

A review on the Electrodeposition of CIGS Thin-Film Solar Cells

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Abstract:

Solar energy is one of the renewable energies being researched extensively owing to the scarcity of fossil fuels, besides the global concern on climate change. Consequently, intensive research activities have been conducting on solar cell material technology. Chalcopyrites (i.e., CIS, CISE, CIGS and CZTS) are suitable candidates for future improvement of solar cell technology as they provide a low-cost alternative to Si thin-film solar cells. Amongst the chalcopyrite family, copper indium gallium diselenide (CIGS) is considered to be a leading thin-film solar cell material. In this paper, a review of the electrodeposition process as a fabricating method for CIGS thin-film solar cells has been presented. The potential challenges encountered while depositing the absorber layers, and the effects of adding complexing agents to overcome such encountered challenges have been discussed. Moreover, past and record efficiencies, in addition to state-of-the-art research in the areas of finding alternative possibilities to overcome the issues with the selenization step as well as suitable solutions to deal with the issues associated with gallium incorporation have been reviewed. Future probable solutions have also been provided to these challenges. In short, this review brings together all the aspects related to CIGS solar cells to enrich the field and support the interested industry and researchers.

Keywords:

Photovoltaics, CIGS thin-film solar cells, Electrodeposition, Gallium accumulation, Complexing agents.

1. Renewable energy and solar energy:

Nowadays, the global warming phenomenon has become a headline issue since the consequences of increasing earth temperatures might cause catastrophic natural disasters and adverse effects, such as flooding, desertification, ice melting, extinction of many species, and deforestation wildfires. Accordingly, many countries are striving to pursue the development of clean, renewable energy resources to minimise the emission of greenhouse gases (as CO₂) from hydrocarbon sources and human-made pollution. However, nature provides many alternative sources of clean energy that could be generated from abundant solar radiation, ocean waves, and wind; thus, solar energy is remaining vital. Photovoltaic (PV) is a term used to describe the direct conversion of solar energy to electrical energy using solar panels, whereas fossil fuels are incredibly costly, as well as limited and scarce.

Moreover, they also emit greenhouse gases. Due to these reasons, the attractiveness of renewable energy has increased considerably in the world energy-based economies (Ellabban, Abu-Rub et al. 2014). The worldwide primary energy consumption was increased by 2.2% in 2017 from 1.2% in 2016 and the highest since 2013 owing to the scarcity and rapid depletion of conventional energy sources and increasing energy demand (2018). It is predicted that by 2050, PV electricity would cover more than 20% of the energy demands (Razykov, Ferekides et al. 2011). To reduce carbon dioxide emissions by the middle of the century, it has become necessary to use PVs and other renewables as a source of electricity.

In solar cells or photovoltaic devices, a semiconductor with another metal forms a rectifying junction. This structure is called a PN-diode or a Schottky diode. When the junction is illuminated, if the energy $h\nu$ of the incoming photons is more significant than that of the band gap of the semiconductor, it absorbs the incoming photons. The absorbed photons are converted into electron-hole pairs. The holes drift to one electrode and the electrons to the other one. This created a potential for the current to flow (Stone 1993, Shah, Torres et al. 1999).

There is a considerable demand for thin-film solar cells and the market for these devices is expected to grow significantly over the next few years (Razykov, Ferekides et al. 2011). In terms of dimensions, thin-film solar cells are ahead of their competition, and they also present a wide variety of choices in terms of device design and fabrication. Currently, amorphous Si, CdTe, CuInSe₂, and their alloys with Ga and/or S are the leading low-cost materials of interest among the various thin-film absorbers (Saji, Choi et al. 2011). Si-wafer-based solar cells are currently abundantly found in the market currently owing to their high efficiency. Si-wafer-based solar cells are considered to be first-generation solar cells and were initially single crystalline (mono-Si) solar cells, which later on developed to poly-crystalline (poly-Si or multi-crystalline Si) cells (Jackson, Wuerz et al. 2016). Polycrystalline Si (pc-Si) thin-film solar cells have been developed to provide high-production capacity with reduced material consumption and energy input in the fabrication of PV cells and integration in the structure of modules via deposition. This consequently leads to a reduction in costs for large-scale terrestrial applications. Traditional Si solar cells have disadvantages such as high cost and low efficiency. To elaborate, the following are the main disadvantages of traditional Si solar cells:

- i. They require expensive fabrication technologies.
- ii. Growing and sawing of ingots is a highly energy-intensive process.
- iii. It is reasonably easy for an electron generated in another molecule to hit a hole left behind in a previous photoexcitation.
- iv. A significant portion of the energy from the higher-energy photons, particularly at the blue and violet ends of the spectrum, is wasted as heat (Jackson, Wuerz et al. 2016).

CdTe is a newer addition to the thin-film family. CdTe is considered to be an auspicious material for thin-film solar cells (Lincot 2005). CdTe cells having a small area with efficiencies of more than 15% have been developed (Glasstone 1960, Zank, Mehlin et al. 1996). Moreover, large-area monolithic CdTe modules have the added advantages of high performance and the ability to attract production-scale capital investment (Huang, Li et al. 2001). However, the conventional SnO₂/poly-CdS/poly-CdTe device structure used for more than 30 years has limited further improvement in the performance and reproducibility of CdTe cells (Goossens and Hofhuis 2008). Another disadvantage of using CdTe is that Cd is exceptionally toxic; therefore, environmental regulations imposed on its usage make it less attractive.

In addition to CdTe, chalcopyrites (CuInSe₂/CuIn_{1-x}/Ga)Se₂ (CIS/CIGS) are also relatively new in this field and are conceivably the most promising material in this category with a maximum reported laboratory efficiency of approximately 23.35% (Nakamura, Yamaguchi et al. 2019). There are several methods for the production of CIGS solar cells including evaporation (Jung, Ahn et al. 2010, Sastré-Hernández, Calixto et al. 2011), sputtering (Lin, Chen et al. 2013, Liu, Zhuang et al. 2013), spray pyrolysis (Babu, Velumani et al. , Ho, Zhang et al. 2014), printing (Kapur, Bansal et al.), molecular beam epitaxy (Grindle, H. Clark et al. 1980), and electrodeposition (Bhattacharya, Wiesner et al. 1997, Bhattacharya RN 1998, J. Sebastian, Calixto et al. 1998, Duchatelet, Sidali et al. 2013). CIGS offers many advantages compared to other PV technologies. It has a high energy yield, low temperature coefficient of power loss, low sensitivity to shadowing, and short energy payback time (Makrides, Zinsser et al. 2010, Ellabban, Abu-Rub et al. 2014, Bhandari, Collier et al. 2015). Vacuum-based methods for the production of CIGS solar cells pose cost and technological barriers to the production of low-cost PV cells, even though they have achieved efficiencies above 20%. CIGS thin-film solar cells have mostly been deposited on glass/Mo substrates; moreover, for a long time, CIGS solar cells deposited on flexible substrates such as plastic film or metal foil could not reach similar efficiencies (Chandran, Panda et al. 2018)

Thin-film solar cell	Highest efficiency obtained (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Features	Typical device structure	Company	Year	Reference																														
Crystalline Silicon	26.7	0.738	42.65	84.9	Interdigitated back contacts, amorphous Si/crystalline Si heterojunction		Kaneka	2017	(Yoshikawa, Kawasaki et al. 2017)																														
GaAs	29.1	1.1272	29.78	86.7	Single junction, lightweight, flexible, excellent UV and radiation resistance	<table border="1"> <tr> <td>p-ohmic</td> <td>p-GaAs</td> <td>500 nm</td> </tr> <tr> <td>Back Surface Field</td> <td>p-InGaP</td> <td>50 nm</td> </tr> <tr> <td>Base</td> <td>p-GaAs</td> <td>3500 nm</td> </tr> <tr> <td>Emitter</td> <td>n-GaAs</td> <td>100 nm</td> </tr> <tr> <td>Window</td> <td>n-InGaP</td> <td>30 nm</td> </tr> <tr> <td>n-ohmic</td> <td>n-GaAs</td> <td>300 nm</td> </tr> <tr> <td>Buffer</td> <td></td> <td></td> </tr> <tr> <td>Sacrificial</td> <td>u-AlAs</td> <td>20 nm</td> </tr> <tr> <td>Buffer</td> <td></td> <td></td> </tr> <tr> <td colspan="3">p-GaAs (100) substrate 2°-off toward [111]</td> </tr> </table>	p-ohmic	p-GaAs	500 nm	Back Surface Field	p-InGaP	50 nm	Base	p-GaAs	3500 nm	Emitter	n-GaAs	100 nm	Window	n-InGaP	30 nm	n-ohmic	n-GaAs	300 nm	Buffer			Sacrificial	u-AlAs	20 nm	Buffer			p-GaAs (100) substrate 2°-off toward [111]			Alta Devices	2018	(2014, Moon, Kim et al. 2016, 2018)
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CIGS	23.35	0.734	39.58	80.4	Rigid, heterojunction system, direct band gap material, high absorption coefficient, Cd-free, Zn(O,S,OH) _x /Zn _{0.8} Mg _{0.2} O double buffer layers		Solar frontier	2018	(Nakamura, Yamaguchi et al. 2019)																														
CdTe	21	0.8759	30.25	79.4	Rigid, high absorption coefficient, direct band gap		First Solar	2014	(2014, Burst, Duenow et al. 2016)																														

