Electrochemical Synthesis and characterization of Copper Indium Gallium Selenide (CIGS) absorber layer for solar cells

A thesis submitted in partial fulfilment of the requirement
for the award of degree of

Masters of Technology

In

Metallurgical and Materials Engineering

Submitted by

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Odisha, India
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Certificate

This is to certify that the thesis entitled **"Electrochemical Synthesis and characterization of Copper Indium Gallium Selenide (CIGS) absorber layer for solar cells"** submitted by Rajneesh Pandey (213MM1473) in partial fulfillment of the requirements for the award of Masters of Technology in Metallurgical and Materials Engineering with specialization in "Metallurgical and Materials Engineering" at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university/Institute for the award of any Degree or Diploma.

Prof. Archana Mallik Date
Assistant Professor
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Place: Rourkela Rajneesh Pandey
Date: May 2015

Abstract:

The quest for searching alternative energy resource is of current interest due to the scarcity of the conventional energy sources, which are major pollutants of the atmosphere. Research on renewable energy has gained attention due to its advantageous features sides like no noise, impollutant, static working parts and long life time. The much matured technology in solar cells is silicon (Si). Thought it have gained a dominant place in commercial aspects, it recedes in terms of cost effective purification process, defect tolerance, Indirect band gap nature (less absorption coefficient), which made researchers to thin for a better alternative direct band gap semiconducting materials like CIGS and CdTe. CIGS have gained much attention in last two decades due to their high absorption coefficient (direct band gap nature). Photovoltaics utilizing CIGS (Copper indium gallium Selenide) material is considered to be the most efficient solar energy converter of any thin film device. They exhibit the potential to reduce the device fabrication cost when compared to Si-based solar devices. The high efficiency CIGS thin film solar cells 20.5% were reported by NREL (National Renewable energy laboratory,USA) for an aperture area of 1 cm^2. Very recently, featuring news release of Center for Solar Energy and Hydrogen Research Baden-Württemberg) of Stuttgart, Germany have reported 21.7% (0.5 Cm^2) as confirmed by Fraunhofer Institute for Solar Energy Systems ISE. Impressive efficiencies were also reported for mini-modules of CIGS devices of efficiency 18.7% (15cm^2).

The efficiency percentage motivates to give an impressive scope to explore about the material. All the reported high efficiency devices were fabricated by co-deposition technique (Physical Vapor Techniques). Inspite of high efficiency, the cost of production and mass production are the hurdles for the PVD technique. Electrodeposition is one of the promising deposition techniques, have achieved an efficiency of 12.25% and 10% for an area of 102 cm^2 and 1.07 m^2.

The work pertains to the electrodeposition of CIS/CIGS absorber layer using two and three electrode systems. From the linear sweep voltammetry (LSV), the bath composition and deposition potential were optimized for ternary system (CIS). Similar approach was extended to quaternary systems using cyclic voltammetry (CV). Using sodium dodecyl sulphate (SDS) as surfactant , it was found to be beneficial in obtaining crystalline and dense CIS/CIGS thin films which is confirmed by XRD and FE-SEM studies. From the preliminary experiments for CIS electrodeposition in a neutral electrolyte without any complexing agents, it was found that CIS can be conveniently co-deposited between the potential of -1 to -1.3 V. This proposed simplified bath scheme reduces the complexity in bath chemistry. The compositional analysis by EDS for CIS/CIGS absorbers deposited using two electrode system revealed that a potential higher than -2 V is required to obtain near stoichiometric CIS/CIGS films.

Keywords: CIS/CIGS, thin film, linear sweep voltammetry, cyclic voltammetry, Chronoamperometry, X-Ray Diffraction, EDS

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Chapter – 1

Introduction

The present work has been carried out with an aim of synthesis, fabrication and characterization of CIGS solar thin films using electrodeposition technique and study nucleation and growth mechanism, electrochemical behavior of the CIGS thin film

1. Introduction

Since the last two decades with the advancements in technology and growing industrialization, energy requirements has been increasing day by day all over the world. Presently our main resources for power generation are mainly fossil fuels, hydro power and nuclear technology. But the most important and common drawback between all these is that they are available in limited quantities for a particular span of time, and also the pollution which is quite concerning nowadays. With increasing requirement of energy resources we need to find a stable and reluctant source of power generation which can fulfill the utmost requirements in need. Renewable resources for power generation are best match for the long term availability and negligible pollution content. While looking forward in renewable source of energy resources among wind, tidal, geothermal, solar, etc. Sun is the most promising source of energy resource, since wind is irregular and varies between places to places with respect to time also geothermal hotspots are not available all around the globe and tidal energy can only be utilized near coastal areas. On the other hand solar source which is available all around the planet for almost 10 hours a day can be accessible easily. The sun continuously supplies about 1.2×1025 terawatts of energy which is very much greater than any other renewable or non- renewable sources of energy can provide. This energy is much greater than the energy required by human beings which is about 13 terawatts. By covering 0.16% of Earth's land with 10% efficient solar cells would provide 20 Terawatts of energy about twice of fossil fuel consumption of the world including numerous nuclear fission reactors. More than 80% of the power consumption is based fossil fuels. Threat for the fast depleting, nature pollutants and cost effective of the fossil fuels gave significant importance for the alternative green energy resources, such as fuel cells and solar cells[1]

The much matured technology in solar cells is silicon (Si) based solar cells. Thought it has gained a dominant place in commercial aspects, it recedes in terms of cost effective purification process, defect tolerance, Indirect band gap nature (less absorption coefficient), which made researchers to thin for a better alternative direct band gap semiconducting materials like CIGS and CdTe. CIGS (Copper indium gallium Selenide) have gained much attention in last two decades due to their high absorption coefficient (direct band gap nature). Photovoltaics utilizing CIGS material is considered to be the most efficient solar energy converter of any thin film device. They exhibit the potential to reduce the device fabrication cost when compared to Si-based solar devices. The high efficiency CIGS thin film solar cells 20.5% were reported by NREL (National Renewable energy laboratory,USA) for an aperture area of 1 cm^2[2]. The efficiency percentage motivates to give an impressive scope to explore about the material. All the reported high efficiency devices were fabricated by co-deposition technique (Physical Vapor Techniques). Inspite of high efficiency, the cost of production and mass production are the hurdles for the PVD technique. Electrodeposition is one of the promising deposition techniques, have achieved an efficiency of 12.25% and 10% for an area of 102 cm2 and 1.07 m2. The proposed work will be an attempt to electrochemically synthesize CuInGaSe2 (CIGS) thin films from a single bath using CIGS chloride precursors as starting materials.

1.1 Motivation

Polycrystalline thin film solar cells such as $CuInSe_2$ (CIS) and $CuInGaSe_2$ (CIGS) compound semiconductors are important for terrestrial applications because of their high efficiency, long-term stable performance and also potential for the low cost production. Since they have high absorption coefficient $\sim 10^5$ cm^{-1} even a thin layer of approx. ~1μm is sufficient to absorb the useful part of solar spectrum. Electrodeposition is simple and cost effective than other vacuum based deposition techniques. The objective of the project is to obtain CIS/CIGS semiconducting thin films of better morphology and good stoichiometric. The optimization studies were carried at different bath concentration, potential along with an SDS (sodium dodecyl sulphate) surfactant as an extra additive. An attempt to deposit CIS thin films in neutral electrolyte have also been done in this work.

1.2 Objectives

This project is an attempt to synthesize and optimize the CIS/CIGS absorber layer to obtain a good stoichiometric thin film in order to make a high efficiency solar cell device. Fabrication of CIS/CIGS absorber layer is carried by electrodeposition route at different deposition potentials.

The objective of this project work is summarized as follows:

- To obtain good quality CIS/CIGS absorber layer thin film by one step electrodeposition route.
- To study the electrochemical behavior of CIS/CIGS absorber layer via electrodeposition route without using any complexing agents.
- To optimize the CIS/CIGS thin film composition at different deposition potentials in order to obtain good stoichiometry.
- To study the effect of using SDS in bath solution on the morphology of CIS/CIGS absorber layer.
- An effort to optimize CIS absorber layer in neutral bath solution without using additives.
- Understanding the kinetics of nucleation and growth mechanism of CIS/CIGS deposition route with the help of chronoamperometric studies.

1.3 Thesis Outline

The present work has been carried out with aim of synthesis, fabrication and characterization of CIGS solar thin films using electrodeposition technique and study nucleation and growth mechanism, electrochemical behavior of the CIGS thin film.

Chapter 2 is about the literature specified on the different solar technologies, CIGS thin film and its properties, different preparation methods, electrodeposition principle, advantages of electrodeposition over other methods, different techniques to characterize solar thin films, electrochemical study using cyclic voltammetry and Chronoamperometry. This chapter concludes about the aim of the project work.

Chapter 3 gives the detail description of experimental method used to electrodeposit CIGS thin film; electrochemical behavior and synthesis of CIS/CIGS thin film have been described in Linear sweep voltammetry, cyclic voltammetry and Chronoamperometry studies. X-Ray diffraction (XRD) technique carried out for the phase analysis of thin film has been given in detail. Morphological structure of thin films has been observed in FESEM and described in this chapter along with the compositional details of as deposited CIS/CIGS thin film.

Results have been described and discussed in detail in chapter 4, electrochemical behavior, electrodeposition mechanism and nucleation and growth mechanism of CIS/CIGS absorber layer has been studied using Linear sweep voltammetry, Cyclic voltammetric and Chronoamperometry analysis and their results have been interpreted on this chapter. This chapter includes the result from phase analysis done using XRD technique. Structural and compositional study results carried out in FESEM have been illustrated in this chapter.

Detail results have been illustrated and conclusive remarks were included in chapter 5. References has been included that supported the study and results inscribed in the preparation of the thesis.

Chapter – 2

Literature Survey

This chapter covers the literature specified on the different solar technologies, CIGS thin film and its properties, different preparation methods, electrodeposition principle, advantages of electrodeposition over other methods, different techniques to characterize solar thin films, electrochemical study using cyclic voltammetry and Chronoamperometry. This chapter concludes about the aim of the project work

2. The quest for Alternative energy sources:

Human civilization is completely dependent on energy conservative atmosphere nowadays harnessing energy resources provided by Mother Nature. We are utilizing energy resources in every possible way weather it is in the form of renewable or non-renewable, but the larger share goes to non-renewable sources due to their greater effectiveness and energy output with respect to renewable sources. On the serious note this dependency on non-renewable sources like fossil fuels, nuclear materials has led us to shortage of these resources and also degrading our own environment due to pollution caused in the process of generation of this energy. For the sake of our future generation we have to look for alternative source of energy which is available easily and also have little or no effect on environment, this decision is also taken jointly by 172 governments in United Nations Conference on Environment and Development (UNCED) or Earth summit held in the year 2012 where among various environmental issues an issue has been considered to replace the fossil fuels by alternative source of energy [3]

Alternative sources of energy are present in abundant amount in our planet irrespective of availability all around the globe. On looking forward to such reliable and easily available source, solar energy had been proven effective and reliable in spite it is easily available to grasp directly. The potential of solar energy (Fig. 2.1) that we receive per year is around 23000 TW/year which is more than twice we extract from fossil fuels. Solar energy is directly harnessed from the sun light falling in our environment and is utilized either in active form or in passive form. In active form it is directly utilized for solar water heating, concentrated solar power, whereas solar devices are classified as passive form of utilizing sunlight to generate electricity.

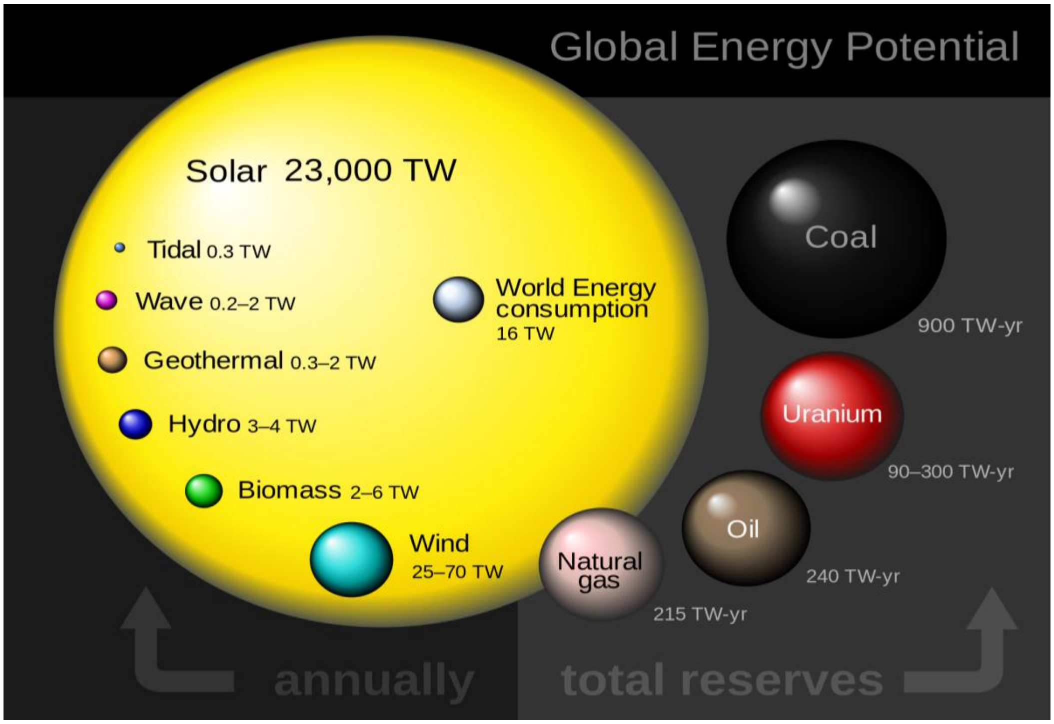

Figure 2.1: Global renewable energy distribution showing individual capacity

2.1 Introduction to solar energy and Solar photovoltaic cell

A Solar cell is a light driven battery. A constant current is obtained when the light is illuminated. The working of solar cells can be explained by 4 steps.

1. Light illumination
2. Electron-hole pair generation
3. Charge separation
4. Charge transportation

The wavelength of the sunlight incident at the earth atmosphere ranges from 200 to 2500 nm. Of this, the wavelength region between 200 nm to 1043 nm contains high energetic radiations. This reason restricts the semiconducting materials in solar cells to have an optimal band gap (Eg) of 1.15 eV. In an ideal case if an incoming photon has an energy $h\nu<E_{gap}$ the no photo generation

will takes place, whereas all the incident light coming with the energy $h\nu=E_{gap}$ will each contribute to the photo generation of electron-hole pairs. The excess photon energy ($h\nu>E_{gap}$) will be lost in the form of heat[4]. A solar power field is shown in Fig. 2.2.

1. 

Figure 2.2: Solar panels established in large field

Solar photovoltaic cells are mainly classified into two group i.e.

