP only. In Figure 6-12, the band gap of CdS grown on Cu(In,Ga)Se₂
substrates for different dip time is plotted with respect to the effective thickness of CdS. As observed in Figure 6-12, there is not any significant shift in the band gap energy with the CdS effective thickness. This observation is opposite to what we saw for CdS on SiO₂ substrate, where the band gap shifted with effective thickness. Since the growth of CdS on soda lime glass (SLG) is totally different than the one on Cu(In,Ga)Se₂ substrate, the transmission measurement (plotted in Figure 6-6) was not helpful in correlating the band gap calculated from ellipsometry measurements.

![Figure 6-13](image)

**Figure 6-13** Amplitude and broadening of the oscillators fitted at the CPs of Figure 6-12.

The amplitude and broadening of the oscillators corresponding to the band gap energy reported in Figure 6-12 are plotted in Figure 6-13. As explained in Chapter 4, under some assumption, the grains size in the thin film is inversely proportional to the broadening. The decrease in the broadening as observed in Figure 6-13 indicates that the average grain size increases as the dip time of the substrate increases. The exact value of the amplitudes of oscillators fitted at CP corresponding to the fundamental band gap of CdS for various thicknesses are plotted in Figure 6-13. Comparison of the amplitude of the Figure 6-12 and Figure 6-6 indicates that the absorption in the CdS on the
Cu(In,Ga)Se₂ substrate was higher than for the CdS on the SiO₂ substrate. This higher value of the amplitude may be contributed to the compact CdS layers on the Cu(In,Ga)Se₂ substrate.

Figure 6-14  AFM images of CdS thin films deposited on Cu(In,Ga)Se₂/SiO₂/Si substrate. The substrate was inside the bath for longer time as we move from “a” to “d”.

The decrease in the surface roughness with the increasing dip time (observed in Figure 6-10) can also be corroborated with AFM measurements. The AFM images of CdS on Cu(In,Ga)Se₂ surface for different dip time are shown in Figure 6-14. As explained in Chapter 4 and Chapter 5, the RMS surface roughness from AFM measurement is not the same as the one from ellipsometry measurements, but has a similar trend. An approximate linear relation \(d_i(SE) = 4.01d_{rms} - 11.09 \text{ nm}\) was found between the roughness extracted by these two measurements. This type of relation was reported for other semiconductors but with smaller slopes [Fujiwara, 2007; Li, 2010].

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The reason for the higher slope here may be due to the small AFM scan area [Fujiwara, 2007].

6.4.4. Comparison between the two substrates

The comparison of \((d_b,d_s)\) plot of Figure 6-4 and Figure 6-10 indicates the formation of more compact and thicker CdS film on Cu(In,Ga)Se\(_2\) surface compared to the SiO\(_2\) surface. Effectively, one has to remember that only half of the thickness for \(d_s\) counts toward the final thickness of the film, leading therefore to a final film thickness of 25 nm on SiO\(_2\) versus 48 nm on Cu(In,Ga)Se\(_2\), which also means a rate twice as fast on Cu(In,Ga)Se\(_2\) since these films were deposited in the same amount of time. This difference in the growth of CdS may be attributed to the substrate morphology on which CdS grows. The AFM images of the Cu(In,Ga)Se\(_2\) and SiO\(_2\) surface are presented in Figure 6-15 and revealed that the surface roughness (or contact surface area) of the Cu(In,Ga)Se\(_2\) film is higher than the SiO\(_2\) surface. The relation between the nucleation rate and the contact surface area is given by [Rieke et al., 1993]:

\[
\frac{d(CdS)}{dt} = K A^n
\]

(6.3)

where the left hand side is the CdS nucleation rate, \(K\) is some constant which depends on \(Cd^+\) and \(S^-\) concentration [Rieke et al., 1993], \(A\) is the surface area in contact with the liquid and \(n\) is the surface geometry factor. According to Equation 6.3, in the case of the Cu(In,Ga)Se\(_2\) surface, the CdS nucleation rate can be higher due to the larger surface area. At the same time, the lattice mismatch between CdS and Cu(In,Ga)Se\(_2\) is small (< 7\%) which also provides a larger number of nucleation sites [Gaiduk et al., 2008]. Due to the large number of nucleation sites, the nucleation centers are close one to another which leads to faster coalescence and to higher growth rate.
At the same time, the grains size of the CdS grown on SiO$_2$ and on Cu(In,Ga)Se$_2$ can be compared. If the broadening reported in Figure 6-12 and in Figure 6-5 are compared, one can see that the broadening for CdS films on SiO$_2$ is smaller than for Cu(In,Ga)Se$_2$. As explained in the literature for the PbS growth on different surfaces [Gaiduk et al., 2008], the growth of thicker film results into smaller grain size compared to thinner (and spatially separated) film. This confirms that due to the faster growth of the CdS on the Cu(In,Ga)Se$_2$ surface, the average grain size of CdS on the Cu(In,Ga)Se$_2$ substrate is smaller compared to the SiO$_2$ substrate. This observation was also confirmed by the GIXRD measurement. The full width at half maximum (FWHM) of the (112) hexagonal/ (311) cubic peak were 0.020 radians and 0.017 radians, indicating the grains size of approximately 9 nm and 12 nm for CdS on Cu(In,Ga)Se$_2$ and on SiO$_2$ respectively.