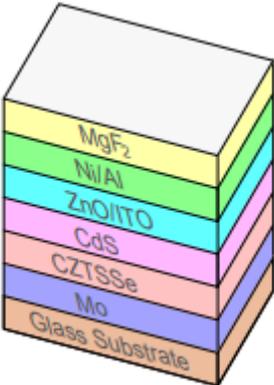
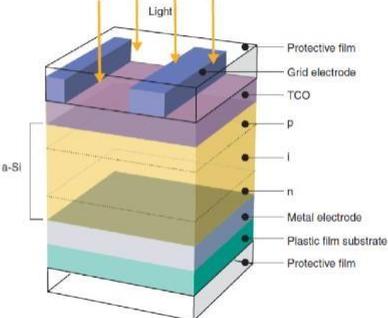
CZTSSe	12.6	0.5134	35.2	69.8	CdS/CZTSSe heterojunction, rigid, direct band gap, high absorption coefficient		DGIST, Korea	2018	(Wang, Winkler et al. 2014)
Amorphous Si	10.2	0.896	16.36	69.8	Double-junction device, rigid		AIST	2015	(Fraas 2014, Matsui, Bidiville et al. 2015)

Table 1: Summary of the characteristics of different thin-film solar cell materials

Table 1 depicts the device structure, highest efficiency obtained, features and vendors of the different types of thin-films available in the market. The optical band gap of CIGS lies within the maximum solar absorption region and varies from approximately 1.05 to 1.6 eV (Gerthoffer, Poulain et al. 2017). The best-in-class devices are typically grown with a Ga/(Ga+In) ratio of 0.25 to 0.35, corresponding to a band gap of approximately 1.1-1.24 eV. Typically, it is required to optimize the band gap energy of the absorber material. The large optical absorption coefficient of CIGS solar cells permits the use of thin layers (1-2 μ m) of active material (Bhattacharya 2003).

The term chalcogen refers to the chemically and technologically essential selenium and tellurium elements of the sulfur sub-group. An ideal absorber material should have the following properties:

- i. A direct band gap (the advantages of direct band gap semiconductor outweighs the advantages of indirect band gap semiconductors. Semiconductors with indirect band gaps do not absorb light as efficiently as those with direct band gaps, and therefore a thick layer of material is needed to achieve sufficient light absorption (Kemell, Ritala et al. 2005). As an example, crystalline silicon should have a thickness of 100 μ m for 90% light absorption in comparison with 1 μ m of direct band gap semiconductor-GaAs (Goetzberger and Hebling 2000))
- ii. High absorption coefficient
- iii. Long diffusion length
- iv. Low recombination velocity
- v. The ability to form a good electronic junction with suitably compatible materials (S. Saji, Lee et al. 2011)

Currently, efforts are underway to develop cheaper deposition methods and increase efficiency by up to 30% (Bhattacharya and Rajeshwar 1986, Bhattacharya RN 1998, D. R. Ludwig, Gruhn et al. 2010).

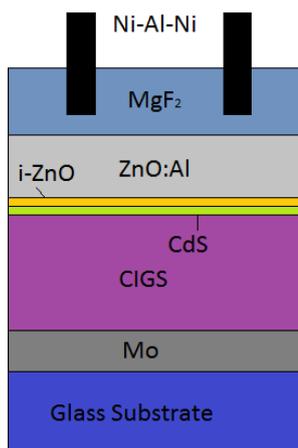


FIGURE 1 - Schematic of a standard CIGS solar cell

The fabrication process involves the deposition of different layers including the contact, absorber buffer, reflector, and window layer, as shown in Figure 1. The overall efficiency of final such cells depends on the processed quality of the layers and their interfaces (S. Saji, Lee et al. 2011). The layer after the CIGS layer is the molybdenum (Mo) back contact layer, which acts as the optical reflector to reflect the light back to the absorber layer in CIGS solar cell (Rostan, Mattheis et al. 2005, Pradhan, Aryal et al. 2015). There are several advantages of using Mo as the back contact material. It does not react strongly with CIGS; further, it forms a low-resistivity ohmic contact with CIGS, and the conductivity of Mo does not degrade during the deposition of CIGS at high substrate temperature; it has high conductivity and is more chemically and mechanically stable during CIGS growth (selenization) (Raud and Nicolet 1991, Ashour, Alkuhaimi et al. 1993, Moons, Engelhard et al. 1993, Orgassa, Schock et al. 2003, Romeo, Terheggen et al. 2004, Huang, Gao et al. 2016, Li, Yan et al. 2016).

Expensive rigid glass or flexible metal/polymer could be utilised as substrates. However, most of the commercially available thin-film solar modules are being produced on rigid glass substrates. Nevertheless, processing on flexible, lightweight substrates, like metal foils or polyimide films is possible owing to the low thickness of thin-film solar cells (Wuerz, Eicke et al. 2009). Related studies were carried out using flexible substrates, such as steel foils (Wuerz, Eicke et al. 2009) and enamelled steel (Wuerz, Eicke et al. 2012), polyimide (Chirilă, Reinhard et al. 2013), ecologic ceramic (Fraga, Stoyanova Lyubenova et al. 2016), and ultra-thin glass substrates (Gerthoffer, Poulain et al. 2017). Thus, the highest efficiency achieved till now on a glass substrate is 23.35%, hitherto (Nakamura, Yamaguchi et al. 2019). The experiments conducted recently proved that by using flexible polyimide, the efficiency gap between Si-wafer-based cells and CIGS solar cells can be reduced significantly. The highest cell efficiency of 18.7% was obtained by using a flexible polyimide film in 2016 (Jackson, Hariskos et al. 2011).

2. Electrodeposition of CIGS thin film solar cells:

The processes that employ electrodeposition as a fabrication method for CIGS thin films fall into two categories:

- i. Single-stage: fabrication of the complete, crystalline film in one electrodeposition step.
- ii. Two-stage: electrodeposition of metallic precursor followed by sulfurization/selenization step.

As vacuum-based methods are rather expensive and pose challenges in controlling the compositional homogeneity for producing a large-area CIGS thin film, there have been several studies conducted on non-vacuum-based techniques, such as chemical bath deposition (Huang, Li et al. 2001), spray deposition (Goossens and Hofhuis 2008), and electrochemical deposition. Electrodeposition is the process of coating a thin layer of one metal on top of a different metal to modify its surface properties. It is done to achieve the desired electrical and corrosion resistance, reduce wear and friction, and improve heat tolerance. Electrodeposition is also an

essential process for the synthesis of semiconductor thin films and nanostructures, especially chalcogenides and oxides. However, it is still challenging to obtain electrodeposited CIGS with the adequate composition, thickness and optical properties (Bhattacharya, Wiesner et al. 1997, Lincot, Guillemoles et al. 2004).

Electrodeposition is a well-known process for the deposition of metals and metallic alloys at the industrial level. The applications to electrodeposition are ranging from large area surface treatments (i.e. Zn electroplating) to more advanced applications (Cu deposition on chips, magnetic heads, and the like). Moreover, the fabrication of thin-film absorber layers is one of the electrodeposition applications, which is a low-cost method for the formation of the absorber layers. It allows for the deposition of uniform large-area materials and also allows for easy adjustment of the film for obtaining the desired chemical and electrical properties. These applications are significant advantages that make electrodeposition very suitable for fabricating of thin-film solar cells. Bhattacharya (N. Bhattacharya 1983) reported the first electrodeposition of a CIS film. When the applied potential exceeds the standard reduction potential of the copper, indium, gallium or selenium ion, metal ions are converted to metal atoms and deposited on the cathode surface (Glasstone and American Electroplaters 1943).

Electrodeposition of CIGS layers is possible via a one-step or two-step process as mentioned earlier. In a simultaneous one-step deposition process, the concentration and pH of the electrolyte ought to be adjusted such that the electrode potentials of all the individual elements may come closer to each other. In the two-step process, stacked layer structure deposition of pure elements or combinations with binary or even ternary films can be done, followed by a selenization/sulfurisation treatment. One-step deposition is often preferred as it simplifies the deposition process and reduces harmful emissions. Electrodeposition has several advantages including low equipment and material costs, high deposition speeds, resourceful utilization of raw materials, and feasibility for fabricating large-area films (Bhattacharya and Rajeshwar 1986, N. Bhattacharya 2010). It could also be used in the deposition of films on substrates with various shapes and forms (wire, tapes, coils, and cylinders) with minimum waste generation (Neale 2016). Intensive research is being carried out and pilot scale processes are being conducted to deposit the CIGS absorber layer via electrochemical deposition with good success (Bhattacharya RN 1998, Lincot, Guillemoles et al. 2004, Taunier, Sicx-Kurdi et al. 2005, Rousset, Saucedo et al. 2011, Duchatelet, Sidali et al. 2013, Jackson, Wuerz et al. 2016).