1. Bulk (Crystalline Si cells) and
2. Thin film solar cells

2.1.1 Bulk solar films

Crystalline Si cells are most prevalent bulk material for solar cells also called "solar grade silicon" [5](fig. 2.3). They are basically traditional, wafer based cells made of conventional crystalline Si are commercially predominant photovoltaic cell technology. The thickness used for fabrication of Si-based solar cells usually ranges in 300µm. Since silicon exhibits poor defect tolerance, the fabrication process is not cost effective and often to be carried at clean room environment.

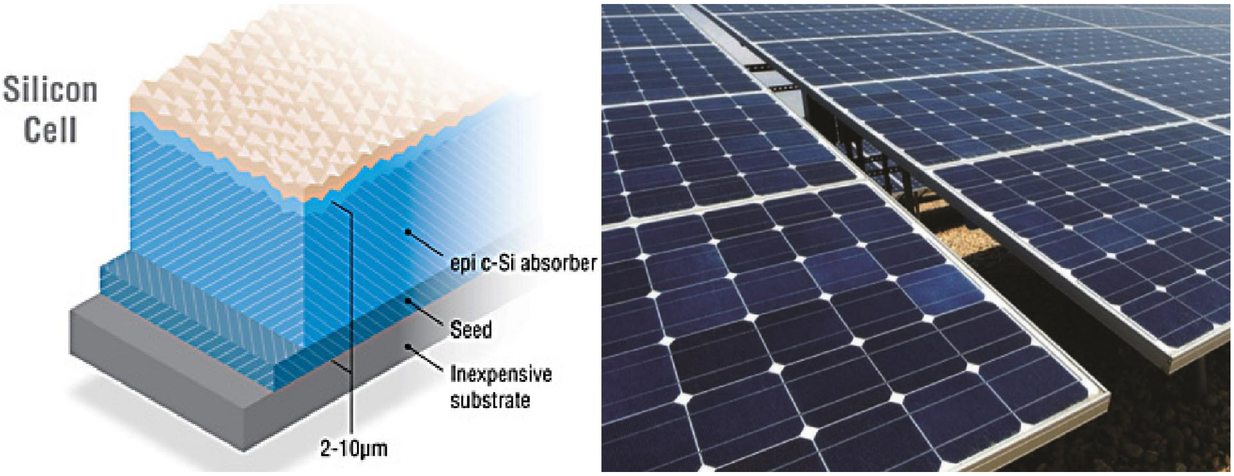

Fig 2.3: Schematic of Si based solar cell (left) and a well-established bulk sonar panel field (right)

Table 2.1: PV summary –Advantages of thin film PV devices over Si

	a-Si	CdTe	CIGS
Best research efficiency	13.4%	19%	20.4%
Best solar module efficiency	8.1%	14.4%	14.5%
Thin film market share	32%	43%	25%
Advantages	Matured technology, Excellent for small devices (calculators)	Low cost manufacturing Fabrication can be carried in glass & flexible substrates	High efficiency Fabrication can be carried in glass & flexible substrates
Disadvantages	Low efficiency & High cost equipment	Medium efficiency & Cadmium is toxic	• Market share expected to grow • Only less Cadmium is required than CdTe Solar cells
Major manufactures	Sharp solar	First Solar	Solar Frontier

2.1.2 Thin film solar cell

A thin-film solar cell (TFSC) is a second generation solar cell that is made by depositing one or more thin layers, on substrates, such as glass, plastic or metal. The Film thickness varies from a few nanometers (nm) to tens of micrometers (µm), much thinner than thin-film's rival technology, the conventional, first-generation crystalline silicon solar cell (c-Si) that uses silicon wafers of up to 200-300 µm. This allows thin film cells to be flexible, lower in weight, and have less drag. It is used in building integrated photovoltaics and as semi-transparent, photovoltaic glazing material that can be laminated onto windows. Fig. 2.4 shows the comparison of CIGS absorber with other thin film materials.

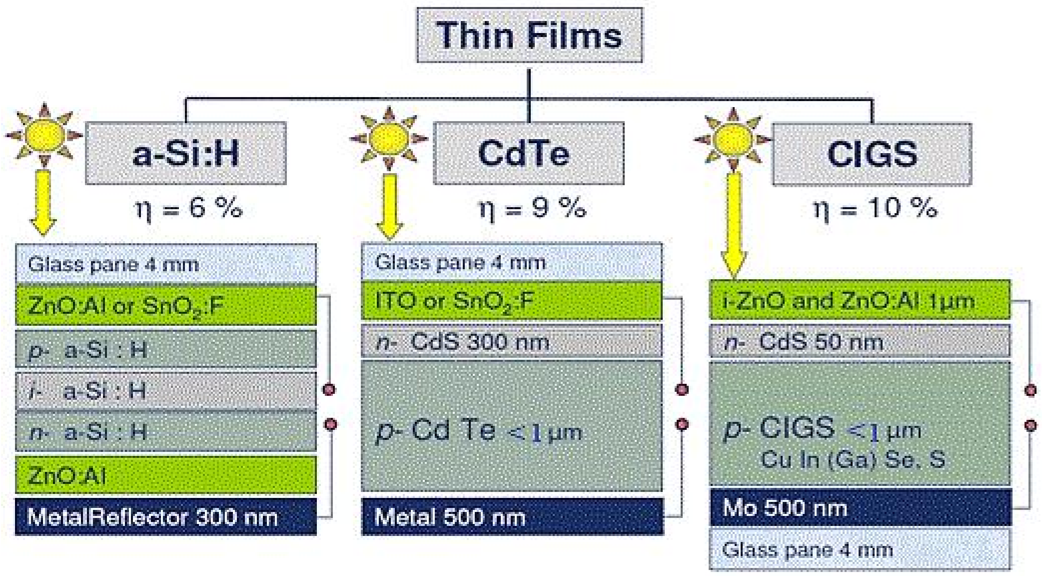

Figure 1.4: Shows specification and type of solar thin films

Thin-film has always been cheaper but less efficient than conventional c-Si technology. However, they significantly improved over the years, and lab cell efficiency for CdTe and CIGS are now beyond 21 percent, out-performing multicrystalline silicon, the dominant material currently used in most solar PV systems. Despite these enhancements, market-share of thin-film never reached more than 20 percent in the last two decades and has been declining in recent years to about 9 percent of worldwide photovoltaic production in 2013.

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Already commercialized PV modules are compared in the aspect of advantages and their market values in the table1 till 2011. An Indo-US Collaborative program for solar cell research have been initiated recently, program named "SERIIUS". One of the research thrust is developing & processing of low cost CIGS thin film solar cells by ink printing technique [7]

2.2 Copper Indium Gallium Selenide (CuInGaSe2)

CIGS is a chalcopyrite alloy of CIS (CuInSe) and CGS (CuGaSe). The chemical formula for the compound is $CuIn_xGa_{(1-x)}Se_2$ where x varies from 1 (CuInSe) to 0 (CuGaSe)[8]. The highest solar cell efficiency recorded is 20% with 0.5 cm^2 area which is fabricated by National Renewable Energy Laboratory (NREL) [9]. In the figure 2.5 progress report of solar cell technologies are shown till year 2010 where we can see that in thin film technologies $Cu(InGa)Se_2$ is the most efficient thin film technology but it's growth rate with time have become somewhat constant that means there's no considerable improvement took place since year 2004. For CIGS, the period from 2004 to till date concentrates much more on materials property rather on efficiency. $CuInGaSe_2$ solar cells have resistance towards high energetic radiations when compared to crystalline silicon solar cells [10]. This feature enables its application for making lightweight absorber layer on flexible substrates which seems promising for space applications. There is a huge scope in CIGS based thin film technology in comparison to other technologies due to following main reasons:

- High absorption coefficient (~ 10^5 cm^{-1})
- Low production cost
- Tunable band gap (from ~1 to 1.7 eV)
- Shows a high tolerance against defects
- Long term opto-electronic stability
- High radiation resistance
- Minimal amount of material required and high efficiency compared to other thin film technologies

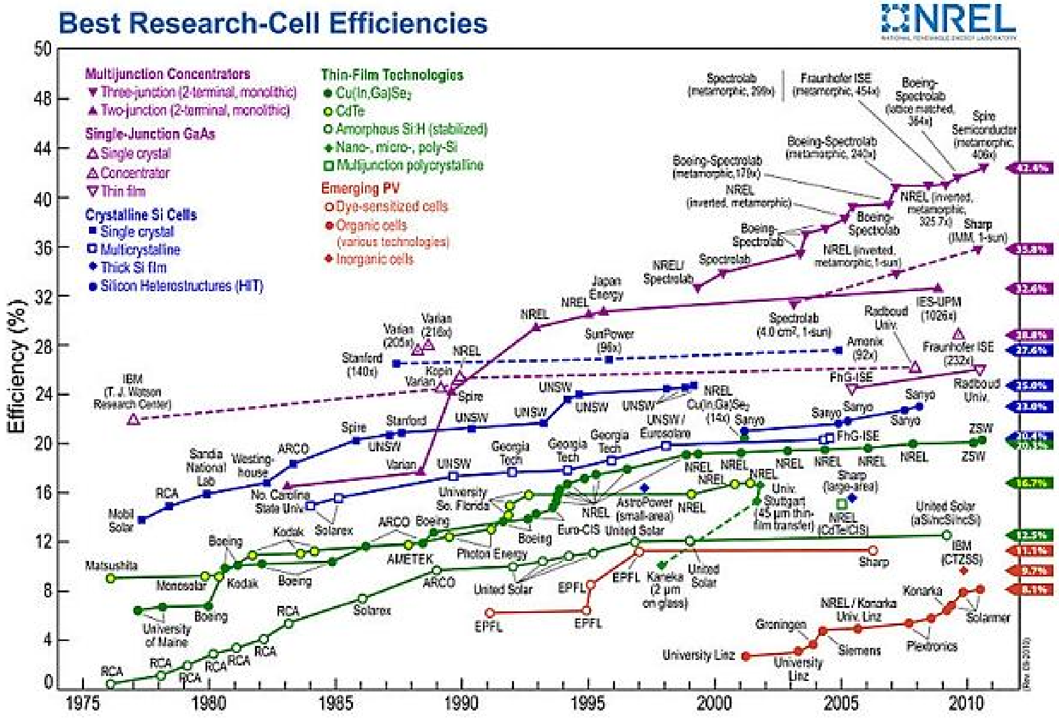

Figure 2.5: National Research Energy Laboratory (NREL) report on progress in solar cell technologies

The

very first $CuInSe_2$ solar cell was made in Bell Laboratories in the early 70s, but its manufacturing and fabrication procedure were first stated by Hahn in 1953 [10]. When Boeing first demonstrated thin film $CuInSe_2$ solar of high efficiency, 9.4% a lot of attention was given to it[11]. Boeing fabricated devices using $CuInSe_2$ deposited by coevaporation i.e. evaporation from separate elemental sources [12]. The solar cell configuration implemented by Boeing gave the basis for various developments that provided high efficiency device technology. The key improvements to the technology are as follows:

- The CIS absorber layer have the band gap of 1.02 eV which is increased to 1.1-1.2 eV by adding Ga into the composition hence increasing the efficiency[13].
- The (CdZn)S layer of 1-2 µm thick doped was replaced by less than <50 nm thin layer of undoped CdS and a conductive ZnO current carrier layer[14]. This change increased cell current by increasing the short wavelength (blue) response.
- Ceramic or borosilicate glass substrate has been replaced by soda lime glass. This decreased the cost and has good thermal expansion match to $CuInSe_2$[15].

2.2.1 Structure of Solar cell device

A thin film solar cell/photovoltaic device of CIGS type has the following structure as shown in figure 2.6. Molybdenum serves as an ideal ohmic back contact (for hole transportation) is coated by thermal evaporation. CIGS thin films is a p-type semiconductor works as an absorber layer. The electron-hole generation upon incident photon is drifted towards the n-type material and the current is collected at the contact. Cadmium sulphate acts as the n –type layer and ZnO for the window layer. Usage of ZnO has added advantages like 1) protects CdS/CIGS interface from diffusion of metal atoms during thermal evaporation 2) High transparency towards the spectra due to its large band gap. Molybdenum / Al acts as the anode and cathode for the measurements and current collection.

Table 2.1: Individual components installed and its function

Components	Functions
Glass (SLG)	Sodium source increase the charge carrier density, enhances open circuit voltage (V_{OC}) and Fill Factor (FF)
Mo coating	Assist in deposition by making substrate layer conductive
CIGS	Main absorber layer, electricity generation takes place
CdS	Buffer layer, Optimizes band gap, creates p-n junction
ZnO:Al	stops shunting of the absorber layer, works as conductive transparent electrical contact

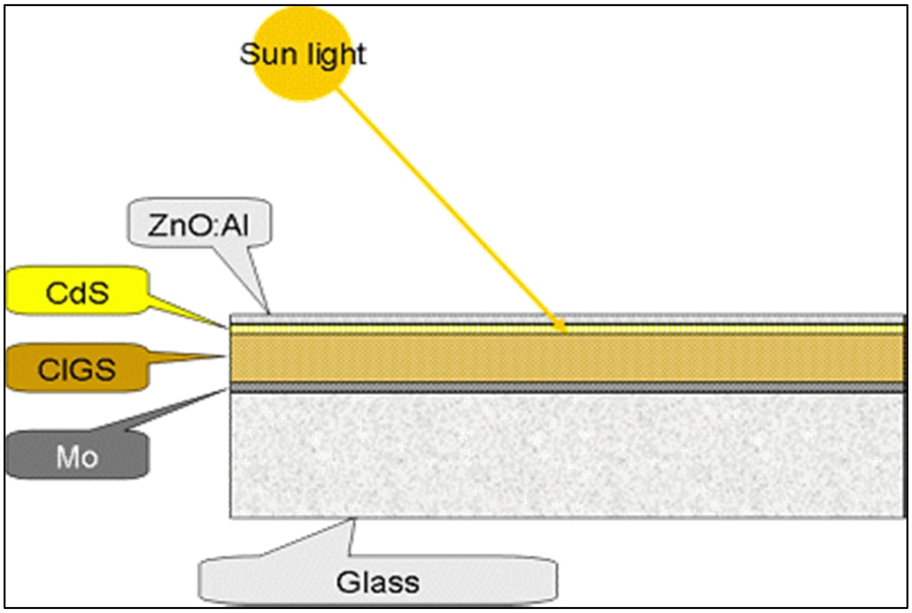

Figure 2.6: A schematic of CIGS based solar cell device

2.2.2 Composition and its influence on the CIGS electrochemistry

Copper Indium gallium selenide ($CuInGaSe_2$- CIGS) material have been explored extensively for the past two decades. The CIGS exhibit a chalcopyrite structure with an adjustable direct band gap nature. The graded thin films can be obtained by varying the composition of Ga and Se or S with respected to the deposition voltage. The stoichiometry of the CIGS thin films is calculated by the ratio between the atomic weight percent of In, Ga, Se with respect to copper (In,Ga,Se/Cu). Obtaining ideal stoichiometry of $CuIn_{0.7}Ga_{0.3}Se_2$ (1:0.7:0.3:2) by electrodeposition is difficult due to many influential parameters.