### 6.5 Conclusions

In this chapter, we reported for the first time ellipsometry study of the growth of CdS by chemical bath deposition process (CBD) on a Cu(In,Ga)Se$_2$ substrate. Also we used this opportunity to compared the growth of CdS on the rougher Cu(In,Ga)Se$_2$ surface to the growth of CdS on smoother surface like SiO$_2$. 
The XRD and GIXRD analysis indicates that the CdS grown on Cu(In,Ga)Se₂ have predominantly an hexagonal lattice structure, whereas the CdS on the SiO₂ have predominantly a cubic structure. On the other hand, spectroscopic ellipsometry analysis in corroboration with the AFM measurement indicates that the morphology and the growth of the CdS layers strongly depend on the nature of the substrate. The growth of CdS on the SiO₂ substrate leads to spatially separated clusters, whereas the Cu(In,Ga)Se₂ substrates were covered by compact CdS layers. These spatially separated clusters lead to quantum confinement as observed by ellipsometry. Also, the CdS deposited on Cu(In,Ga)Se₂ substrate were thicker than those deposited on SiO₂. The ellipsometry analysis revealed that the average grain size for the CdS deposited on the Cu(In,Ga)Se₂ substrates was smaller than the one deposited on the SiO₂ substrates. We think that the reason for the different growth mechanism is due to the surface morphology of the Cu(In,Ga)Se₂, which provides a larger number of nucleation and growth sites compared to the SiO₂ substrates.
Chapter Seven

Conclusions and Future Considerations

1-stage, 2-stage and 3-stage co evaporation processes were used to deposit thin films of Cu(In,Ga)Se₂ for high efficiency photovoltaic devices. Among these three processes, the 3-stage process proved to be the best for growing device quality Cu(In,Ga)Se₂ thin films. Material properties of Cu(In,Ga)Se₂ thin films deposited by 1-stage, 2-stage and 3-stage processes were examined and compared using different optical and electrical characterization techniques such as spectroscopic ellipsometry (SE), Auger electron spectroscopy (AES) etc. SE helped in finding the band gap, thickness and roughness of films deposited by 2-stage and 3-stage process. By analyzing the SE data, we were able to find the Ga grading in CIGS thin film deposited by 3-stage process. This is the first time that SE data was used to extract a Ga grading and this was in good agreement with AES data. Analysis of SE data indicated that there was loss of signal in case of measurement performed on the CIGS thin film deposited by 1-stage process. We concluded that this loss of signal was due to the high surface roughness of CIGS grown by 1-stage process. Atomic force microscopy measurement on this film revealed that the surface roughness was around 80nm. The solar cells processed from these films were also characterized to compare the efficiency, voltage and current. Current-voltage and
quantum efficiency measurements on these solar cells helped us in understanding the reason for different efficiencies for devices processed from 1-stage, 2-stage and 3-stage processes. We concluded that the grain size, better interface between CIGS and n-type CdS as well as Ga grading were some of the reasons for better efficiency of solar cells processed from CIGS deposited by 3-stage process.

The inability to extract any information from SE data taken on CIGS deposited by 1-stage process, as well as our future goal to use the spectroscopic ellipsometry for monitoring and controlling the CIGS growth, motivated us to use real time spectroscopic ellipsometry (RTSE) studies of CIGS thin films deposited by 1-stage co evaporation process as a function of Cu at.% and Ga at.%.

Series of polycrystalline CIGS were deposited on 25 nm thermal oxide covered crystal Silicon substrates by 1-stage co evaporation process. During all these depositions, spectroscopic ellipsometry data were acquired. To study the effect of Cu at.% on the properties of CIGS, Ga/(In+Ga) ratio in all these CIGS films were kept constant and only Cu at.% were varied. Irrespective of Cu at.%, the initial nucleation stages of these films show island growth or the Volmer-Weber (V-W) process. Bulk layer and surface roughness thickness extracted from RTSE data analysis were confirmed by other ex-situ techniques such as atomic force microscopy (AFM), i.e. decrease in the surface roughness with increase in the Cu at.% in the CIGS film. The roughness from AFM measurements were not exactly the same as the one from RTSE but followed the same trend.