Duchatelet et. al. studied the impact of reducing the thickness of electrodeposited stacked Cu/In/Ga layers on the performance of CIGS solar cells. To decrease the thickness, it is not enough to merely reduce the deposition time of the CIG layers without changing the composition and deposition parameters of the thin films. Three different thicknesses were investigated: 2100nm, 650nm and 370 nm. Results showed that it was possible to significantly improve the open circuit voltage in electrodeposited ultrathin CIGS solar cells by increasing the Ga content in the layer. For a 0.37- μm -thick absorber layer, an absorber efficiency of 8.7% was observed because as the thickness is reduced, the efficiency of the CIGS solar cell also decreases (Duchatelet, Letty et al. 2017). This is because when the thickness of the CIGS absorber layer thickness increases, several photons are absorbed (Heriche, Rouabah et al. 2017).

Although electrodeposition process has the advantage that it is an inexpensive method for the fabrication of CIGS thin film solar cells, however, it is difficult to control when compared to the co-evaporation process. Therefore, it is important to develop methods to control the system properly and efficiently. This paper provides a comprehensive review of several topics that come under the electrodeposition of CIGS thin film solar cells including past efficiencies obtained, effect of deposition parameters and challenges encountered while depositing the CIGS thin-films.

3. Efficiencies obtained in different studies on fabrication of CIGS thin-film solar cells:

As a quaternary chalcopyrite compound, CIGS has become one of the most promising materials for fabricating high-efficiency thin-film solar cells (Jaffe and Zunger 1984). Studies have been conducted to achieve the maximum possible efficiency for CIGS solar cells. Ribeaucourt et. al. reported efficiencies up to 9.3% via one-

step electrodeposition of CIG alloys under acidic conditions (at pH 2) as precursor layers for preparing CIGS thin-film solar cells. The layers were deposited potentiostatically followed by annealing under a Se atmosphere. This study investigated the effect of adding sodium citrate as a complexing agent. Apart from this, partial single or binary electrodeposition systems Cu, In, Ga, Cu-Ga, Cu-In were studied followed by Cu-In-Ga ternary electrodeposition systems. From these speciation studies, it was observed that Cu-Ga and Cu-In electrodeposition proceeds mainly through the formation of binary phases. Scanning electron microscopy (SEM) studies showed dendritic morphology. However, with intermediate thermal treatment, dense absorbers with adequate properties could be obtained (Ribeaucourt, Savidand et al. 2011).

Solar cells with an efficiency of 12.4% were achieved from an atmospheric-based deposition process for CIGS synthesis, involving electrodeposition of a Cu-In-Ga mixed oxide/hydroxide layer from an aqueous solution, at room temperature, followed by thermochemical reduction and selenization. Electrodeposition was carried out without the addition of any complexing agent in a nitrate based electrolyte. The advantages of this process included fast growing rates through the one-step co-deposition of the three elements and precise control of composition as it is a mass-transfer-controlled process. A mixture of In and $\text{Cu}_9(\text{In,Ga})_4$ metals results from the reduction of the layer in a pure hydrogen atmosphere. The main advancement was eliminating Ga depletion by avoiding it, which occurs because of GaMo_3 formation at the back contact. The $\text{CuIn}_{0.85}\text{Ga}_{0.15}\text{Se}_2$ phase was obtained after selenization. The results proved the suitability of the Cu-In-Ga oxide/hydroxide electrodeposition and reduction process. This represented a new path for enhanced wet technologies (which can also be termed non-vacuum fabrication methods) and more cost reduction. The whole electrodeposition process took just a few minutes to be completed (Duchatelet, Sidali et al. 2013).

Londhe et. al. investigated the effect of electrodeposition potential on the growth and properties of CIGS layers. They deposited the CIGS thin film solar cells from non-aqueous bath using one-step electrodeposition. The authors found that films deposited at lower potential (-0.9V) tend to drive the growth of CIGS favouring (112) crystal orientation, whereas the films deposited at -1.6V show the orientation along (220/204). It was observed that the films deposited at -1.6V with (220/204) orientation showed high efficiency as compared to the film deposited at -0.9V with (112) orientation (Londhe, Rohom et al. 2018).

High efficiencies of up to 15.8% in Mo/CIGS/CdS/i-ZnO solar cells terminated with an electrodeposited ZnO:Cl window layer were also reported. ZnO is used for transparent conductive oxide applications (TCO) owing to its structural and optical properties. The more cost-intensive sputtering technique was replaced by the low-cost electrochemical deposition technique for synthesizing the ZnO front contact of the CIGS-based solar cell (Rousset, Saucedo et al. 2011). Efficiencies of 20% have been reported for Mo/CIGS/CdS/i-ZnO/ZnO:Al structures terminated with a sputtered Al-doped ZnO layer (Jackson, Wuerz et al. 2016). Bhattacharya reported efficiencies of 11.7% in CIGS-based solar cells fabricated directly from electrodeposited precursor films, eliminating the expensive Physical vapour deposition (PVD) step. Electrodeposited CIGS absorber layers were fabricated from stacked Cu/In/Ga layers (Bhattacharya 2013). Bhattacharya et al. also reported Cu-In-Ga-Se precursor thin films prepared via electrodeposition on molybdenum substrates. Using the precursor electrodeposited Cu-In-Ga-Se layers, ZnO/CdS/CuIn_{1-x}Ga_xSe₂ device was fabricated with an efficiency of 12.3%. In another paper, efficiencies of 15.4% and 12.4% have been reported for CIGS-based devices fabricated from electrodeposited (ED) and electroless deposited (EL) precursors. The final film composition is adjusted by a Physical Vapor Deposition step. The authors concluded that the ED and EL processes are simple and fast, and they can synthesize binary or multinary precursors for subsequent processing into high-quality CIGS thin-film absorbers for solar cells. Furthermore, it was decided that the quality of CIGS-based films and devices prepared from ED precursors is very promising which would lead to novel, fast, and low-cost methods for solar-cell absorber growth, and eventual module fabrication (Bhattacharya, Batchelor et al. 1999). A record efficiency of more than 20% was reported by Philip et. al for CIGS thin-film solar cells fabricated via co-evaporation (Jackson, Hariskos et al. 2011). Recently, an efficiency of 22.9% for laboratory-scale CIGS-based solar cells prepared by the two-step process was reported by the National Institute of Advanced Industrial Science and Technology (AIST) (Chirilă, Buecheler et al. 2011, Green, Hishikawa et al. 2019). Record cell and absorber efficiencies of 17.3% and 14%, respectively, for CIGS solar cells prepared via electrodeposition followed by thermal treatment under atmospheric pressure were obtained by NEXCIS (Broussillou, Viscogliosi et al.). A

slight variation in stoichiometric composition results in significant variations in the conductivity, thus dramatically decreasing the conversion efficiency of solar energy to electricity (Yeh, Hsu et al. 2016). The following steps have been undertaken to achieve higher efficiencies:

- i. Very strict standardization of the process flow: By standardizing the fabrication process of the CIGS solar cells, the efficiency can be increased by increasing the quality of the film deposited.
- ii. Usage of cleaner materials, procedures and working environments
- iii. Varying the selenium flow rate: At a relatively high Se flow rate (e.g. 25 A/s), the selenised CGIS cells exhibit improved surface morphology, resulting in increased efficiency of the solar cell (Continenza, Massidda et al. 1992).
- iv. Fine tuning of the cell stack.
- v. Optimization of processing conditions: Optimizing processing conditions leads to a better fill factor and improved open-circuit voltage.
- vi. Minimization of material loss reduces production costs (Jackson, Hariskos et al. 2011).

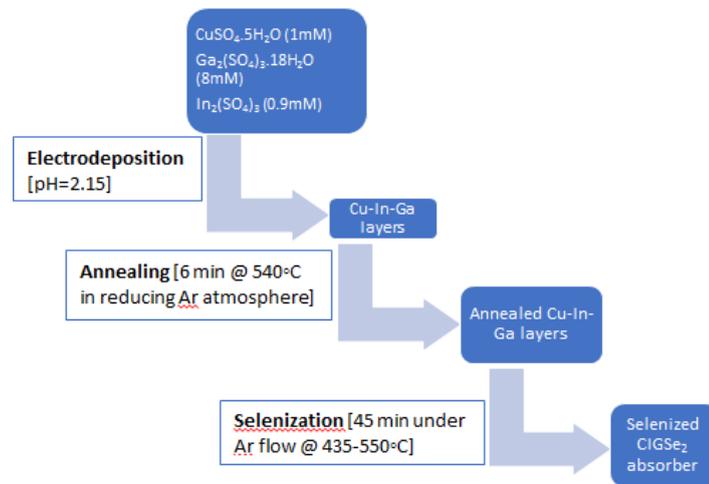


FIGURE 2- An example of the co-deposition method for the production of CIGS solar cells

Figure 2 shows an example of the codeposition process of the elements Cu, In and Ga from their respective solutions to produce 9.3% efficient CIGS thin film solar cells (Ribeaucourt, Savidand et al. 2011).