The bandgap of ternary CIS is 1.04 eV, which is slightly less than the optimal bandgap matching the solar spectrum. However, rapid diffusion of impurities and metals takes place even at low temperatures which leads to degradation and decrease in efficiency. The optimal band gap can be obtained by adding Ga as a substitution in CIS. The electrodeposition of CIGS is usually carried by suing one-step electrodeposition [16]–[21] and multi-step electrodeposition [22], [23]. The disadvantage of multistep deposition technique is, after deposition annealing in selenium atmosphere is required to induce the reaction chemistry between the deposits and for fine crystallization. Comparably, one step deposition is appealing due to its simplicity and it only needs a post annealing in an inert atmosphere for enhancing the film crystallization to reach sufficient photovoltaic qualities.

The co-deposition of CIGS is often complex due to the large variation in the standard potentials of the elements. The incorporation of Ga during co-deposition is much more difficult than indium due to the low standard potential under a constant deposition potential. Hence when deposition under a constant potential is carried, the composition of the thin film will rely much on the mass transfer of the ions in the solution. Also, gallium possesses high affinity with oxygen leading to cracks in the co-deposited thin films. A brief review on the advancements of both CIS and CIGS electrodeposition techniques by various approaches is discussed in this section.

Table 1.2: deposition potential of different ions

Standard potential	Ion/ Element
0.34V	Cu2+/Cu
-0.34V	In3+/In
-0.52V	Ga3+/Ga
0.74V	Se4+/Se

A two-step deposition process involves in successive deposition of Cu-Ga and Cu-In-Se precursor avoiding a post-deposition selenization step[22]. The annealing treatment at 600°C in Argon atmosphere resulted in better crystalline CIS [22]. The influence of varying bath composition, pH and deposition voltage for CIS thin film was extensively studied [16], [23]. In their experiment, the Copper to selenium molar ratio was fixed [Se^{4+} /Cu^{2+}] as 2.08 and [In^{3+}/ Se^{4+}] was maintained to be unity. The Chemical composition analysis results in atomic percentage for as-deposited CIS thin films by inductive coupled plasma (ICP) spectroscopy revealed a copper rich phase (Se-poor) with pH increase. CIS electrodeposition without complexing agent using two electrode system was carried [24], The deposited CIS thin films were of various bandgap. By varying the cathodic potential, CIS conductivity was varied from p, p+, intrinsic (i), n, n+. For low cathodic potential Cu-richness (In poor) films were observed with n-type conductivity and at high cathodic, In-richness leads to p, p+ conductivity. The measurement of potential difference between the dark and light in solid-electrolyte interface enables to identify the conductivity of the semiconductor. The polarity enables to identify the nature of the semiconductor (p or n type) and the magnitude of the current relies on the carrier concentration.

The technique was extended to deposit a CIGS thin films (p-i-n structure) using three electrode system. The PEC signal technique was used to confirm the conductivity behavior of n-CIGS, i-CIGS and p-CIGS during electrodeposition. A device structure comprising of (glass/TCO/n-CdS/n-CIGS/i-CIGS/p-CIGS/Au) gave a V_{oc}~520 mV, J_{sc}~30 mA/cm^2 and fill factor ~0.3 under AM1.5 illumination conditions [25]

2.3 Synthesis procedure

$CuInGaSe_2$ absorber layer are deposited by various deposition processes and fabrication techniques and characterization methods to produce the device. The synthesis processes can be classified in two ways [26]

- **Physical process**: processes which depends on the evaporation or ejection of the material from a source. Like evaporation or sputtering,
- **Chemical process**: Chemical methods depend on physical properties and their structure relationships on a specific chemical reaction. Like electroplating, vapor phase deposition

Here in this thesis we will discuss few important manufacturing processes in brief and electroplating in detail. The methods are summarized in table 2.3 which are often capable of producing thin films i.e. 1 µm or less than 1 µm else comes in the category of thick films. There are techniques capable of producing thick films like printing, glazing, electrophoretic deposition, painting, etc.

Table 2.3: Characterization of thin film technologies

Sputtering	Evaporation	Gas Phase	Liquid Phase
Glow discharge DC sputtering	Vacuum Evaporation	Chemical vapor Deposition	**Electro-deposition**
Triode sputtering	Resistive heating Evaporation	Laser Chemical vapor deposition	Chemical bath deposition (CBD) / Arrested Precipitation Technique (APT)
Getter sputtering	Flash Evaporation	Photo-chemical vapor deposition	Electro less deposition
Radio Frequency sputtering	Electron beam Evaporation	Plasma enhanced vapor deposition	Anodisation Liquid phase Epitaxy
Magnetron sputtering	Laser Evaporation	Metal-Organo Chemical Vapor Deposition (MO-CVD)	Sol- gel Spin Coating
Ion Beam sputtering			Spray-pyrolysis technique (SPT)
AC. Sputtering	Arc		Ultrasonic (SPT)
	7) R. F. Heating		Polymer assisted deposition (PAD)

2.3.1 Physical processes

2.3.1.1 Physical Vapor Deposition (PVD):

Physical vapor deposition is a process carried out in high temperature range between 150^{o} C to 500^{o} C and high vacuum.

- The elemental powders is either evaporated by applying heat or by bombardment with ions (sputtering) to vaporize , followed by deposition on the substrate
- Process like sulpharisation or selenization, can also be carried (e.g. by purging reactive H2se gas or by evaporating elemental sulphur or Selenium source) to modify the composition during deposition.
- In order to obtain a uniform coating thickness, the substrate holder is rotated at uniform speed around 360°.

  The other PVD processes include arc evaporation, sputtering, ion plating, and enhanced sputtering.

2.3.1.2 Thermal evaporation

Thermal evaporation technique uses a metal powder as starting materials which are to be deposited over the substrates. The powders are placed in a highly stable tantalum or molybdenum crucible. Evaporation is carried at either high vacuum range (10^{-5} mbar) or in ultra-high vacuum range ($>10^{-6}$ mbar). By resistive heating, the Ta or Mo crucible generates heat which facilitates the powders to evaporate and deposit over the substrates.

2.3.1.3 Sputtering

Sputtering technique is used to deposit thin films over the substrates. The inert gas such as Argon is used to create plasma. These high energetic ions colloids with the target material erode to generate either individual or cluster of atoms and molecules which deposits over the substrate.

2.3.2 Electrochemical and chemical process

2.3.2.1 Chemical vapor deposition

Chemical vapor deposition (CVD) is a process in which solid material gets deposited by a vapor with the help of a chemical reaction on or in the vicinity of the container where one or more heated substrates are kept to be deposited. Chemical reactions take place on or near the surface of the high temperature substrate hence deposition of the thin film. By changing the physical variables like substrate material, substrate temperature, composition of the reaction of gas mixture, etc., we can deposit the films with different properties. There are so many chemical reactions that are utilized in CVD technique for the formation of solids those are pyrolysis, oxidation, reduction, hydrolysis, etc.

2.3.2.2 Chemical bath deposition

Chemical bath deposition is a very simplest technique in comparison to all the physical methods that has been discussed previously. It is also known as Chemical Solution Deposition (CSD) and is the simplest method to deposit a thin film. The chief requirement for this method is a bath solution (mainly aqueous solution) in a vessel and a substrate on which deposition is to be carried out. Complicated part for this method is to check the mechanism for stirring and to maintain a specific constant temperature of thermostated bath solution[27]. Chemical reaction takes place either on the surface of the substrate or within the solution itself subsequently there will be a requirement of mixing of components on the surface of the substrate to be coated.

2.3.2.3 Electroplating or Cathodic deposition

Electrodeposition is a simple inexpensive technique which does not require much apart from the precursor metal ions. Using a two or three electrode system, the deposition can be carried conveniently by varying the electrical parameters [voltage or current]. The most commonly used anode [Counter electrode] is Pt or graphite rod and cathode [Working electrode] can be any conducting substrate on which deposition is done.

The electrodeposition setup consists of following

1. Electrolyte (containing dissolved ions)
2. Anode (Platinum rod)
3. Cathode (Glass/Molybdenum)

By applying a D.C (Direct current) between anode (Pt) and cathode (Glass/Mo), positively charged ions will get attracted towards the cathode and gets reduced by receiving electrons reference electrode. Fig. 2.7 shows schematic of electrodeposition setup.

When operating in the potentiostatic mode, the potential is applied to the working with respect to reference electrode (V vs.SCE). Due to the inertness and fixed potential of the reference, the potential drop taking place between the cathode and reference can be measured accurately, with an output in the form of Voltage (V/SCE) Vs. Current (mA).

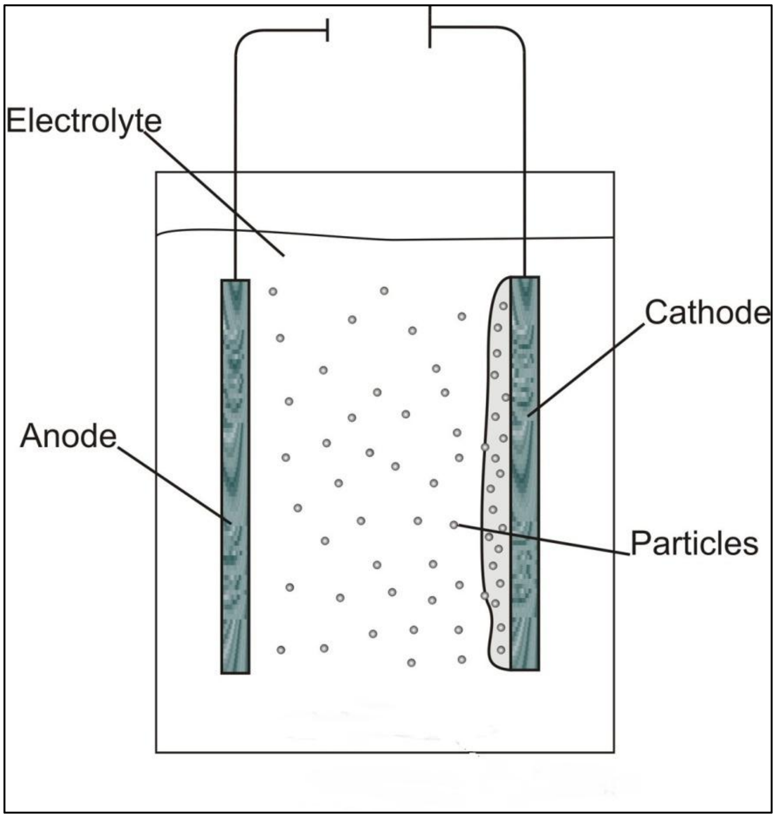

Figure 2.7: Schematic of electrodeposition

For the electrochemical studies, such as analyzing the redox behavior the ions, three electrode systems are used frequently. For large scale deposition, a conventional D.C source is used in practice.

Electrodeposition has many advantages over other deposition techniques:

- Compositionally and structurally controlled alloys can be deposited which is very difficult and complex in other deposition techniques.
- Generally deposition is carried out in room temperature making a way to form the semiconductor without interdiffusion.
- Complex shape depositions can be done easily
- No toxic gases or chemicals are formed unlike other techniques.

- Composition , thickness, stoichiometry can be controlled by adjusting the variables like current, voltage, temperature, time of deposition to get good quality thin films.

2.3.3 Electrodeposition of Binary/Ternary/Quaternary alloy

For a single element deposition (ex-standard reduction potential of Cu^{2+}=+0.34 V/SHE), metal ions are reduced on the cathode surface when the applied potential exceeds the standard reduction potential. But it will be difficult to carry co-deposition such as Cu-Se, In-Se, Ga-Se binary system. Due to their vast difference in the EMF series, when a voltage is applied, it will be favorable for certain ions to deposit and not for others. In quaternary electrodeposition, the trend of reduction of the metal ions of desired concentrations can be predicted by Nernst equation [equation (1)].

$$E = E_m^0 + \frac{RT}{nF} \, Log a_m^+ / a_m^0 \qquad \text{----- (1)}$$

Where E- Equilibrium potential of the electrode (/SHE), E^0- reduction potential of metal ions at standard condition, R is the gas constant, T is the absolute temperature, n-number of electrons involved in the reduction, F-Faradays constant,a_m^+ is the activity in the electrolyte and $a_m^0$is the activity of the reduces solid species (unity). Adjusting the pH and concentration enables to bring the potential of individual ions together for simultaneous electrodeposition.

The theoretical thickness of the deposited film (d) can be calculated by formula in Eqn (2)

$$d = \frac{JMt}{nf\rho} \qquad \text{----} \qquad (2)$$

Where,

J- Current density (mA/Cm2)

M-molecular weight (gm)

t- Deposition time (sec)

n- Number of electrons transferred

f- Faradays constant

ρ – Deposited material density

The bath chemistry and electrodeposition approaches to deposit ternary and quaternary CIS/CIGS semiconductors are discussed below.

2.3.3.1 CIS/CIGS Electrodeposition

The electrodeposition of CIS and CIGS involves in the electrochemistry of metal ions of Cu, In, Ga, Se dissolved in the electrolyte. Initial stages of preparing the bath for CIGS involves dissolving the chlorides or sulfate salts of the respective metals as starting precursors. The electrolyte of choice is usually double distilled water. Excess concentration of Se (IV) leads to precipitation and hence highly acidic media (pH1-4) is necessary to prevent hydroxides formation and also to enhance solubility. Based on the bath concentration, the pH is to be adjusted (more acidic) to ensure proper solubility and oxides/hydroxides prevention. After a few depositions, due to the depletion of H^+ ions, pH of the solution increases slightly which results in oxide/hydroxide precipitation. Hence to sustain the bath pH throughout the deposition, buffers (pHydrion etc.) are used[28]

In quaternary CIGS deposition, when a favorable potential is applied for In and Ga elemental deposition, the noble elements (Cu, Se) will be diffusion limited and hence stirring helps in improving the stoichiometry and film quality under low current density deposition regime [28]. To shrink the deposition potential during a one-step electrodeposition and to obtain smooth films, organic compounds such as ligands, complexing agents, brighteners and buffers are used in the bath solution [29]. The deposition will not be any more diffusion limited when a complexing is good between the ions used in the bath, since specific charge will be a dominant controlling parameter in deposition. Hence the study of complexing capability of the substance with the individual ions plays a significant role in co-deposition process. A high stability constant between the noble metal ions (Cu, Se) and the active substance and least for In and Ga is a prerequisite to have good control over the deposition potential and stoichiometry.

The simplest way of CIGS formation is depositing in the form of individual elemental thin film stacks followed by annealing in H_2Se or Se atmosphere to obtain a chalcopyrite CIGS phase. This technique is practically inconvenient and thus improved to deposit binary stacks (Cu-In, In-Se, Ga-Se) followed by high temperature selenization.