To find the shift in the critical points (CPs), change in broadening etc., the dielectric functions extracted from RTSE modeling were analyzed by fitting critical point parabolic
oscillators in the second derivative of the dielectric function. We found that there was not any significant shift in the CPs when Cu at.% in the CIGS film varies from 22.5 to 27.5. The broadening of these CPs decreased as Cu at.% increased in the CIGS thin film. If the broadening in the oscillator was due to the grain boundaries then the reason for this decrease in the broadening was an increase in the grain size. Fitting of the Drude oscillators in these dielectric functions below the band gap allowed us to distinguish the Cu-rich phase of the CIGS from the Cu-poor phase of CIGS. The findings of RTSE were corroborated by different ex-situ characterization techniques such as scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), etc. This correlation of the RTSE results with these well established ex-situ techniques confirmed the accuracy of the RTSE. We also concluded that the carrier density increased in the CIGS thin film with increasing Cu at.% in the Cu poor film; this also induces an increase of the efficiency.

For RTSE study of the effect of Ga at.% on the CIGS thin films, series of polycrystalline CIGS were deposited on 25 nm thermal oxide covered crystal Silicon substrates by a 1-stage co-evaporation process. Cu at.% in these films was kept constant at 23.5 while Ga/(In+Ga) ratio was varied between 0.0 to 0.55. The RTSE data were acquired during all of these depositions. Irrespective of Ga at.%, the initial nucleation stages of these films showed island growth or the Volmer-Weber (V-W) process. For each of these films, bulk layer and surface roughness thickness extracted from RTSE data analysis were confirmed by profilometry and atomic force microscopy (AFM). The roughness from AFM measurements was not exactly the same as the one from RTSE but followed the same trend, i.e. no effect of the Ga/(In+Ga) ratio on the roughness of the
CIGS. To find the shift in the critical points (CPs), change in broadening etc., the dielectric functions extracted from RTSE modeling were analyzed by fitting the critical point parabolic oscillators in the second derivative of the dielectric function. From these analyses, we found that the CPs shifted towards high energy as the Ga/(In+Ga) ratio increases from 0.0 to 0.55. This result was consistent with the earlier finding at room temperature. This analysis of the dielectric function helped in identifying several new CPs (these CPs were not identified earlier even at room temperature) corresponding to higher energy transitions. We were not able to resolve the $E_0(A)$ and $E_0(B)$ transition due to the negligible crystal field splitting. At the same time, we were able to find the spin-orbital splitting as a function of the Ga content. We also found that for a given Ga/(In+Ga) ratio, there was shift in the band gap when comparing room temperature and 570 $^\circ$C. This effect motivated us to compare the CPs of CuInSe$_2$ (CIS) at two different temperatures i.e. room temperature and 570 $^\circ$C. To understand the effect of Ga at.% on the solar cell performance, CIGS films were deposited on Mo coated soda lime glass and processed for complete devices. J-V and QE measurements were performed on these devices. We found that the addition of Ga above the Ga/(In+Ga) ratio of 0.3 had a detrimental effect due to the increase in the defect densities.

As n-type heterojunction partner to p-type CIGS, optical and electrical properties of the CdS play a very important role in the CIGS based PV devices. First we studied the growth and material properties of CdS on the CIGS surface and then used this opportunity to compare the growth and material properties of CdS on the CIGS and SiO$_2$ surfaces. The XRD and GIXRD analysis indicates that the CdS grown on Cu(In,Ga)Se$_2$ have predominantly an hexagonal lattice structure, whereas the CdS on the SiO$_2$ have
predominantly a cubic structure. The spectroscopic ellipsometry data analysis revealed a quantum confinement in the case of CdS on SiO₂. No such effect was observed in the case of CdS on a CIGS surface. Also, the spectroscopic ellipsometry analysis in corroboration with the AFM measurement indicated that the morphology and the growth of the CdS layers are strongly dependent on the nature of the substrate. The growth of CdS on the SiO₂ substrate led to spatially separated clusters, whereas the Cu(In,Ga)Se₂ substrates were covered by compact CdS layers. We think that the reason for the different growth mechanism was the surface morphology of the Cu(In,Ga)Se₂, which provided a larger number of nucleation and growth sites compared to the SiO₂ substrates. Also, the CdS deposited on Cu(In,Ga)Se₂ substrate were thicker than those deposited on SiO₂. The ellipsometry analysis revealed that the average grain size for the CdS deposited on the Cu(In,Ga)Se₂ substrates was smaller than the one deposited on the SiO₂ substrates.