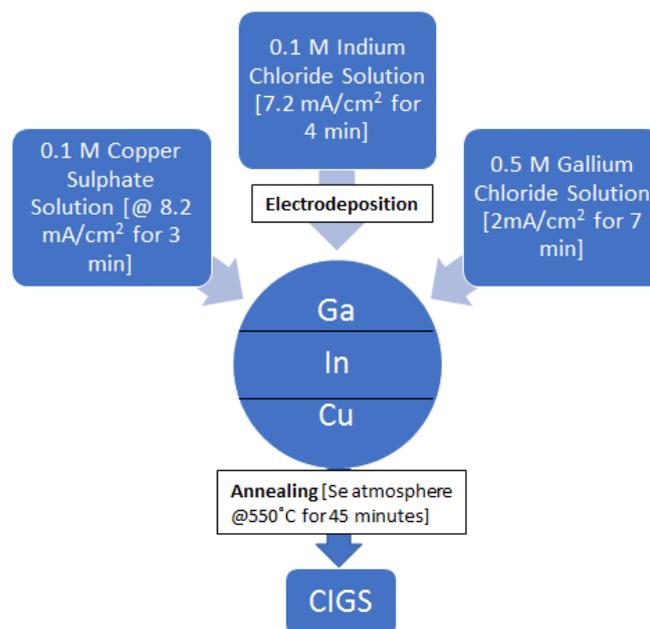
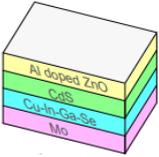
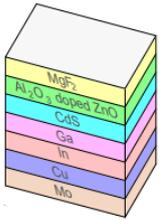
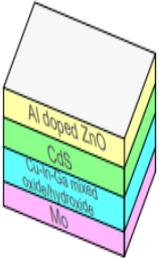
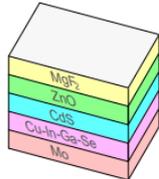
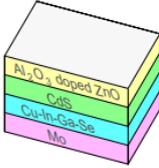
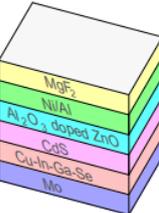
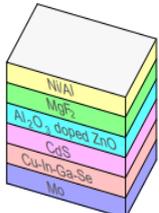
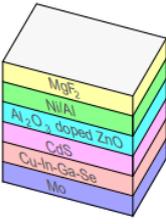
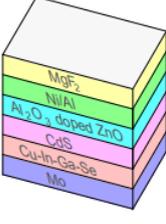
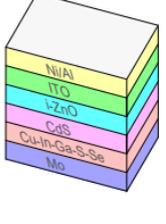
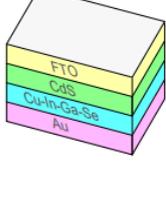


FIGURE 3- An example of the Cu, In and Ga multi-step electrodeposition method for the production of CIGS solar cells

Figure 3 shows an example of the multi-step electrodeposition process of the elements Cu, In and Ga from their respective solutions to produce 11.7% efficient CIGS thin film solar cells (Bhattacharya 2013).

Deposition method	Available Device Structure	Absorber material	Substrate	Fill factor (%)	Open circuit voltage (mV)	Short circuit current flux (mA/cm ²)	Cell Efficiency, η (%)	Ref.	Additional information	Year of Publication
Electrodeposition of Cu-In-Ga alloys followed by selenization		CIGS	Mo/glass	62	456	33	9.3	(Ribeau court, Savida nd et al. 2011)	Electrodeposit ion conducted in acidic medium; complexing agent used: Sodium Citrate	2011
Electrodeposition of stacked Cu/In/Ga layers followed by selenization		CIGS	Mo/glass	66	480	37.3	11.7	(Bhatta charya 2013)	Eliminates expensive PVD step	2013
Electrodeposition of Cu-In-Ga mixed oxide layer followed by thermochemical reduction followed by selenization		CIGS	Mo/glass	72.7	539	31.8	12.4	(Ducha telet, Sidali et al. 2013)	One-step co-deposition of the three elements	2013
Electrodeposition and electroless deposition of CIGS solar cells followed by PVD step to adjust the final film		CIGS	Mo/glass	75.6, 66.1	666, 565	30.51, 33.27	15.4, 12.4	(N. Bhattac harya, Batchel or et al. 1999)	Compared with 17.7% PVD device	1999

composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$										
Electrodeposition of Cu-In-Ga alloys followed by thermal annealing in Se atmosphere		CIGSe	Mo	45.6	300	31.7	4.35	(Ganchev, Koiss et al. 2006)	Addition of complexing agent: KSCN	2006
Electrodeposition of CIGS followed by PVD step to adjust the final composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$		CIGSe	Mo/glass	74.1	656	29.03	14.1	(Bhattacharya RN 1998)	Four electrodeposited devices were fabricated. Results presented here are for Ga/(In+Ga) ratio device of 0.24. Results were compared to 17.7% PVD device	1998
Electrodeposition of CIGS followed by PVD to adjust the final composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$		CIGSe	Mo/glass	71.6	689	27.65	13.7	(Bhattacharya, Batchelor et al. 1998)	Three devices were fabricated. Ga/(In+Ga) content = 0.39. Compared with 17.7% efficient device	1998
Electrodeposition of CIGS followed by selenization at 550°C		CIGSe	Mo/Cr/glass	67.9	550	-26.6	10	(J. Sebastian, Calixto et al. 1998)	-	1998

Electrodeposition of CIGS followed by PVD step to adjust the final film composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$		CIGS e	Mo/glass	66.93	540	13.95	12.3	(Bhattacharya, Wiesner et al. 1997)	Two sets of absorber layer were prepared and compared. Absorber layers had different final composition adjusted by PVD	1997
Electrodeposition of CIGS followed by the PVD step to adjust final film composition		CIGS e	Mo/glass	66	430	38.7	10.9	(Bhattacharya, Oh et al. 2012)	Three stage electrodeposition process: 1. Electrodeposition of CIGS, 2. Electrodeposition of Cu, 3. Electrodeposition of In layer	2012
Electrodeposition of CIG metal precursors followed by annealing with H_2Se , followed by thermal treatment (Ar) and annealing with H_2S		CIGS Se	Mo/glass	54	676	27.1	9.8	(Malaquias, Berg et al. 2015)	Different absorbers were prepared with $0.10 \leq \text{Ga}/(\text{Ga}+\text{In}) \leq 0.72$. To avoid Ga segregation, a deep eutectic solvent and 3-step annealing was used.	2015
One-step electrodeposition of CIGS from a non-aqueous bath of ethylene glycol		CIGS e	Fluorine-doped tin oxide-coated glass	34	460	58	9.07	(Londhe, Rohom et al. 2018)	These results are at a potential of -1.6V. For a potential of -0.9V, efficiency=4.90	2018

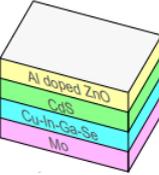
<p>Electrodeposition of Cu-In-Ga stack followed by thermal treatment at atmospheric pressure with Selenium and Sulphur</p>		<p>CIGS Se</p>	<p>Mo/glass</p>	<p>74.7</p>	<p>621</p>	<p>37.3</p>	<p>17.3</p>	<p>(Brousillou, Viscogliosi et al.)</p>	<p>Manufactured by NEXCIS. Module efficiency achieved=14%. This method produced the highest cell efficiency till date</p>	<p>2015</p>
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Table 2: Comparison of past studies with different efficiencies of CIGS solar cells fabricated by electrodeposition process

Table 2 gives a summary of different electrodeposition processes for fabrication of CIGS thin-film solar cells with different efficiencies.

4. Growth mechanism and cyclic voltammetric studies of electrodeposited CIGS:

4.1 Growth mechanism

In a voltammetric study conducted by Carbonnelle and Lamberts, the formation of copper selenide from a binary acid bath containing Se(IV) and Cu(II) ions by electrodeposition process was studied. A qualitative mechanistic scheme was proposed for the formation of CuSe based on the experimental results. This study back in 1992 was the first step in understanding the mechanism of Copper Selenide electrodeposition to understanding the copper indium diselenide deposition from a ternary bath. According to the authors the study of copper selenides is particularly interesting because this material is an intermediate or precursor for copper indium diselenide synthesis (Carbonnelle and Lamberts 1992).