The electrodeposition of CIGS is usually carried using one-step electrodeposition [22], [24], [30]–[33]and multi-step electrodeposition[34]–[38]. The potential region for one step deposition is highlighted in fig.2.8. The disadvantage of multistep deposition technique is, after deposition annealing in selenium atmosphere is required to induce the reaction chemistry between the deposits and for fine crystallization. Comparably, one step deposition is appealing due to its simplicity and it only needs a post annealing in an inert atmosphere for enhancing the film crystallization to reach sufficient photovoltaic qualities.

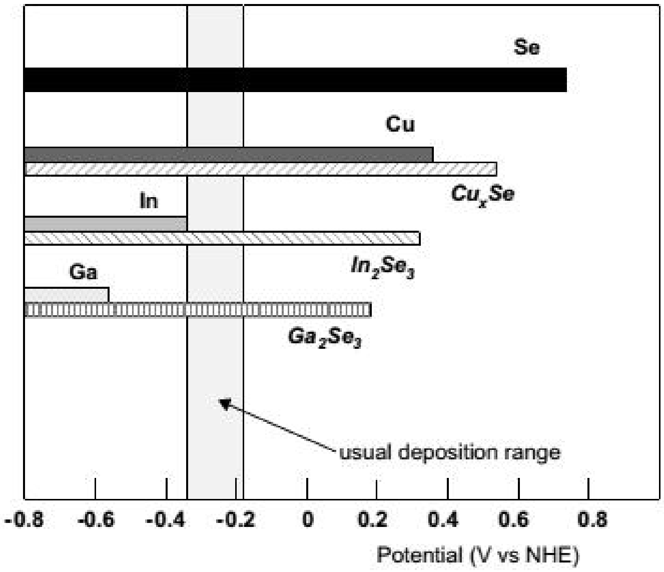

Figure 2.8: Thermodynamic diagram of the Cu-In-Ga-Se codeposition system

2.3.3.1.1 CIS/CIGS formation mechanism:

Many literatures have examined the formation mechanism of CIS/CIGS. A generalized mechanism will be discussed in brief.

During CIS/CIGS deposition, the initial deposits are usually Cu-Se rich phases like CuxSe. Though CuxSe phase exists in various phase (Cu3Se2, Cu2Se, and CuSe), for simplicity they are mentioned here as CuxSe. During a one-step deposition process, the CuxSe phase formed will be acting like catalytic sites for the In (III) assimilation in the form of In_2Se_3 over these sites to form a stable CIS phase. The In inclusion takes place when Se/Cu ratio is greater than 1 [39]. The global formation of $CuInSe_2$ takes place by co-deposition along with the elemental Se (0) and binary Cu-Se formation simultaneously which is supported by [40]. Similar formation mechanism was proposed for Ga_2Se_3 [31].

To conclude on the CIS/CIGS deposition mechanism (fig 2.9), In^{3+} and Ga^{3+} inclusion takes place, by reducing over Cu_xSe phase and H_2Se at lower and higher cathodic potential respectively. Having excess In^{3+} composition facilities direct reduction of In. Whereas, Ga^{3+} follows an alternate mechanism of Inclusion as Ga_2O_3.

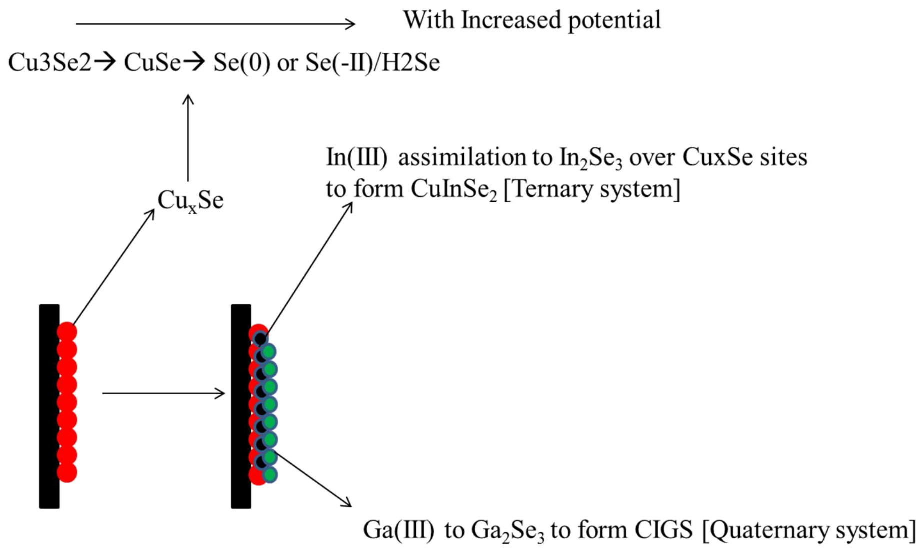

Fig 2.9: Schematic of CIS/CIGS formation mechanism

Chapter – 3

Experimental

This chapter gives the detail description of experimental method used to electrodeposit CIGS thin film; electrochemical behavior and synthesis of CIS/CIGS thin film have been described in Linear sweep voltammetry, cyclic voltammetry and Chronoamperometry studies. X-Ray diffraction (XRD) technique carried out for the phase analysis of thin film has been given in detail. Morphological structure of thin films has been observed in FESEM and described in this chapter along with the compositional details of as deposited CIS/CIGS thin film

3. Experimental details

3.1 Experimental setup

Electroplating and electrochemical studies of absorber layer has been carried out in thermally sputtered Mo (30 nm) coated soda lime glass substrate. All the substrates were cleaned with acetone and rinsed with deionized water and, dried subsequently. Electrochemical experiments for current-voltage studies has been carried out in potentiostat/galvanostate (Eco Chemie Netherland, Autolab PGSTAT 12) system having computer interface of GPES software and three electrode electrochemical cell. Electrodeposition of $CuInGaSe_2$ has been carried out in two electrode setup DC power source where Mo substrate acts as cathode whereas Pt acts as anode while for electrochemical studies Calomel (Saturated Calomel Electrode) is used as a reference electrode, Pt as counter electrode and Mo coated glass substrate as working electrode. Before all experiments substrate was cleaned and dried properly. The pH of bath solution was measured before and after experiments with digital pH meter [pH brand and model]. Figure 3.1 (below) showing schematic of experimental arrangement in three electrode setup.

Figure 2.1: Showing Electrochemical arrangement for three electrode setup connected with Potentiostat

3.2 Electrolytic bath preparation

Electrochemical bath for absorber layer deposition is composed of chloride salts of Cu, In, Ga and H_2SeO_3. Conc.sulfuric acid was added in double distilled water to maintain the pH value equal to 2. All the chemicals used are of high purity and used as received with no further purification. All the bath solutions were prepared in double distilled water at room temperature maintaining a constant pH. Electrodeposition of absorber layer has been carried out with and without adding Sodium Dodecyl Sulphate (SDS) to study the morphology of the absorber layer. The bath composition used for preparing absorber layer has been given in the table 3.1 below.

Table 3.1: Bath composition for absorber layer deposition

Type of thin film	$CuCl_3$ (µl)	$InCl_3$ (µl)	$GaCl_3$ (µl)	H_2SeO_3 (µl)	H_2SO_4 (µl)	SDS (µl)
CuInSe	75	180	-----	165	30	----
CuInSe	75	180	-----	165	30	200
$CuInSe_2$	**120**	**60**		**120**	------	------
$CuInSe_2$	120	60		120	20	------
CuInGaSe2	40	80	80	80	10	----
CuInGaSe2	40	80	80	80	10	200

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3.3 Electrochemical synthesis

Solar cell absorber layer synthesis include electrodeposition route to fabricate solar cell device in a two electrode setup. Electrochemical synthesis studies have been carried out in potentiostat where a setup is prepared composed of electrolytic bath immersed with working electrode, counter electrode and a reference electrode. Bath pH has been maintained to 2 and the bath temperature is maintained at 25^{o} C. Effect of different deposition potentials for binary, ternary and quaternary components has been studied with the help of cyclic voltammetry and Chronoamperometry studies. Structural and morphological studies have been conducted for absorber layer under both conditions i.e. with SDS and without SDS.

3.4 Electrochemical Studies

Electrochemical studies include current-voltage behavior and reduction potential of binary, ternary and quaternary phases which is going to be examined with help of cyclic voltammetry while nucleation and growth mechanism is to be studied with the help of chronoamperometric analysis. The basic principle on which CV and CA studies rely on are given below which is used in the synthesis of the CIS/CIGS absorber layer.

3.4.1 Linear Sweep Voltammetry

Linear sweep voltammetry is carried out to check the reduction potential of individual ions to be deposited. In LSV, the electrode potential is varied at a constant rate throughout the scan. The current at the low cathodic potential is quite small which helps to maintain a double layer charging at the electrode surface, sometimes this current is called charging current. As the potential increases further an electrochemical reaction will take place at the electrode surface or in other terms electrons will transfer from the electrode surface to the hydrogen ions in the solution to cause a reduction of H^+ ions to H_2 following increase in current.

3.4.2 Cyclic Voltammetry

Cyclic voltammetry is a very multipurpose electrochemical technique which provides us to probe the reduction, oxidation and transport mechanism of a system in the solution (Fig. 3.2).

This electrochemical technique is well versed with a three electrode setup where a reduction potential of the depositing species is scanned to a working electrode relative to some reference electrode. While scanning of deposition potential is on the run, the resulting current which will be flowing through a counter (or auxiliary) electrode is examined in quiescent solution. This technique is well suited in case of binary, ternary and quaternary system where reduction potential of every single identity can be studied separately at each point which allows us to get the desired stoichiometric composition.

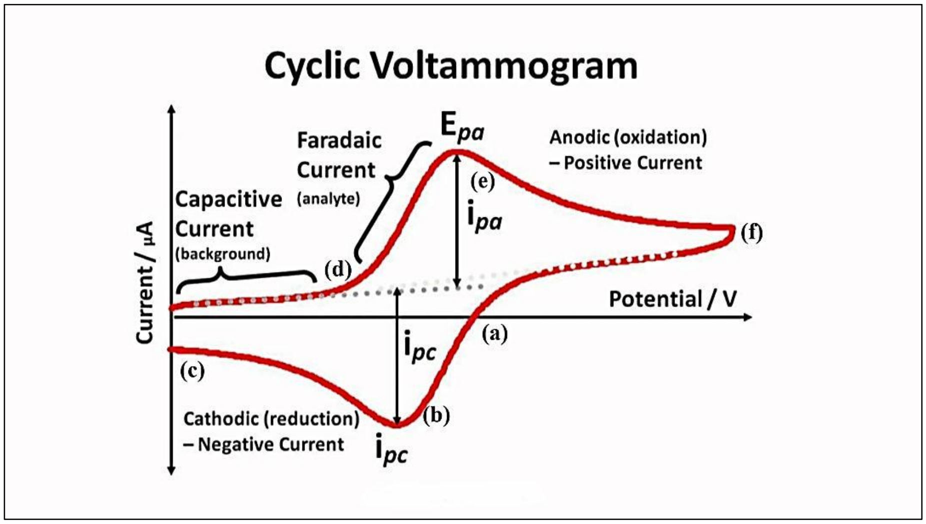

Figure 3.2: A schematic of a cyclic voltammogram graph showing oxidation and reduction peak

When the potential of working electrode is more positive than the redox couples present in the solution then the corresponding species tends to oxidize i.e. electrons going from the solution to anode and produces an anodic current. Similarly, on the return scan as the working electrode potential is more negative than the redox couples then reduction occurs to cause a cathodic current.

3.4.3 Chronoamperometry analysis

Chronoamperometry is a useful tool for determining diffusion coefficients and for examining kinetics of nucleation and growth mechanisms. In this analysis when a potential step sufficiently large enough to cause an electrochemical reaction is applied to an electrode, the current change with time is plotted in the digital screen. The study of current response as a function of time [fig.3.4] is called Chronoamperometry (CA). Chronoamperometry is a square wave pulsed voltammetric technique. The identity of the electrolyzed species can be obtained from the ratio of the peak oxidation current versus the peak reduction current. However, as with all pulsed techniques, Chronoamperometry generates high charging currents.

3.5 Characterization techniques

$CuInGaSe_2$/CuInSe2 absorber layer have been deposited at different potentials to optimize the composition and to analyze the results of the stoichiometry of thin films several characterization techniques have been used. X-Ray diffraction (XRD) technique has been employed to study the structural planes and molecular phases present in the absorber layer. Scanning Electron Microscopy (SEM) has been done to analyze the surface morphology of the thin film absorber layer; Electron Dispersive Spectroscopy (EDS) has been used to check the chemical composition of the deposited thin film absorber layer.

3.5.1 X-Ray Diffraction (XRD)

X-Ray diffraction has been carried out for CIS/CIGS at the scan range of 20^o to 80^o to cover all the traces of each phase at the scan rate of 20^o/min with the step size of 0.05 at CuKα radiation ($\lambda = 1.5406\ A^o$) using RIGAKU Japan Model : ULTIMA IV. X-Ray crystallography is analytical technique to determine the phase of a crystalline material and gives information of the cystallographic planes on a unit cell dimension.

The X-ray diffraction is based on the principle of constructive interference of monochromatic X-Rays and a crystalline sample. These rays are generated using thermoionic gun filtered to yield monochromatic radiation and is collimated to concentrate towards the sample. The incident rays hits the sample and produces a constructive interference and a diffracted ray when it satisfies the Bragg's law.

3.5.2 Field Emission Scanning Electron Microscopy (FESEM)

FESEM analysis has been carried out in [Model: FEI Nova NanoSEM 450].A field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. This imaging technique is used for applications which demand the highest magnification possible. It has following applications:

- Semiconductor device cross section analyses for gate widths, gate oxides,film thicknesses, and construction details
- Advanced coating thickness and structure uniformity determination
- Small contamination feature geometry and elemental composition measurement

Chapter -4

Results and Discussion

Results have been described and discussed in detail in this chapter, electrochemical behavior, electrodeposition mechanism and nucleation and growth mechanism of CIS/CIGS absorber layer has been studied using Linear sweep voltammetry, Cyclic voltammetric and Chronoamperometry analysis and their results have been interpreted on this chapter. This chapter includes the result from phase analysis done using XRD technique. Structural and compositional study results carried out in FESEM have been illustrated in this chapter

4. Results and discussion

4.1 Electrochemical analysis: Deposition potential and bath composition optimization

To optimize deposition potential for CIS, linear sweep voltammetry (LSV) experiments were carried for unitary, binary and ternary systems Cu, Cu-Se, In-Se and Cu-In-Se without any complexing agents on a sputtered molybdenum substrate (glass/Mo) are shown in fig.4.1. The pH of the bath was maintained to be 2.45 by adding conc.sulfuric acid.