In this thesis, we were able to use ex-situ SE data analysis to distinguish between the Cu-rich and Cu- phase of CIGS. One of our goal is to find these phases by RTSE during the deposition, i.e. we have to develop a model so that we can distinguish Cu-rich and Cu-poor phases during the 2-stage and 3-stage process. For this modeling, we would have to develop a library of the dielectric functions of (In,Ga)₂Se₃ compound as well as of CIGS for a wide range of Cu concentration.
References

Abushama et al., 2001

Albin et al., 1991

Albin et al., (Solar cells) 1991

Al-Thani et al., 2002

Alonso et al., 2001

Alonso et al., 2002

An et al., 1990

Arwin et al., 1984

Barreau *et al.* 2009

Birkholz 2006

Bohm *et al.*, 1985

Brus, 1986

Cao *et al.*, 2007

Chaisitsak *et al.*, 2002

Chapin *et al.*, 1954

Chen *et al.*, 1980

Collins, 1990
Collins et al., 1998

Collins et al., (TSF)1998

Collins et al., 2001

Collins et al., 2005

Collins and Yang, 1989

Crisp et al., 2004

DOE, 2005

DOE, 2010

Dullweber et al., 2001

Durante Rincon et al., 2001

Eaton *et al.*, 2010

Feng *et al.*, 1989

Fujiwara *et al.*, 2000

Fujiwara 2007

Gabor *et al.*, 1994

Gabor et al, 1996

Geiss, 1992

Gödecke *et al.*, 2000

Gray, 2003
Green et al., 2010

Grimm et al., 1926

Guenter, 1990

Gaiduk et al., 2008

Han et al., 2005

Hariskos et al., 2005

Hegedus et al., 2004

Hermann et al., 2001

Hernandez-calderon 2002

Hodes 2002
Jackson 1999

Jaffe et al., 1983

Jaffe and Zunger, 1983

Jian Li, 2010

Jones et al., 1975

Kasap, 2005

Kaur, I., et al. 1980

Kawashima et al., 1998

Kazmerski et al., 1976

Kazmerski, 1983

Kazmerski, 2006
Kessler et al., 1993

Kessler et al., 2000

Kessler et al., 2001

Khallaf et al., 2008

Kim et al., 1995

Kitaev et al.1965

Kolodinski et.al, 1993

Leamy,1982

Lee et.al, 1998

Leng et al., 1998
Li et al., 1996

Li et al., 2005

Lincot et al., 1992

Lu et al., 2008

Lundberg, 2003

Lundberg et al., 2003

McCandless et al., 2003

Murai et al., 2005

Newman 1986

NREL AM1.5
URL: http://rredc.nrel.gov/solar/spectra/am1.5/

Naufi et al., 1984

Nguyen *et al.*, 1993
Nguyen, H.V., and Collins, R.W., "Finite-size effects on the optical functions of silicon microcrystallites: a real-time spectroscopic ellipsometry study."

Ninomiya *et al.*, 1995

Oladeji *et al.*, 2000

Park, 2000

Patterson, 1939

Paulson *et al.*, 2003

Philibert, 2005

PVCDROM
URL: http://pvcdrom.pveducation.org/index.html

Rau *et al.*, 1998

Rau *et al.*, 1999,

Rau *et al.*, 2000

Rau, 2001

Rau *et al.*, 2001

Repins *et. al.*, 2005

Rieke *et al.*, 1993

Rincon *et al.*, 1986

Rockett, 2005

Ross *et al.*, 1982;

Rossetti *et al.*, 1983

Ruckh *et. al.* 1996

Schock, 2004

Scholdstrom *et al.*, 2005

Schmid *et al.*, 1996

Schroder, 2006

Scofield *et al.*, 1994

Scofield *et al.*, 1995

Shafarman *et al.*, 1996

Shafarman *et. al.*, 2003

Song *et al.*, 2004

Stewart et. al. 1987

Suri et al. 1989

Suryanarayana et al., 1998

Sze, 1981

Tarrant et al. 1993

Tell et. al. 1975

Tennakone et al. 2001

Tisdale et al., 2010

Turcu et al., 2006
Tuttle et al., 1993

Vickerman, 1997

Voss et al., 2004

Wada et al., 1997

Wada et al., 2001

Wei et al., 1995

Wei et al., 1998

Wooten, 1972

Würfel, 2002

Yan 2001

Zeleya-Angel et al., 1997
Zeleya-Angel, O., Castillo-Alvarado, F.L., Avendano-Lopez, J.,

ZSW 2010
URL: http://www.zsw-bw.de/index.php?id=109&L=1