In another paper, Calixto et. al. proposed a growth mechanism for electrodeposited CIS and CIGS films keeping under consideration the cyclic voltammetry, composition and GIXRD data obtained from the experiments. The authors state that at a bath pH of ~2.5, H₂Se is the likely phase of dissolved Se²⁻. According to the authors, the liberated H₂Se will react with In³⁺ (aq) forming In₂Se₃, which, due to a favourable free energy of formation will rapidly assimilate into the growing CuInSe₂ film through reaction with Cu_{2-x}Se. The Cu generates further copper selenide through reaction with H₂Se or other Se species. The authors also predict that the inclusion of Ga into the growing films may occur via a similar mechanism to In uptake, via the formation and assimilation of Ga₂Se₃ (Saji, Jung et al. 2015).

Chassaing et. al. carried out a voltammetric investigation using a rotating disk electrode to determine the deposition mechanism of the CIGS absorber layer. The polarisation curve obtained showed specific features. From figure 4 curve 1, for potentials in the range of -0.55 to -0.65V, a peak similar to the passivation peak is observed. Indication of deposition controlled by mass transfer of Cu(II) and Se(IV) species is observed. A second current peak is observed for higher polarisations. This peak corresponds to the reduction of Se(0) in the deposited layer into Se(-II). Reduction of the solvent occurs at higher polarisations. From -0.3 V to -0.55 V, only Cu and Se exists in the deposit. The Se/Cu ratio increases from a composition close to Cu₃Se₂ up to CuSe₂. No indium is deposited in this region. Indium insertion starts at potentials close to -0.6 V (Chassaing, Ramdani et al. 2008).

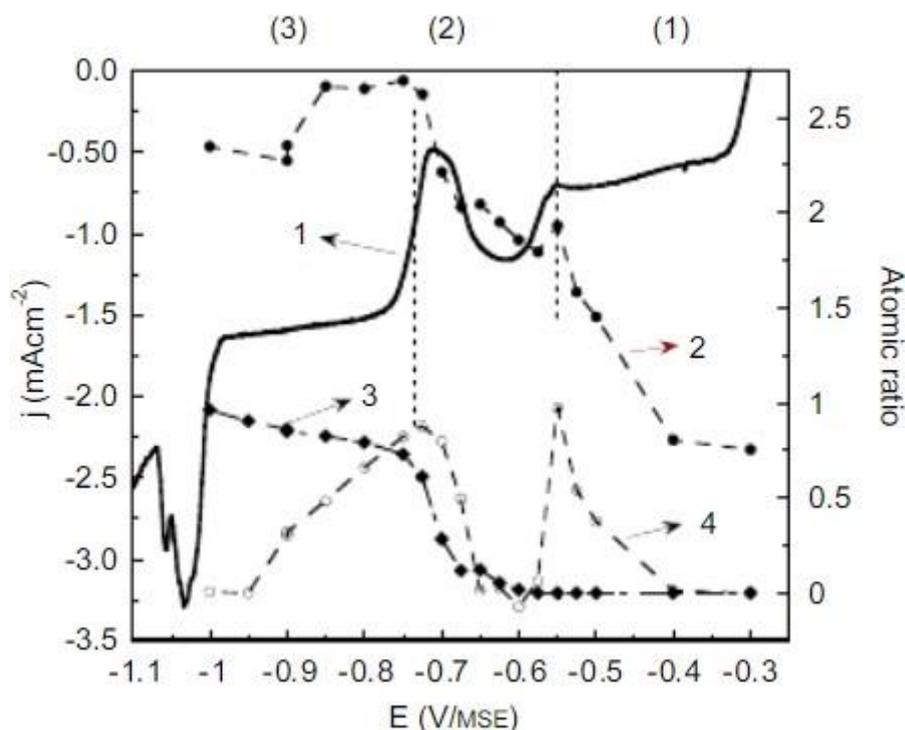


FIGURE 4- Potential dependence of the current density (curve 1) and the composition of the layers. Curve 2: Se(total)/Cu atomic ratio, curve 3: In/Cu atomic ratio, curve 4: Se(0)/Cu atomic ratio (Chassaing, Ramdani et al. 2008).

Sidali and co-authors, in their paper investigate the nucleation and growth mechanisms taking place during co-electrodeposition of Cu-In-Ga oxide/hydroxide films. The authors showed that the co-deposition is triggered by initial formation of 3D nuclei of metallic copper on the Mo electrode. These nuclei encourage the growth of Cu-In-Ga oxide films. Precipitation of Cu-In-Ga hydroxide takes place due to an increase in the pH which enables the reduction of nitrate catalysed from freshly deposited copper. After the heat treatments under hydrogen atmosphere, the oxide film is reduced to metallic phases. The XRD characterisation indicates a presence of Cu-In-Ga phase, metallic In and GaMo₃ phases. By increasing the selenization temperature, it was observed that better thermal mixing of the elements is achieved and allows a better incorporation of Ga into the CIGS layer (Sidali, Duchatelet et al. 2015).

A plausible growth mechanism of the CuIn_xGa_{1-x}Se₂ film is illustrated in Fig.5. The Cu/Ga/Cu/In/Cu/Mo-glass sample has a stacked layered structure. Upon pre-alloying at 150°C. Cu-In, Cu-Ga, Cu-In-Ga, In_mGa_n, elemental Cu, and In phases result in the alloyed precursor film. When selenizing the alloyed precursor film at 250°C, the CuInSe₂/CuIn_{rich}Ga_{poor}Se₂ phases is generated from the Cu-In, Cu-Ga, and Cu/In_mGa_n phases. Elemental Cu and In are selenized into Cu₂Se and In_aSe_b, respectively while some crystalline metallic phases such as Cu₁₁In₉ and elemental In phases are still observable in the film. By setting the selenization temperature to 350°C, the CuInSe₂ and CuIn_xGa_{1-x}Se₂ phases are formed along with Cu₂Se still existing in the sample. When the selenization temperature is increased to 450°C, the Ga-containing phases are completely selenized and they form another distinct layer below the CuInSe₂/CuIn_{rich}Ga_{poor}Se₂ layer. The Cu₂Se phase is significantly reduced after additional thermal annealing at 550°C in Ar. The overall composition of the final film is CuIn_{0.67}Ga_{0.3}Se_{2.03} (Yeh, Hsu et al. 2016).

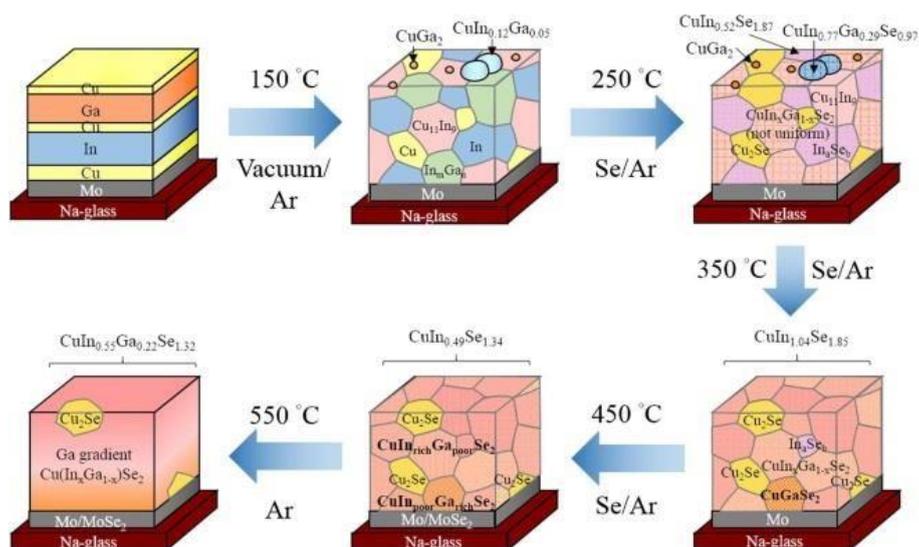


FIGURE 5- A plausible growth mechanism of a sequentially electrodeposited $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ tin film selenized in RTP (Yeh, Hsu et al. 2016).

4.2 Cyclic voltammetry studies:

Cyclic voltammetry studies enable us to estimate the extent of hydrogen evolution and more information can be retrieved regarding the specific behavior of each element in CIGS cells [52]. The peaks at the reduction potential should be in agreement with the equilibrium potential obtained using the Nernst equation given below. This equation below relates the potential of an electrochemical cell (E) to the standard potential of a species (E^0) and the concentrations of the oxidized (Ox) and reduced (Red) analytes in the system at equilibrium.

$$E = E^0 + \frac{RT}{nF} \ln\left(\frac{[Ox]}{[Red]}\right)$$

where F is the Faraday's constant, R is the universal gas constant, n is the number of electrons, and T is the temperature (Elgrishi, Rountree et al. 2018).