For unitary Cu, the peak centered at -0.34 V can be assigned as the reduction of Cu2+ to Cu [41]. For Cu-Se, three peaks appear mainly at positions A, B and C. The apparent reduction current starting at 0V to -0.15 V (peak-A) can be due to the Cu_3Se_2 phase followed by its reduction to Cu_2Se/CuSe phase at higher negative potential (peak-B). As suggested by Rajeshwar et.al, CuSe formation is more likely than the direct deposition of Se (IV) [52] and the order of deposition is Cu>Se, where the Cu nuclei serves as an active site for the formation of Cu-Se compounds. At still higher cathodic potential (peak-C), Cu_2Se will further reduce to Cu and H_2Se. [31]

The Chronoamperometry (CA) study was carried at -0.6V (C) [data not shown] for Cu-Se system resulted in formation of a blackish colloidal gel on the substrate followed by immediate dissolution in the electrolyte. The excess Se over Cu_2Se gets reduced to soluble [Se (-II)] form leads to the poor adherence on the substrate [42]. At acidic pH H_2Se is the dissolved form of Se (-II). The same scan was run down for the binary system In-Se with the same pH for the same potential range from 0V to 1V at the scan rate of 0.0099V/sec. For the In-Se binary system, the potential ranging from 0V to -0.4V, the peak centered at -0.34V is due to the formation of In_xSe_x alloy. From the figure 4.2 it can be seen that beyond -0.4V, diffusion limited deposition of In_xSe_x takes place followed by electrolyte discharge.

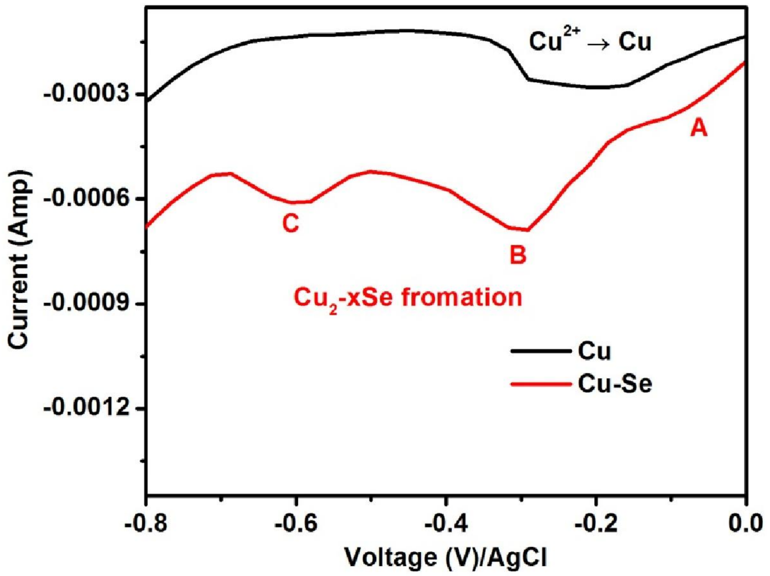

Figure 4.1: Linear sweep voltammetry scan of unitary Cu and Cu-Se binary system

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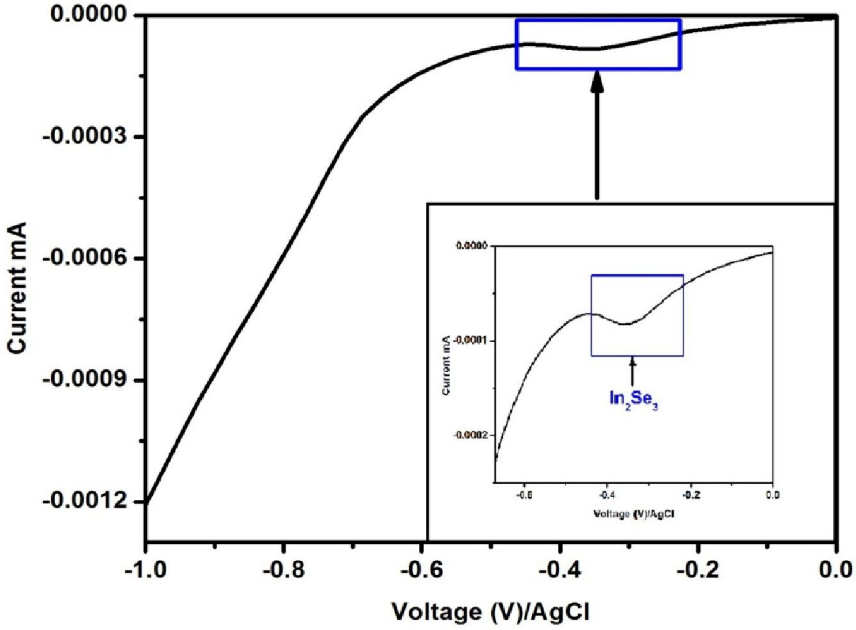


Figure 4.2: Linear sweep voltammetry scan of In-Se binary system with enlarged peak given in the insat

After determining the Cu-Se and In-Se deposition mechanism and reduction potential of both the alloys a ternary system of CuInSe was employed to study under the same potential range of 0V to 1V maintaining the same pH at the scan rate of 0.015V/sec given in the figure 4.3

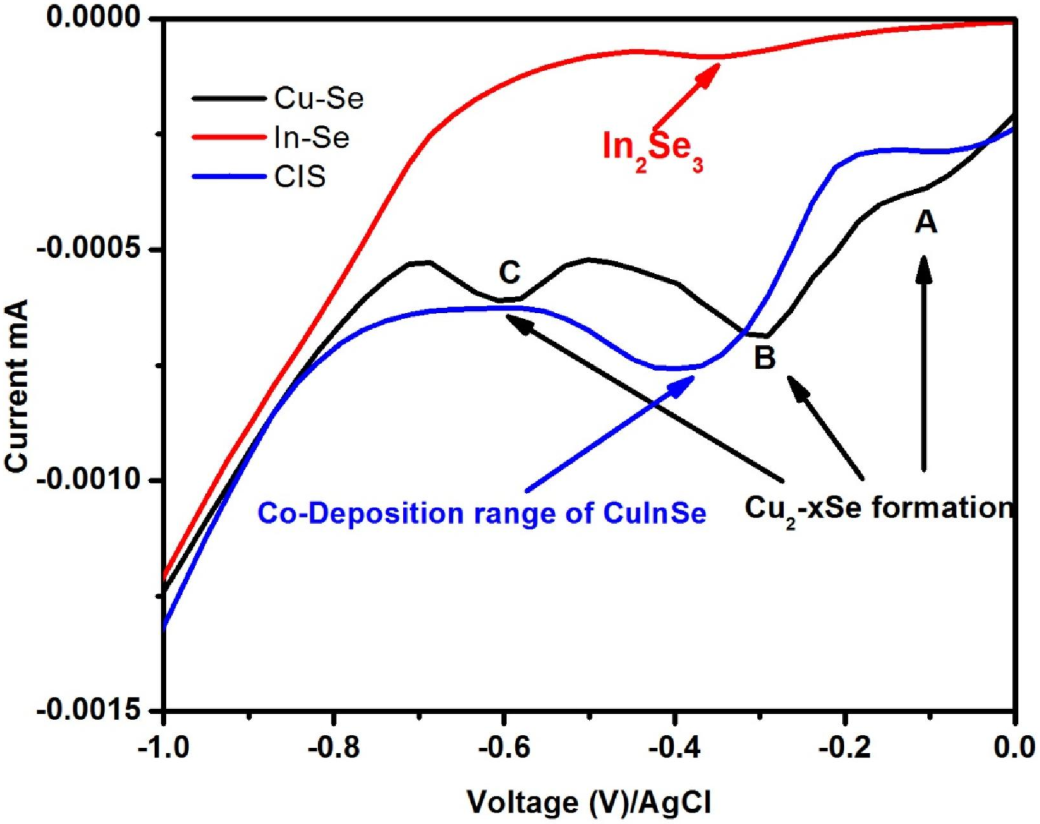


Fig. 4.3 LSV of Cu-Se, In-Se, Cu-In-Se systems

Significant changes were observed upon the addition of In^{3+} ions to Cu-Se system. Between -0.2 V to -0.58 V, In_2Se_3 formation takes place over the CuxSe phase due to its low free energy if formation, thus following the Kröger's mechanism [Kroger ref]. The order of deposition of CIS in this case is given as Cu>Se>In. The peak position 'C' in Cu-Se LSV disappeared upon the addition of In^{3+} ion in the ternary system. From -0.6 V to -0.7 V, In (III) reacts with H_2Se to form In_2Se_3, followed by assimilation over CuxSe to form growing CIS films. The global formation of

$CuInSe_2$ takes place by co-deposition, along with the elemental Se (0) and binary Cu-Se formation simultaneously. [43]

The $CuInSe_2$ compound formation can be due to any of the following reactions mentioned below:

$$Cu_3Se_2 + 3In^{3+} + 4H_2SeO_3 + 16H^+ + 19e^- \leftrightarrows 3CuInSe_2 + 12H_2O \quad (1)$$

$$Cu_3Se_2 + 3In^{3+} + 4Se + e^- \leftrightarrows 3CuInSe_2 \text{ (under excess In(III) concentration)} \quad (2)$$

$$3In^{3+} + 4H_2SeO_3 + Cu_3Se_2 + e^- \leftrightarrows 3CuInSe_2 + 8H^+ \quad (3)$$

$$2Cu^+ + In_2Se_3 + H_2SeO_3 + 4H^+ + 8e^- \leftrightarrows 2CuInSe_2 + 3H_2O \quad (4)$$

$$2Cu^+ + In_2Se_3 + Se + 4e^- \leftrightarrows 2CuInSe_2 \quad (5)$$

It is very difficult to confirm the particular reaction by linear sweep voltammetry only due to the complexity in the quaternary system. For understanding the co-electrodeposition mechanism of quaternary system in detail cyclic voltammetry analysis has been done in the later section.

4.1.1 Deposition potential optimization of CIS with and without SDS

Surfactants enable to provide smooth and compact films during electrodeposition. Hence CIS deposition was carried along with Sodium dodecyl sulphate (SDS) (Fig.4.4) to study the effect of SDS in CIS morphology. CIS deposition was carried with same concentration and pH [0.004:0.008:0.008 M & pH=2]. The concentration of SDS used is 0.01 M. Successive scans were carried on the same substrate to understand the deposition behavior. In the initial linear sweep behavior [Scan-1] of CIS was much similar to that of without SDS [Fig.4.2]. A decreased current density at the lower cathodic potential shows that CuxSe phase is inhibited after the addition of SDS. During successive scans, it was observed that the peak centered at -0.45 V disappeared followed by appearance of reduction peaks between -0.6 V to -0.9 V [11, 12].The cathodic peak centered at -0.4 V corresponds to the CIS formation as explained earlier. On the subsequent scans, the deposition of CIS at -0.4 V is less pronounced and hence the dominant mechanism of In^{3+} ions (aq) uptake for CIS formation must be by reacting with dissolved H_2Se or with Se (0).

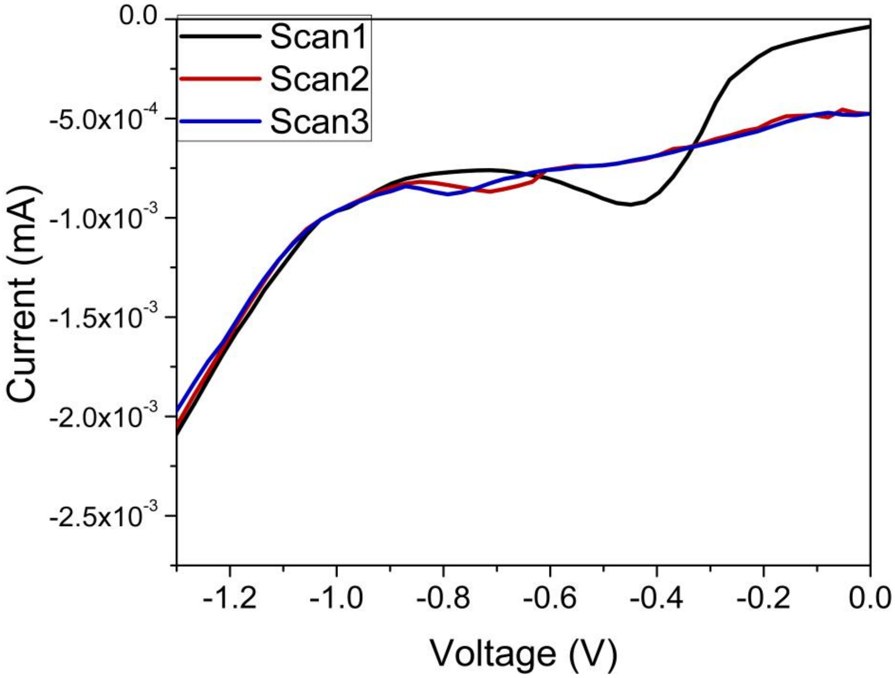


Fig.4.4 Successive LSV scans for CIS-SDS

4.1.2 Bath composition and deposition potential study of CIS in neutral bath solution

Most of the CIS deposition studies were carried in acidic media [pH-1-4]. Some reports on In-Se and Ga-Se stack deposition in alkaline media [pH-10] were carried. As In3+ and Ga3+ were prone to oxides and hydroxides formation, (white precipitation will form when these ions are mixed in D.I water), complexing agents are necessary to enhance their solubility and to inhibit hydroxide formation.

A preliminary study on CIS electrodeposition was carried using a neutral electrolyte without any complexing agents. The CIS LSV studies were also carried for neutral bath solution with a molar ratio of 1:0.5:1 (M). For the fabrication of superstrate devices of structure glass/ZnO/CdS/CIS/Metal, a neutral electrolyte is required to avoid any redox reaction between ZnO/CdS. Fig.4.5 shows the deposition behavior of CIS in slightly alkaline media [pH-6.35]. For comparison the deposition were also carried at a pH of 3. The concentrations of In and Se has been optimized to minimize the effect of solubility and oxide/hydroxides formation issues. At lower cathodic potential [0V to -0.2V], the formation of Cu_xSe phase takes place. In alkaline or neutral bath, the standard reduction potential of selenite species is -0.357 V which is close to that of In (III) [-0.34 V]. [44]. By compositional analysis, In inclusion initiated above -0.25 V/AgAgCl. The plateau region starting from -0.35V to -1V may be assigned for the deposition of $CuInSe_2$ by In^{3+} assimilation over Cu_xSe to form a stable CIS phase. At higher cathodic potential [-1V to -1.25 V], CIS co-deposition takes place by reaction of In (III) with Se (0), and CuxSe species followed by H_2 evolution. The corresponding phase formation regimes are marked in the LSV plot. Te shift in the CIS co-deposition window is different for pH of 3 and 6.35 which can be attributed as pH effect. Though much compositional studies have not been carried in this preliminary study, it is interesting that CIS can be co-deposited conveniently at high cathodic potential without any additives. A detailed study on this deposition scheme is necessary to have a simplified the bath chemistry.