Several cyclic voltammetry studies have been conducted on unitary, binary, ternary and quaternary systems of copper, indium, gallium and selenide. Alcanfor et al. recorded cyclic voltammograms for indium electrodeposition on a copper substrate under different temperatures (25, 45, 65 and 80°C) at 25 mVs⁻¹. In the cyclic voltammograms, a single reduction peak in the forward scan (cathodic sweep) was observed which was related to the electrochemical reduction of In^{3+} species to elemental In. At all temperatures, a cathodic current crossover loop between the forward and reverse sweep was observed. This indicates that electrodeposition is controlled by a nucleation-growth mechanism as the electrodeposition of In on Cu substrate requires an overpotential to start the nucleation and growth of the bulk In film. The peak in the oxidation process corresponds to the stripping of the electrodeposited In. The anodic current peak was smaller than the cathodic one. This shows that the In coating was removed partially in the reverse sweep. From the voltammograms it was inferred that the cathodic peak current increasing with an increasing bath temperature, suggesting that the rate of In electrodeposition increases with the working temperature (Alcanfor, dos Santos et al. 2017). Huang et al. also studies indium electrodeposition from a sulphate solution on a PVD copper seed. One cathodic current peak and three anodic current peaks were observed in the potential range used in the study. The cathodic peak corresponds to the deposition of indium. The first anodic peak corresponds to the stripping of the indium deposit. The two other anodic peaks are at more positive potentials, indicating the stripping or anodization of two different, nobler materials (Huang, Reuter et al. 2011)

Another study was carried out by Yanqing et al. regarding the effect of adding a complexing agent (sodium citrate) on the cyclic voltammograms of unitary, binary, ternary and quaternary systems of CIGS. On comparing the cyclic voltammogram of a CuCl_2 solution with that of a CuCl_2 +sodium citrate solution, it was found that the Cu^{2+} reduction peaks shift to more negative values and the maximum peak height decreases. This result is

indicative of the citrate anion and copper cation forming a complex compound. In the case of InCl_3 , the cyclic voltammogram is not significantly affected by Na-citrate. There is no significant difference in the reduction potential of In^{3+} in both the solutions. There is no shift in the In^{3+} peak caused by the citrate component because of the weak complexation of the citrate ion and In^{3+} . There was no peak found for the reduction of Ga^{3+} to Ga. The peak found corresponded to the reduction of H^+ to H_2 . There was no evidence from the cyclic voltammograms that gallium was electrodeposited on the electrode surface. Thus, it was concluded that the electrochemical insertion of gallium is very difficult to achieve in an electrolyte bath owing to the highly negative reduction potential of Ga. For selenium, the reduction peak was too weak to discern. The cyclic voltammograms indicate that the citrate component can significantly shift the reduction potential of H_2SeO_3 toward the negative direction. For a binary solution containing GaCl_3 and H_2SeO_3 , the reduction of H_2SeO_3 to Se begins earlier. The formation of indium and gallium selenides proceeds the reactions of Ga^{3+} and In^{3+} with H_2Se , respectively (Lai, Liu et al. 2009).

Another study by Viswanathan et. al. focused on performing cyclic voltammetry of unitary, binary, ternary and quaternary compositions of copper, selenium, indium and gallium and comparing them at different concentrations. In the cyclic voltammograms, four peaks could be observed, where the first two peaks were copper reduction peaks, the third was the surface oxide's reduction peak and the fourth corresponded to the hydrogen evolution process. Four concentrations were studied: bare (0.6 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$), 10 μM , 50 μM and 100 μM of the respective solutions of copper, indium, gallium and selenide. For copper, at greater than 50 μM , the first two reduction peaks along with the corresponding oxidation peaks were highly noticeable. At concentrations less than 50 μM , only one Cu reduction peak was noticeable. Copper deposits formed can completely cover the oxide surface at high Cu(II) concentrations. This makes the active sites on the oxide surface less available for the redox process associated with the third reduction peak. For selenium, the first reduction peak could be attributed to the surface oxide's reduction, and the second reduction peak to H_2Se formation. No oxidation peaks were observed. On using different Se(IV) precursors (H_2SeO_3 or SeO_3), the nature and appearance of the first reduction peak was different. For both, indium and gallium, there were no major reduction peaks observed other than the surface oxide's reduction peak, which was similar to the bare electrolyte (Saji, Jung et al. 2015).

5. Role of deposition parameters on electrodeposition of CIGS:

Stoichiometric CIGS (Cu, 25%; In, 12.5%; Ga, 12.5%; and Se, 50%) can be electrodeposited by using appropriate additives/supporting chemicals, complexing agents along with pH of the solution due to the wide differences in equilibrium potentials of Cu, Se, In and Ga. Moreover, additional In and Ga can be incorporated in CIGS by electrodepositing at higher negative potentials, -0.9 V and above, vs. Ag/AgCl. The pH of electrolyte can play an important role to reduce the electrodeposition potential due to the availability of more OH^- ions, which can either form the complex with noble elements or reduce the open circuit potentials (Rohom, Londhe et al. 2014). A higher deposition rate can be achieved by using the electrodeposition process if the thickness of the film, particle size, and stoichiometry can be controlled (Chauré, Samantilleke et al. 2005, Palacios-Padrós, Caballero-Briones et al. 2010, Yang, Liu et al. 2012)

5.1 Effect of adding supporting electrolyte:

Ribeaucourt et. al. studied the nature of the supporting electrolytes (sodium sulfate vs. sodium chloride) through speciation diagrams, cyclic voltammograms and SEM characterisation on unary, binary and ternary systems of Cu-In-Ga. The authors concluded that the nature of the supporting electrolyte has a marked influence on the voltammograms. The species distribution in the two supporting electrolyte solutions was different. Even though at pH 2.15, both electrolytes were found to be stable, chloride bath enables higher solubility of In(III) and Ga(III) (Ribeaucourt, Savidand et al. 2011). Morphology is also affected by the nature of the electrolyte. Chlorides show dendritic growth because Cu deposition is diffusion controlled. The dendritic growth is observed to be less in sulfates as Cu deposition in this case is mass transfer limited (Ribeaucourt, Chassaing et

al. 2011). Vishakha et. al. used lithium sulfate as a supporting electrolyte for their solution to bring the deposition potential of all species closer for a better co-deposition of Cu, In and Se (Dhanwate and Chaure 2013). LiCl is also used as a supporting electrolyte to control the ionic conductivity of the bath and as a pH adjuster (Lee, Lee et al. 2014). Moreover, it was found that LiCl was helpful to incorporate more Ga in the precursor and to improve the film morphology (Bhattacharya RN 1998).

5.2 Effect of adding buffering agent:

Buffering agents help in bringing the deposition potential of Cu toward the negative direction, as well as to buffer the aqueous solution at an adequate pH. Lee et. al. used Sulfamic acid and Potassium hydrogen phthalate as buffering agents in varying concentration (from 0 to 10 mM), to find the optimal concentration of the buffering agent (Lee, Lee et al. 2013). Pern et. al. used Ethylenediamine as a buffering agent and found that the composition and quality of the thin films were found sensitive to the concentration of the buffering agent. It was used to stabilize the solution acidity. A decrease in ethylenediamine concentration results in higher deposition rate and hence copper-rich films (Pern, Goral et al. 1988). Even though, usage of pH buffer solution has the above mentioned advantages, it also results in poorer morphology than non-pH buffered baths. Non-pH buffered baths, according to Sene et. al. resulted in denser and smoother CIS films. Therefore, best devices were obtained from non-pH buffered baths (Sene, Calixto et al. 2008).

5.3 Effect of adding complexing agents:

Chelation is a process of reversible binding or complexation of a ligand. In the industry, common complexing agents are organic compounds that form stable and soluble complexes with metal ions (PIRKANNIEMI).

Complexing agents can be added for a variety of purposes which include:

- i. To increase the viscosity of the salt solutions for using deposition techniques other than spraying
- ii. To prevent the formation of oxides of Cu, Ga and In in the alkaline pH regime
- iii. To chelate with metal ions in Cu-Ga and Cu-In phases
- iv. To improve the surface morphology of films (reduce the number of cracks on the surface)
- v. To bring the deposition potentials of metal species closer for a better co-deposition environment
- vi. To improve the crystallinity of the CZTS/CIGS thin films
- vii. To bring the reduction potential of Cu, In and Ga closer to that of the Se

Tri-sodium citrate is the most attractive complexing agent. Lia et al. showed that citrate ions produce a complexing effect on Cu^{2+} and H_2SeO_3 through cyclic voltammetric studies. They also showed that this ion had no effect on In^{3+} in the electrodeposition of CuInSe_2 .

Additionally, citrate is non-toxic and readily available (Lai, Liu et al. 2009). Chraibi et. al. also studied the effect of sodium citrate as a complexing agent on the electrodeposition of pure copper, indium, selenium and of their ternary alloy. Similar results were obtained and it was observed that the presence of citrate in the electrolyte improves its crystallinity (Chraibi, Fahoume et al. 2001). Serdar et. al. presented electrodeposition methods and chemistries for the deposition of several thin films including Cu-Ga, Cu-In, Cu-In-Ga, In-Se, Ga-Se and Cu-In-Ga-Se obtained from alkaline plating solutions containing complexing agents. The complexing agents solubilised Cu, In and Ga ions at high pH, enabling preparation of electrolytes to obtain adherent and high quality metallic films with controllable molar ratios. It was observed that no appreciable complexation occurs between Se and the complexing agents (Aksu and Pinarbasi 2011). The potential-pH diagrams for Cu, Ga and In show that all three metals are expected to form oxides in the alkaline pH regime (Bi, Gao et al. 2018) therefore, complexing agents were needed. J. Sun et. al. investigated the effect of using different suitable acids as complexing agents. These included oxalic acid, acetic acid and hydrochloric acid. It was found that oxalic acid was the most effective additive because the CIS film deposited was the densest and yielded the highest photocurrent (Sun, Batabyal et al. 2014).

5.4 Effect of deposition potential:

There have been studies conducted on the variation of composition and morphology of the deposited films with applied potential (Sang, Quang et al. 2013, You, Lew et al. 2014). Composition is dependent on potential which can be shown from cyclic voltammetric results. Sang et.al showed that for certain concentrations of the electrolytes (specifically 120 ml deionized water, 20 mM CuCl₂, 30 mM InCl₃, 40 mM Ga(NO₃)₃, 20 mM H₂SeO₃ and 350 mM LiCl), the concentration of Copper increases as the deposition potential decreases to -0.5 V, then decreases as the deposition potential decreases continuously. The peak composition of Cu at -0.5V is associated with copper deposition reduction process: Cu²⁺ → Cu⁰ at -0.4 V and to the low concentration of In and Ga in the samples deposited at the negative potential above -0.7V, then as the potential decreases, the concentration rises rapidly to a maximum value of 18.14% at -1.0 V. The insertion of In can be achieved at -0.5 V, that is more positive than the desired deposition potential of Ga. Potentials from -0.8 to -1.0V, the concentration of all the constituents is quite unaffected. The highest concentration of In and Ga are also obtained in this potential range. This potential range is the best choice for obtaining films with desired and stable stoichiometry (Sang, Quang et al. 2013).

5.5 Effect of bath parameters on grain morphology:

An improvement in current indicates a decrease in grain boundaries and defects. Cells grown using the co-evaporation method result in homogeneous grain composition and narrower grains. Cu rich CIGSe is known to have large sized grains. A Cu rich step would be preferable if large sized grains via recrystallization are needed due to active recombination at grain boundaries (Raghuwanshi 2015). This means grains are larger in depth as compared to width and hence size of grains with depth are referred to grain length. The surface roughness appear to decrease as grain size get larger with higher annealing temperature (Long, Wang et al. 2009). A new method called pulsed current (PC) electrodeposition, in comparison to DC electrodeposition can help in achieving suitable manipulation of diffusion layer, grain size and nucleation by proper choice of variable such as duty cycle and amplitude of pulsed current potential. Grain size and grain boundaries of CIGS layers decrease with increasing Ga content (Kodigala 2010). Sodium can easily diffuse from soda-lime glass (SLG) substrates into the growing CIGS layer and help in increasing the efficiency. Presence of sodium increases the grain size and texture during growth. However, incorporation of sodium at “high” doses leads to small grain sizes and porous films and is detrimental for cell performance (Rudmann 2004).

5.6 Effect of pH

The effect of pH can be understood by the factors dominated in an electrodeposition process such as dissolution of the freshly deposited metal atoms on the substrate because of acidic electrolyte, formation and absorption of metals (M. Harris, L. Wilson et al. 1999). According to Rohom et. al., the dissolution of freshly deposited metals and the formation and adsorption of metal hydroxide is favoured at lower pH value (1.2) and vice versa for higher pH values (2.5). Low pH also suppresses indium deposition. Also, it results in hydrogen evolution at lower cathodic potential. The structural, morphological, optical, compositional, and electric properties of CIS film is greatly influenced by the pH of the bath (Rohom, Londhe et al. 2014). Calixto et. al. studied the effect of pH on film properties such as thickness and quality. It was observed that as the pH increased the thickness decreased. Rohom et. al. indicated that a low pH of the bath may not be suitable to obtain the stoichiometric CIS thin films due to hydrogen evolution at lower cathodic potential. Hydrogen evolution is helpful to passivate the oxidation of precursor layer during the growth, whereas heavy hydrogen evolution prepares amorphous, powdery, and patchy films with very rough surface. The electrodeposition potential for stoichiometric CIS films was found to be shifted towards higher cathodic potential as the pH of the bath increases (Rohom, Londhe et al. 2014).

5.7 Effect of deposition time:

Esmaeili et. al. observed in through their experiment that the morphology and particle size of the products is greatly affected by the deposition time. According to the authors, for their electrolyte bath comprising of 30 ml deionized water with 0.001 M CuSO₄, 0.001 M InCl₃, 0.008 M GaCl₃ and 0.003 M SeCl₄, as the deposition time increases from 30 to 45 minutes, crystallinity of the as-prepared products is decreased. As the deposition

time increases from 30 to 60 minutes, the size of obtained nanostructure is increased. As the deposition time is increased from 30 to 45 minutes, nanoparticles come together and flower-like particles are formed, so with prolonging the reaction, aggregated CIGS flower-like nanostructures were produced instead of CIGS nanoparticles. From SEM images, it is clear that the deposition time is a function of CIGS grain size growth. Cross-section micrographs show that increasing of deposition time can lead to increasing of CIGS layer thickness (Esmaili, Behpour et al. 2015).

6. Challenges encountered in the production of CIGS solar cells:

5.1 Selenization of ED CIGS solar cells

In the selenization process, the surface of the material is exposed to a selenium-containing atmosphere at a high temperature. The surface then reacts and forms a new compound incorporating selenium. As electrodeposition is performed at low temperatures in most cases, all ED CIGS films need a selenization step. Feng et. al. studied Se-poor and Se-rich CIGS precursors electrodeposited on Mo/glass substrates from two different types of electrolyte baths, namely a thiocyanate complex bath and simple chloride bath, respectively; then they were selenized by exposure to selenium vapors. Through XRF, XRD, SEM and illuminated I-V measurements, the enhancement in film crystallinity and concentration of incorporated gallium and the improvement of conversion efficiency were confirmed for the film grown from Se-poor ED precursor as compared with the film grown from Se-rich ED precursor (Kang, Ao et al. 2010). However, the selenization process is environmentally unfriendly owing to the toxicity of Se. Hu et. al. studied the preparation of CIGS layers through selenization of CIG precursors and the effect of adding a thiocyanate complexing agent on the deposition potentials of In and Ga. The best structure of the selenized CIGS thin film gave a conversion efficiency of 10.3%. A classical selenization procedure is carried out using Se vapor or H₂Se. Among these, H₂Se is preferred over elemental selenium as the compositional change and material loss during the selenization is a major problem when using elemental Se vapors. However, this stage is toxic. It was suggested by Bamiduro et.al that there is a need for developing other methods to enhance cell efficiency (Bamiduro, Chennamadhava et al. 2011). Shinde et. al. in their recent research conducted in 2017, have proposed an alternatives for absorber preparation to reduced hazardous and storage risks associated with Hydrogen selenide. They used a mixture of hydrogen and diethyl selenide as an alternative for the selenization step in the deposition of the absorber layers. Solar cells with device efficiency 9.2% were obtained from Diethyl selenide processed absorber layer (Londhe, Rohom et al. 2018).

5.2 Difficulties in incorporating gallium:

Ga substitution for In (CIGS) is probably the best option for increasing the band gap (from 1.04 eV in CIS to 1.7 eV in CGS) to the desired value and increase the current conversion efficiency (Shafarman, Klenk et al. 1996, Jayapayalan, Sankaranarayanan et al. 1999, Birkmire 2001). However, Ga accumulation results in a bi-layered structure with CuInSe₂ layer (E_g = 1.0 eV) on the top surface and CuGaSe₂ layer (E_g = 1.68 eV) at the bottom of the film. Owing to the absence of gallium near the p-n junction, it results in a film surface energy bandgap lower than the ideal bandgap of 1.3-1.5 eV. This results in a lower open circuit voltage and an increased operating current. Thus, in order to fabricate high quality CIGSe thin films and solar cells, gallium homogenisation during post-selenization is vital (Bi, Gao et al. 2018). Without Ga, the efficiencies have a record value of 15% (J. AbuShama). However, Ga incorporation is associated with several difficulties. Difficulties in Ga incorporation are one of the factors responsible for the reduced efficiency of 17.4% in electrodeposited CIGS solar cells compared to the certified efficiency of 23.35% (Nakamura, Yamaguchi et al. 2019). Moreover, the incorporation of Ga by electrodeposition is yet more difficult than that of In due to its higher electronegativity (Hibberd, Chassaing et al. 2010). Therefore, it is important to take steps to overcome these challenges.