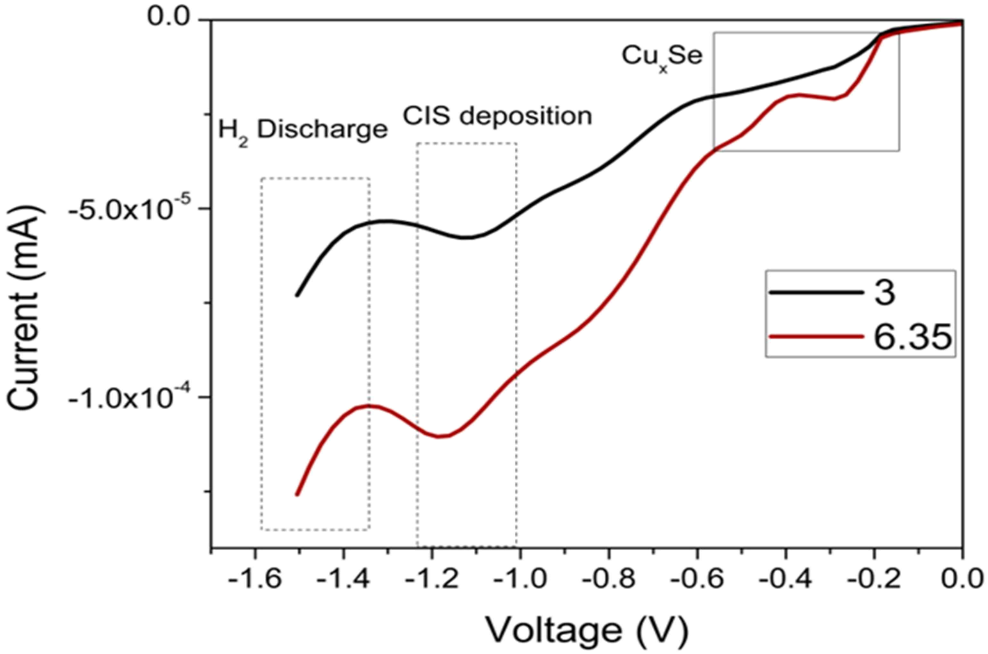


Fig.4.5 LSV-CIS deposition at pH= 3, 6.35

4.1.3 Cyclic voltammetry analysis of quaternary CIGS system

Cyclic voltammetry has been carried out in Mo coated glass substrate at the range of [-2 V to 1.5V] to study the electrochemical behavior during the co-deposition of CuInGaSe at the scan rate of 5mV/sec. Figure 4.6 illustrates the cyclic voltammograms of the CIGS bath solution without using Sodium Dodecyl Sulfamate (SDS). In the given figure 4.6 cathodic reduction potentials of quaternary system can be seen where Cu, Se, In, Ga deposited at -0.025V, -0.102V, -0.277V and -0.612V respectively. This value is concluded from the cyclic voltammogram of quaternary Cu-In-Ga-Se system and the film composition has been confirmed by Electron dispersive spectroscopy (EDS) analysis given in the table 4.1. The voltammogram was initially at zero potential and started to scan towards negative potential where negative current started to increase right from the beginning of the reduction consecutively showing successive peaks showing the deposition mechanism.

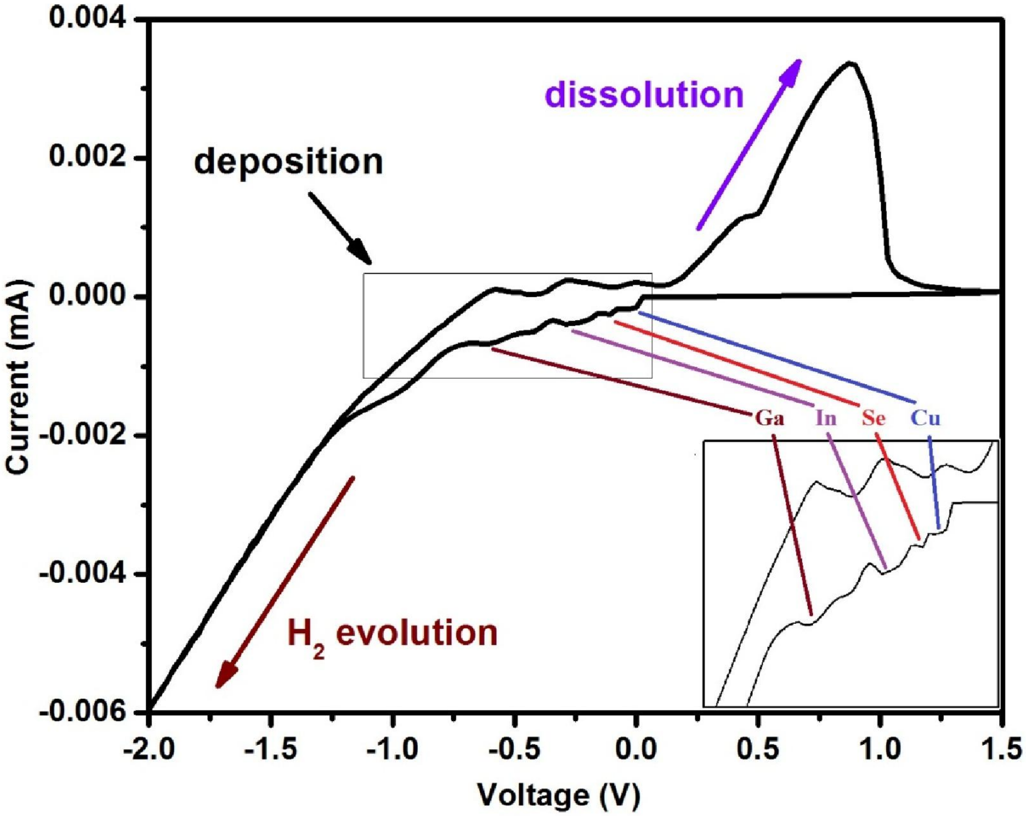


Figure 4.6: Cyclic Voltammogram of quaternary CuInGaSe system without using SDS

According to their active nature of deposition Cu will deposit first where a small positive shift in the reduction potential of Cu^{2+} from 0.2V in unitary solution to 0.025V in quaternary solution. Proceeding to somewhat increased potential Se will make a compound with Cu which is more stable than to deposit Se alone as concluded earlier. Cu_2Se compound then will serve as active site to catalyze In deposition over the layer of Cu-Se compound at the recorded potential of -0.27V. In agreement with film composition it can be inferred that slight increase in cathodic current after -0.3V is ascribed as the reduction of In^{3+} and Ga^{3+}. The peak at -0.277 and -0.65V may inferred as the reduction peak of In^{3+} and Ga^{3+}, respectively. From the EDS analysis it can be said that the co-electrodeposition of Cu, In, Ga, Se occurs at higher deposition potential. The morphology of the co-deposited film was rice like structure figure 4.11 given in the later section. The electrochemical mechanism Cu(InGa)Se_2 can be similar to the Cu$InSe_2$ deposition. Furthermore, Cu_3Se_2 phase which has been formed earlier may give rise to underpotential deposition of Ga. This leads to the formation of $CuGaSe_2$ and may continue due to following reactions:

$$Cu_3Se_2 + 3Ga^{3+} + 4Se + e^- \leftrightarrows 3CuGaSe_2 \quad (6)$$

$$Cu_3Se_2 + 3Ga^{3+} + 4H_2SeO_3 + 16H^+ + 19e^- \leftrightarrows 3CuGaSe_2 + 12H_2O \quad (7)$$

The formation energy of $CuGaSe_2$ is more than that of $CuInSe_2$, so there are fair chances that Eqns. (6) and (7) are more likely to happen than Eqns. (1) and (2)[45]. After the cathodic peak when the potential reached to at lower negative potential of cathodic current rises rapidly indicating hydrogen reduction has become the main reaction. Hydrogen evolution weakens the electric double layer on electrode surface which apparently disturbs the film composition. Upon the sweep reversal at the potential of -2 V the cathodic current density gradually decreases until it reaches to the value 0. After sweep in positive direction results in the dissolution of quaternary CuInGaSe system starts and anodic peak forms at the potential of 0.87 V indicating the reactions taking place in reverse order. The current density when reaches to the value 0, that means oxidative dissolution of CuInGaSe is completed at the electrode surface.

4.2 Cyclic Voltammetry analysis of quaternary CIGS prepared with SDS

A Cyclic voltammetry studies for the quaternary CuInGaSe_2 system were carried with and without surfactant sodium dodecyl sulphate (SDS) shown in fig 4.7. As explained for the ternary CIS system, at low cathodic potential 0V to -0.2V, CuxSe deposition takes place. These CuxSe phase acts like catalytic sites for the under potential deposition (UPD) of In(III) and Ga(III) ions. Thus the inclusion of In and Ga initiates after the formation of CuxSe. With increase in cathodic potential, the atomic percentage of In increases highly up to -0.6 V, with a little but considerable Ga inclusion. Beyond -0.6V, Ga(III) inclusion increases rapidly along with In(III) thus forming a stable CuInGaSe2 phase. The generalized mechanistic formation of CIGS has been explained in the introductory section. Upon the addition of SDS, a slight shift in the peaks has been observed which is evident that SDS has complexing behavior with ions. From the crossover potential observed around -0.9 V, it is clear that the Ga (III) reduction potential have been shifted towards less cathodic, which enables CIGS co-deposition.

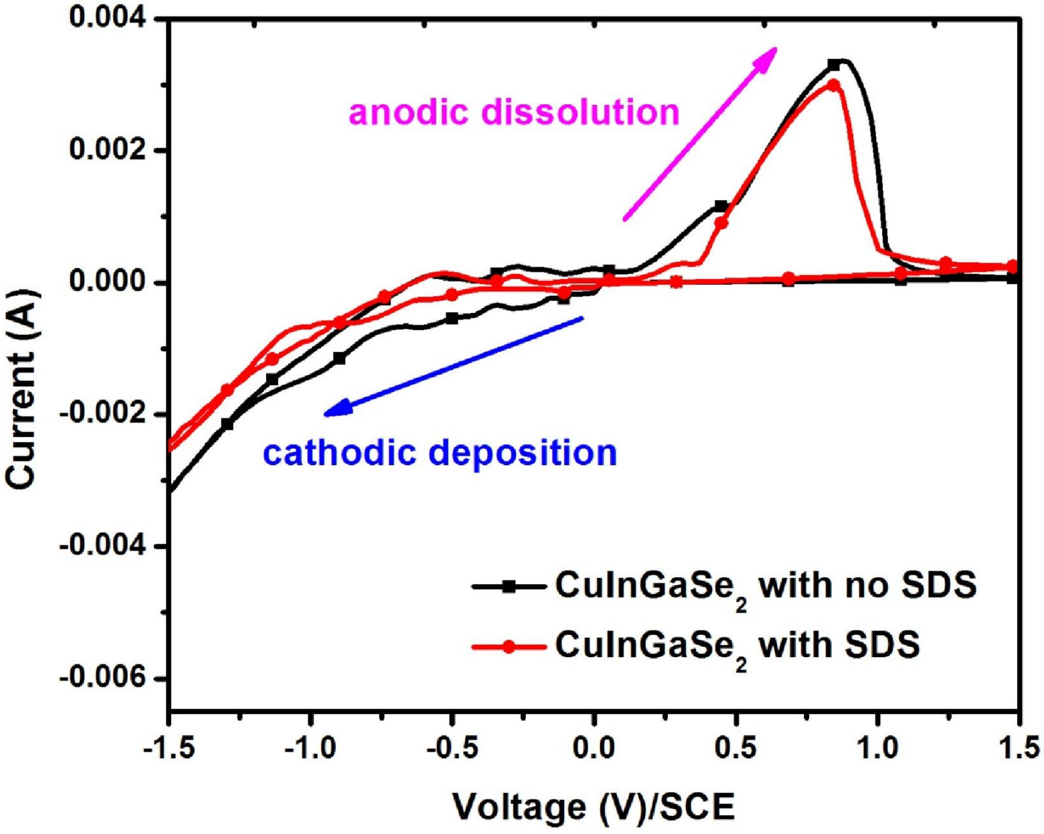


Figure 4.7: A comparison on the cyclic voltammogram of CuInGaSe bath with no SDS and with SDS

4.3 Electrodeposition ternary CIS with and without using SDS

Chronoamperometry study was conducted on ternary CuInSe system and quaternary CuInGaSe system to study the nucleation and growth mechanism. Cyclic voltammograms were considered for selection of deposition potentials for the chronomaperometry. The potential values selected for the Chronoamperometry were taken from negative side of CV peak. For deposition of CuInSe the deposition potential chosen was -0.5V to run the chronoameperometry study. The Chronoamperometry (CA) [Fig.4.8] carried for fresh Molybdenum substrate reveals that CIS formation follows progressive nucleation when SDS is used.

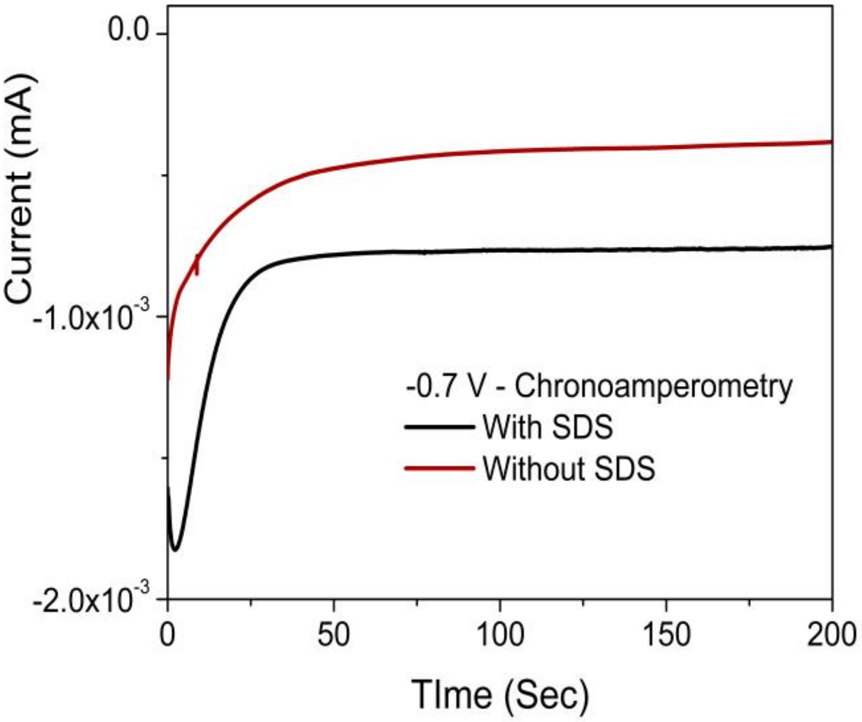


Fig.4.8: CA of CIS with and without SDS

The XRD of the as-deposited CIS films with and without SDS is shown in Fig. 4.9.An increased crystallinity was observed for CIS with SDS. Other unitary and binary phases like In, In_2se_3 and $MoSe_2$ were observed in both the samples. The JCPDS card numbers used are,

a) 23-0207- CIS
b) 45-1042- In_2Se_3
c) 29-0914-MoSe2
d) 05-0642- Elemental In.

Due to the amorphous nature and overlapping diffraction peaks of CIS and some secondary phases, identification of CuxSe and elemental Se phases only with XRD is difficult and hence it requires further supporting studies like Raman spectroscopy and XPS (X-ray photoelectron spectroscopy) to confirm the other phase present. Some of the unidentified peaks might be due to the impurities.

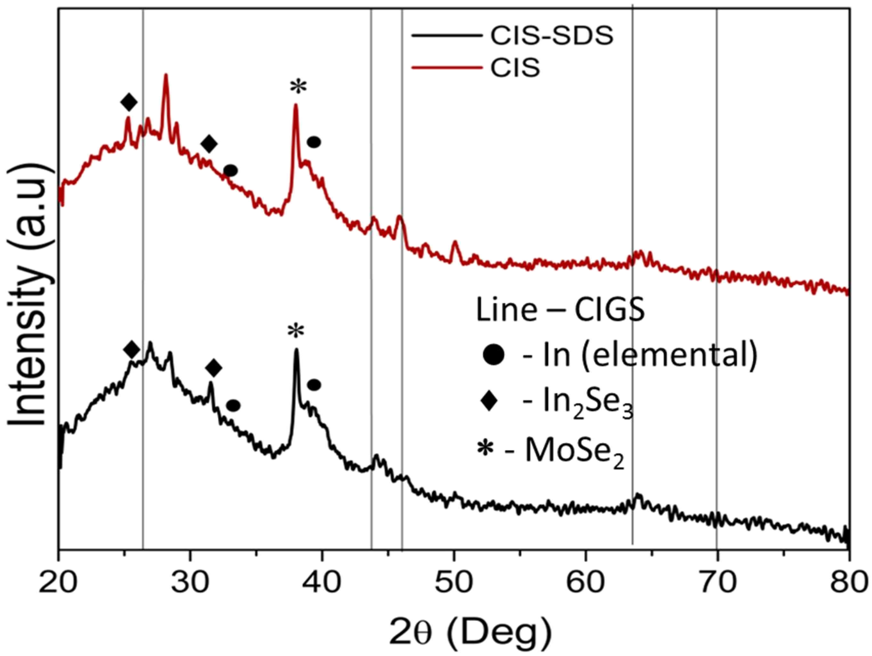


Fig.4.9 XRD of as-deposited CIS films with and without SDS [Lines- CIS phase, diamonds-In2Se3, circles- In, Star-MoSe2]

For the FE-SEM image analysis [fi.g4.10] the CIS deposited at -0.7 V for 20 min with and without SDS were used.

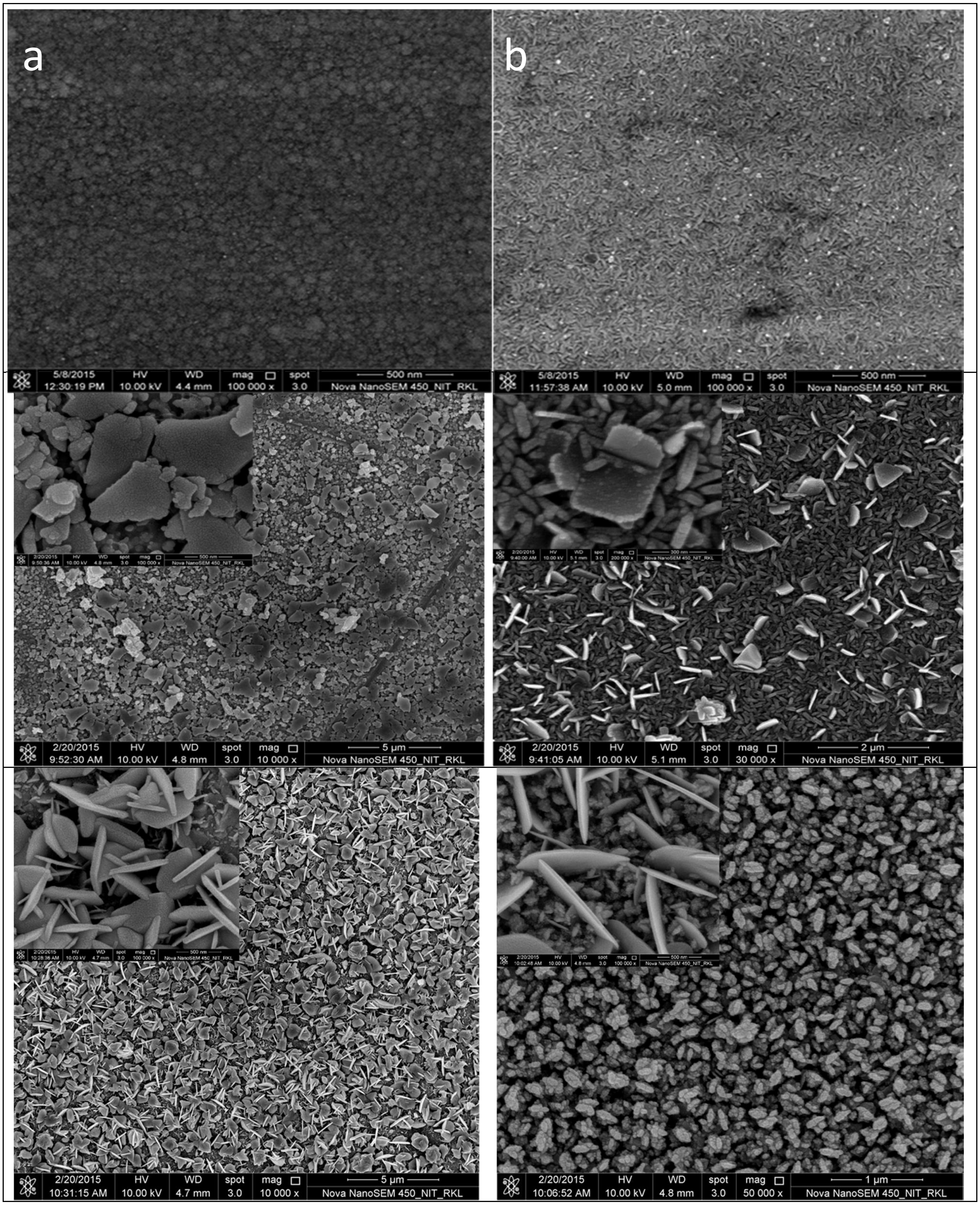


Figure 4.10: FESEM images of CIS thin film at -1.7 V, -1.5 V and -2 V (left) without SDS (right) with SDS respectively

It is confirmed that the CIS deposition in the presence of SDS follows progressive growth behavior, whereas an instantaneous growth behavior for CIS without SDS. A highly dense rice-shaped CIS deposits were obtained when CIS is deposited with SDS surfactant. Comparatively, the CIS films deposited without SDS were less dense and amorphous in nature.

4.4 Electrodeposition of quaternary CIGS with and without SDS

Chronoamperometry analysis then carried out for quaternary CuInGaSe system given the scan done at -1.5V for the time span of 120 sec for two baths, firstly for the bath having no surfactant as SDS and the other bath having SDS. Figure 4.11 shows the current-time response of CIGS absorber layer on Mo coated glass substrate deposited at both conditions i.e. bath with no SDS and bath with SDS. Initial current increases due to sudden increase in surface area in hetereogheneous system whenever the nucleation is involved in both the cases.

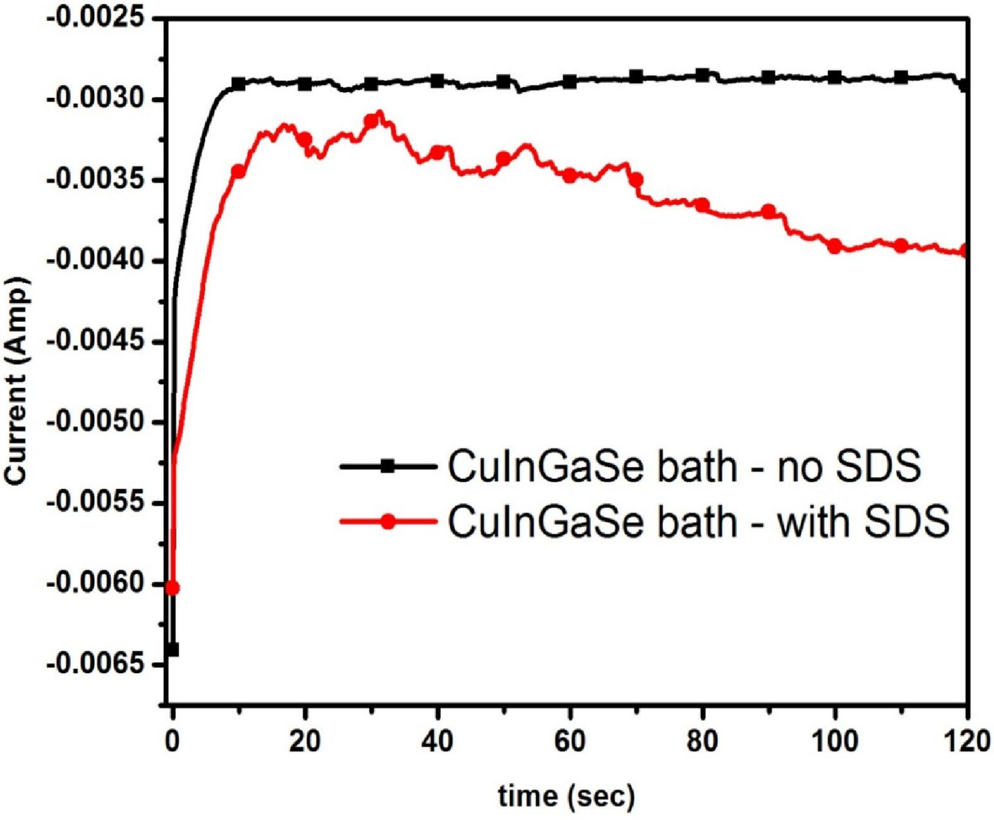


Figure 4.11: Current-time responses recorded for CIGS bath with SDS and with no SDS

In the CIGS electrodeposition there decrease in the reduction current with increasing negative potential in the CIGS bath with no SDS. Later a steady state current-time response gives idea about the development of growth of nuclei species with very little nucleation taking place. While in case of bath having SDS shows initial decrease in reduction current following gradual increase in reduction current shows the simultaneous process of nucleation and growth of new nuclei on active sites of the electrode surface. With increasing reduction current there is also a depletion of ion concentration takes place near the surface of the substrate surface. This concludes that the nucleation time for bath with no SDS was short while the bath with SDS nucleation and growth took place in synchronization.

The obtained CIGS deposited were subjected to XRD studies. The SDS assisted CIGS deposits were crystalline which is confirmed by FESEM (fig.4.13) and also exhibited less secondary phase than CIGS deposited without SDS (fig 4.12). Identification of other secondary phase was difficult due to the amorphous nature of the secondary phase. The possible identified secondary phase are CIGS [Line-JCPDS No: 35-1101], CIS [diamond-80-2189], Cu3Se2 [Circle-72-1421] and $MoSe_2$ [star- 77-1715].

Electrodeposition of quaternary CuInGaSe is carried out in the bath having SDS and in the bath having no SDS and their structural and compositional study has been done by FESEM analysis. Figure 4.13 shows the structural images of CuInGaSe electrodeposited in different deposition potentials i.e. bath with SDS at the deposition potential of -1.5V, -1.7 and -2V.

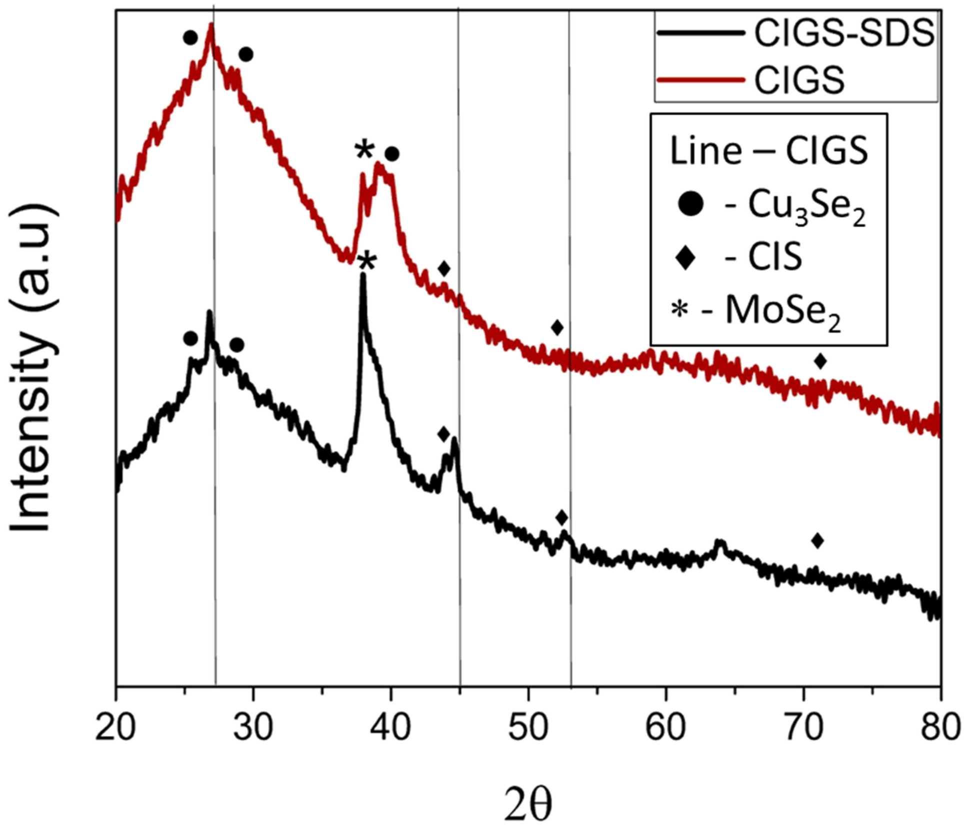
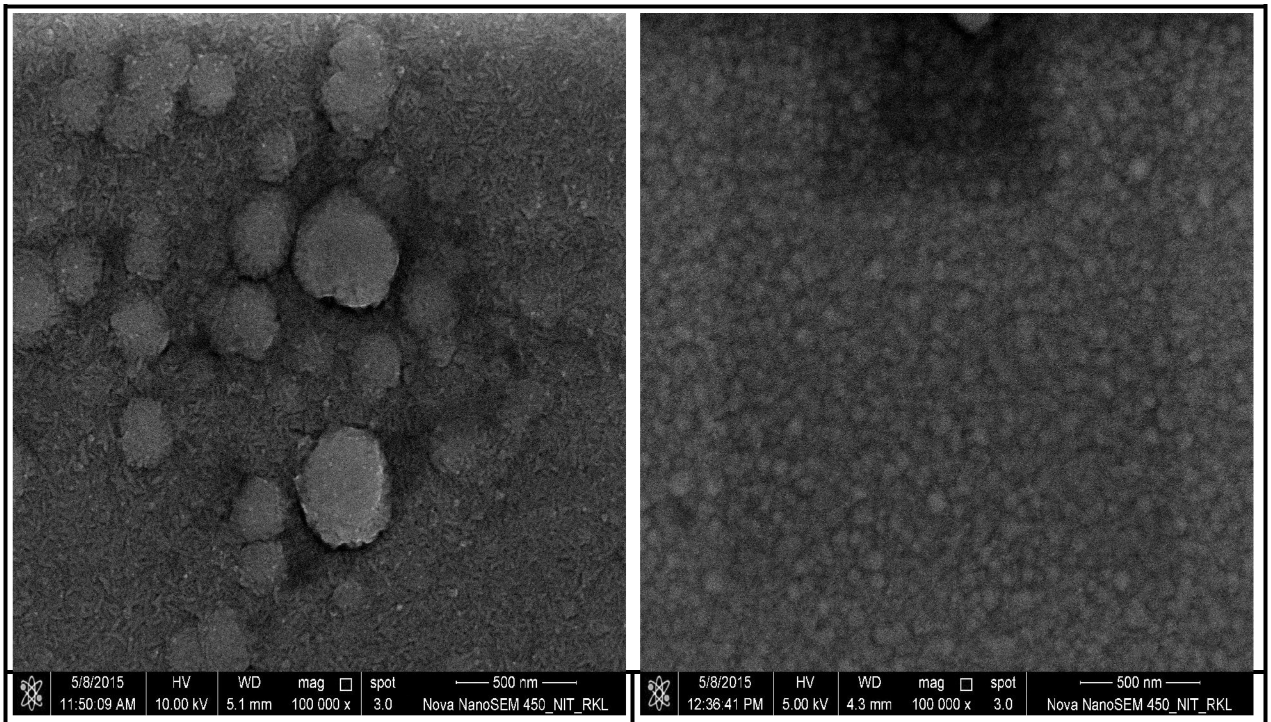


Fig. 4.12 XRD of as-deposited CIGS (with and Without SDS)

Analyzing the images of thin films prepared using SDS at the deposition potential of -2V, uniform rice like grains have been formed above the monolayer (figure 14.13 (a), (b), (c)). Looking into higher magnification, uniformity in the distribution of grains can be seen with average grain size range between 26 - 28 nm. Thin films prepared using SDS at the deposition potential of -1.5V (figure 14.13 (d), (e), (f)) gave completely different microstructure showing cauliflower like structure deposited over a thin deposited monolayer.



-1.5V with SDS

-2V with SDS

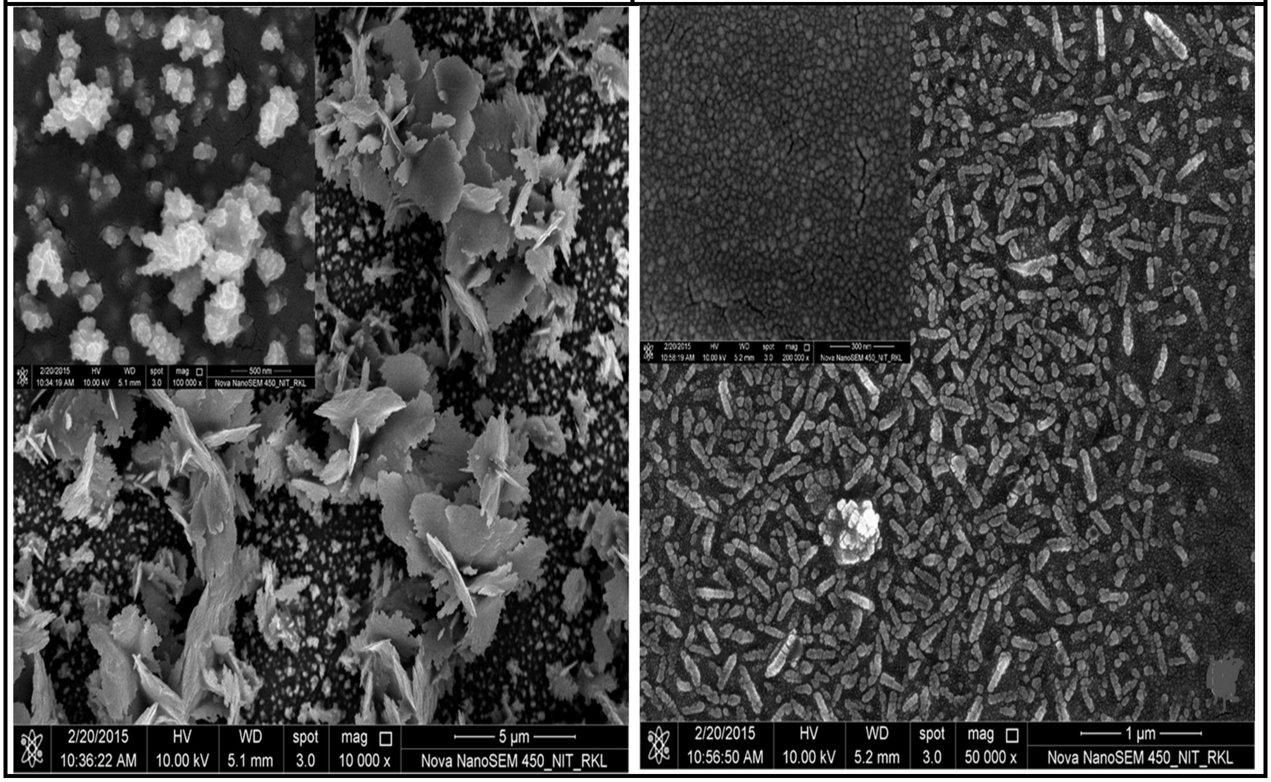


Figure 4.13: FESEM images of CIGS thin film at -1.7 V (left) without SDS (right) with SDS and thin film prepared with SDS at the potential of -1.5 V (left) and -2 V (right)

4.5 CIS/CIGS stoichiometry films obtained by two-electrode system:

CIS and CIGS deposition were carried by using a conventional two electrode system. The composition analysis was carried for $CuInSe_2$ and CuInGaSe2 deposited at -1.5V and -2V with SDS and without SDS. The ideal composition for CuInSe2 is of ratio 1:1:2 and for CIGS is 1:0.7:0.3:2.

Table 4.1: EDS Compositional analysis of CIS electrodeposited at different potentials

Potential/V vs. SCE	Atomic Percentage (%)			Cu/In ratio	Se/(Cu+In) ratio	Stoichiometry
	Cu	In	Se			
-1.5V	21.05	4.47	19.97	4.70	0.78	$CuIn_{0.21}Se_{0.94}$
-1.5V with SDS	28.58	7.32	32.78	3.90	0.91	$CuIn_{0.25}Se_{1.14}$
-2V	17.05	3.99	20.20	4.27	0.96	$CuIn_{0.23}Se_{1.18}$
-2V with SDS	29.80	11.40	41.30	2.61	1.0	$CuIn_{0.3}8Se_{1.38}$

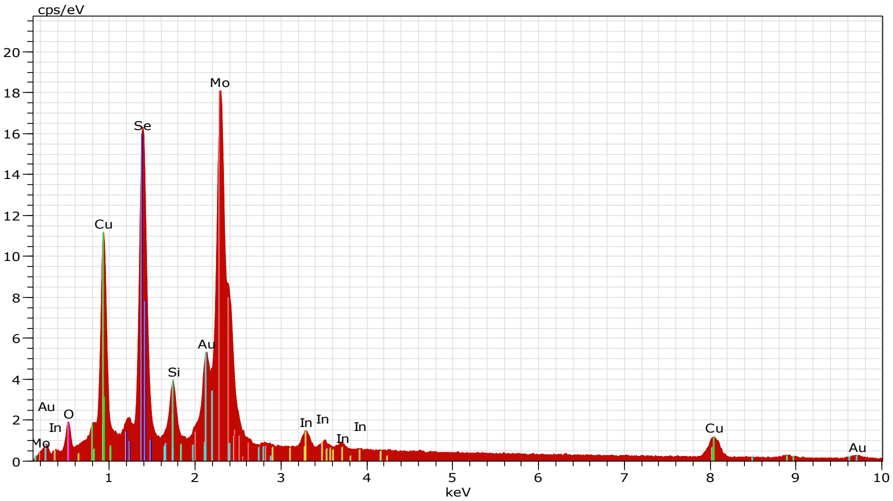


Figure 4.14: EDS spectra recorde for ternary CIS system at potential of -2V

Optimization for obtaining smooth and compact films was achieved. Yet, the potential used for deposition was found to be not suitable for In and Ga inclusion. Further work on composition analysis at higher cathodic potential is required to obtain good stoichiometric CIS/CIGS thin films.

Table 4.2: EDS Compositional analysis of CIGS electrodeposited at different potentials

Potential/V vs. SCE	Atomic percent (%)				Cu/(In+Ga) ratio	Se/(Cu+In+Ga) ratio	Stoichiometry
	Cu	In	Ga	Se			
-1.5V	30.14	14.06	0.67	44.94	2.04	1.00	$CuIn_{0.46}Ga_{0.02}Se_{1.49}$
-2V	22.66	1.30	4.34	20.97	4.01	0.74	$CuIn_{0.05}Ga_{0.19}Se_{0.92}$

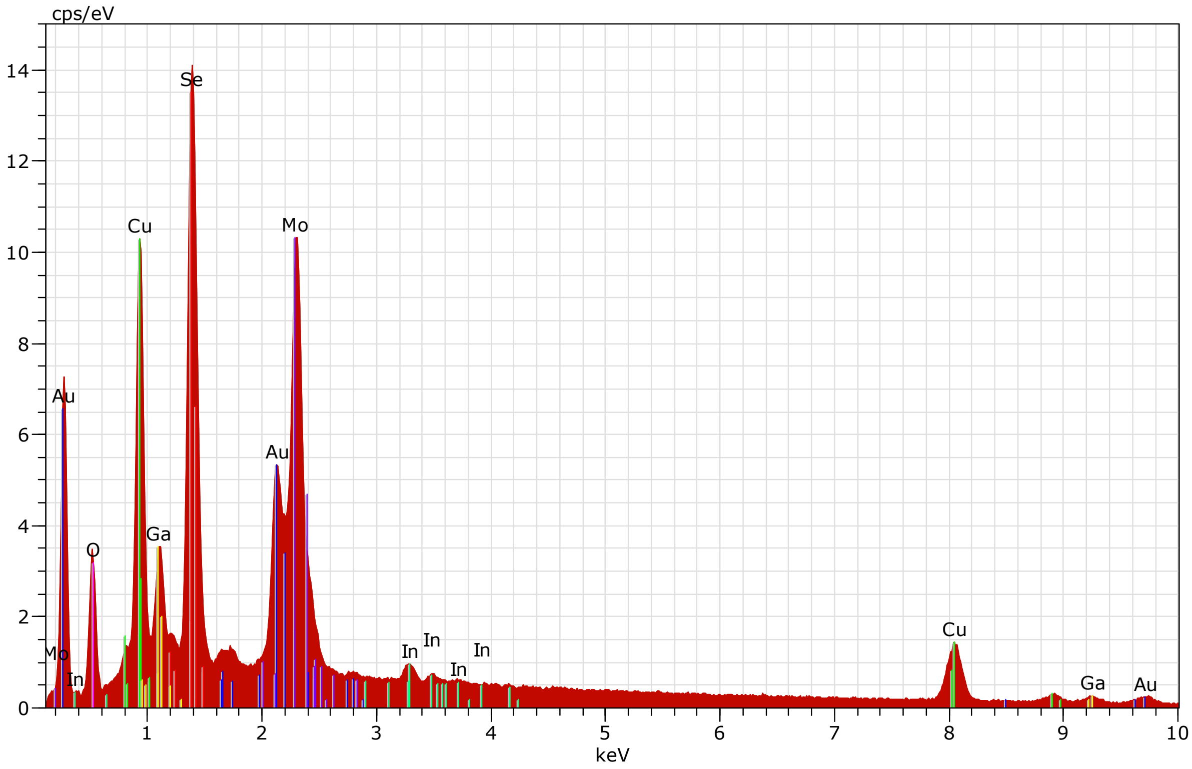


Figure 4.15: EDS spectra recorde for quaternary CIGS system at potential of -2V

Chapter – 5

Conclusions

Experimental results have been illustrated and conclusive remarks were included in this chapter

5. Conclusions

In the present work, the mechanistic deposition behavior of CIS and CIGS has been studied using three electrode systems. Usage of SDS surfactant was found to be beneficial in improving the morphology and helps in obtaining dense thin films. The significant results are summarized below,

1. From the linear sweep voltammetry (LSV) study carried for unitary (Cu), binary (Cu-Se) and ternary (Cu-In-Se) systems, the optimal co-deposition potential range for CIS have been identified. The order of deposition was found to be Cu> Se> In. The formation of CuxSe phase does not follow Kröger's mechanism, whereas In2Se3 formation obeys.
2. Using SDS, the CIS deposits were found to be dense and crystalline in nature which is confirmed by XRD and FE-SEM studies.
3. A preliminary study of CIS electrodeposition was carried in neutral electrolyte without any additives. Interestingly, it was found that CIS deposition can be carried conveniently co-deposited in such neutral bath with the potential range between -1 V to -1.3 V. This simplified deposition scheme reduces the complexity and avoids the usage of complexing agents. Further studies have to be carried to optimize and understand the complete deposition behavior.
4. Addition of SDS enhanced gallium uptake during electrodeposition, which is also confirmed by cyclic voltammetry studies. A cross over with increased current density observed at higher cathodic potential is evident for the enhanced Ga ions inclusion during the co-deposition process. The obtained CIGS films were crystalline and contained less secondary phase like Cu_3Se_2. For both ternary and quaternary systems, the morphology

obtained for SDS assisted CIS/CIGS deposits were rice shaped, which is confirmed by FE-SEM.

5. The CIS/CIGS deposition was also carried using conventional two electrode systems. From the compositional analysis, it was determined that the deposition voltage of -1.5 and -2V is sufficient for In and Ga inclusion. Yet, the films were non-stoichiometric. It is also suggested that a compositional studies for deposition potential greater than -2 V is required to obtain good composition CIS/CIGS films.

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