- i. One of the main challenges for developing low cost electrodeposition processes is controlling the incorporation of Ga in Cu-In-Ga metal precursors for Cu(In,Ga)Se₂ solar cells; this is mainly because of the difficulty in electrodepositing metallic Ga from aqueous electrolytes. This reason for this is the interfering hydrogen evolution reaction (HER), which occurs when electrodepositing Ga from aqueous

solvents. Thus, according to Malaquias, the problem of incorporating gallium efficiently was solved by co-electrodepositing Ga from a deep eutectic solvent. The electrodeposition of Ga from aqueous electrolytes is not a simple process. However, efficient electrodeposition can be achieved by using a deep eutectic solvent based electrolyte since the hydrogen evolution reaction in water does not occur (Malaquias, Steichen et al. 2013).

- ii. Another difficulty encountered during electrodeposition of Ga is its segregation during the annealing step. To avoid the problem, it is possible to employ a three-step annealing procedure, in which a limited quantity of sulphur on the surface of the absorber is introduced. Ga segregation severely hinders solar cell performance owing to open circuit voltage limitations (C. Malaquias, M. Berg et al. 2015). Sidali et al. found that increasing the annealing temperature allows for better homogenization of Ga in the film (Sidali, Duchatelet et al. 2015).
- iii. Jaoa et al. introduced a facile, additive free and robust method of controlling the Ga content solely by tuning the metal concentration in the electrolyte (Malaquias, Regesch et al. 2014).
The control of Ga is highly difficult due to its low melting point. This low melting point of Ga has a negative effect on annealing of CIGS films. Ga segregates toward indium tin oxide layers at high temperatures (Yildirim and Peksoz 2017). Gallium incorporation also limits the optimization of the surface energy bandgap and open circuit voltage of CIGS thin film solar cells.
- iv. In addition to this, the redox potential of Ga is low and it is difficult to avoid the formation of gallium oxide. It is also known that segregation of Ga occurs because Se reacts preferentially with In (Brummer, Honkimäki et al. 2003, Hergert, Jost et al. 2006). This problem can be overcome by introducing suitable complexing agents to the electrolyte.
- v. One of the main factors responsible for the poor efficiency of electrodeposited cells compared to co-evaporated solar cells is gallium accumulation, which leads to the formation of a fine-grained CuGaSe₂ phase near the back contact region (Rodriguez-Alvarez, Mainz et al. 2013, Han, Liao et al. 2014, Mainz, Weber et al. 2015)
- vi. In order to achieve better crystallisation and Ga homogenization in the CIGS layer Lin et al. suggested using an evaporated In film. The results showed that the evaporated In structure was superior than conventional sputtered In structure. According to the authors, an evaporated In structure has an ability to produce a CIGS film with better crystallization, superior structural characteristics, reduced surface roughness, and more homogeneous distribution of elemental Ga (Lin, Yao et al. 2013).
- vii. The presence of cracks in Ga-containing layers (Calixto, Dobson et al. 2006) can be reduced through the use of alcohol-aqueous solutions or supporting electrolytes such as Li₂SO₄ with gelatine as brightening additive (Long, Wang et al. 2008, Oda, Minemoto et al. 2008).

Jinlian et al. studied the influence of Cu content on gallium diffusion and grain growth of CIGS thin films fabricated via electrodeposition and during the post-selenization process [26]. The results showed that the gallium diffused homogeneously through the film with $Cu/(In+Ga) < 0.9$, while with $Cu/(In+Ga) > 0.9$, Ga accumulated at the back contact region. Thus to avoid gallium accumulation at the back contact it is important to have a lower $Cu/(In+Ga)$ ratio. Yeh et al. showed that an additional thermal process in Ar at 550 °C for 2 min improved the Ga distribution in the CuIn_xGa_{1-x}Se₂ thin film and enhanced the light absorbance at the near IR region (Yeh, Hsu et al. 2016). Figure 6 summarises these challenges and their available and possible solutions.

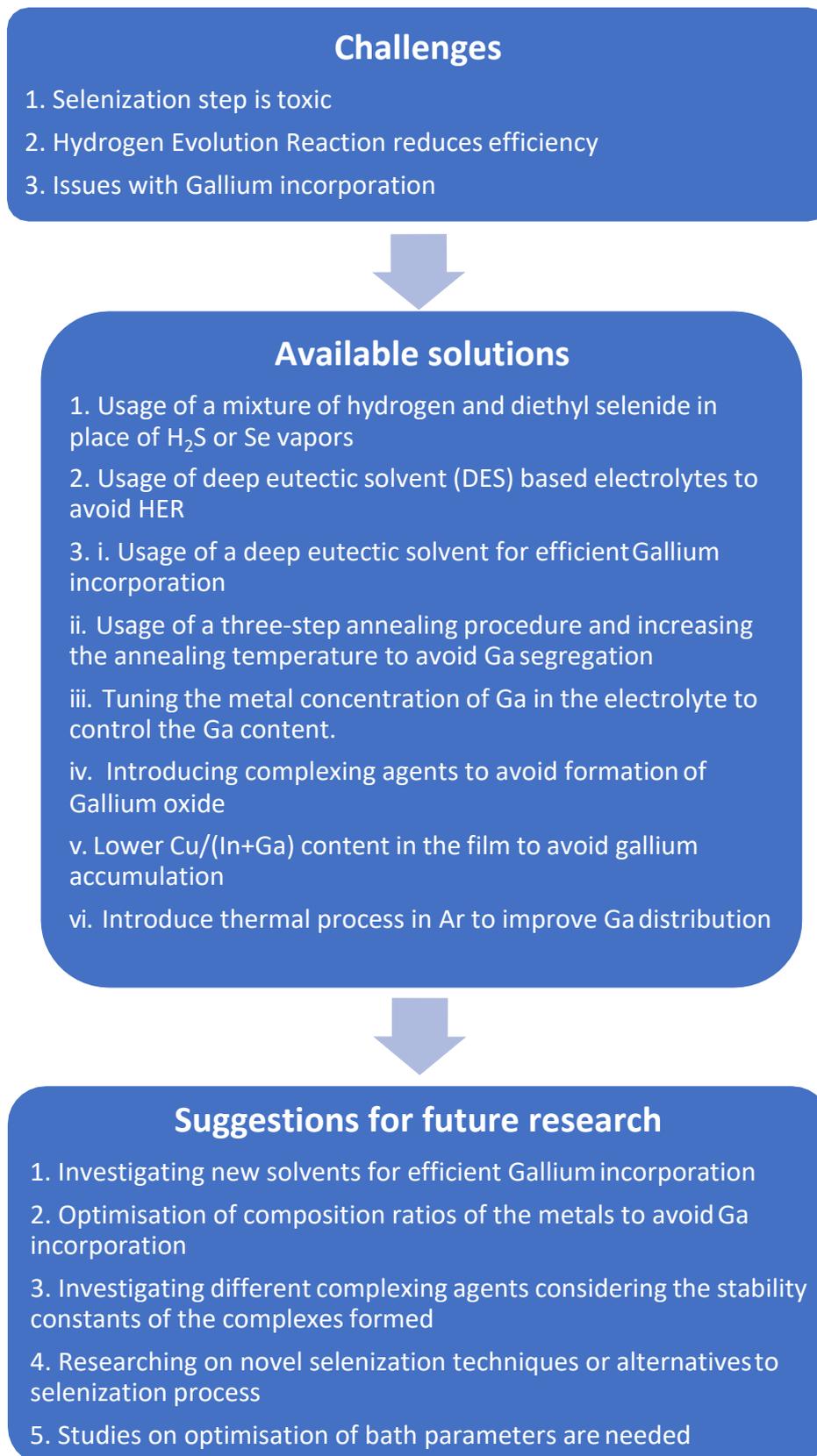


FIGURE 6-Summary of the challenges, available solutions and suggestions for future research to overcome the challenges

7. Conclusion:

This paper presents a comprehensive review on the electrodeposition technique for the fabrication of CIGS thin film solar cells. In recent years, research groups are focusing on electrodeposition as it is a cheap and convenient method for the production of CIGS solar cells. Other thin-film solar cells such as Si and CdTe thin film solar cells have several disadvantages compared to CIGS solar cells. The highest cell efficiency obtained for electrodeposited CIGS solar cells was 17.3% in 2015 by NEXCIS. Several studies reporting different efficiencies of CIGS solar cells were also reviewed. However, several practical challenges need to be overcome for the large-scale commercial production of CIGS thin-film solar cells. Research is underway to develop methods for producing CIGS solar cell with high efficiency on a large scale.

The objective of future research would be to modify the parametric values and optimize them in order to increase the band gap of the absorber material which increases the Voc and FF and decreases the Jsc in order to increase the efficiency to a theoretical maximum efficiency of 30%.

There is also a lack of studies conducted to overcome the challenges associated with gallium incorporation. Gallium incorporation is necessary in order to increase the band gap of the CIGS absorber and in turn increase the efficiency. Therefore it is necessary to carry out studies in this field to overcome the challenges in regards to gallium incorporation. Moreover, there is a need for more studies in the field of determining the growth mechanism through cyclic voltammetry in order to better understand it.

Solar PV energy is vital in mitigating the costs and uncertainties associated with reliance on fossil fuels for electrical power generation. Electrodeposition further provides a cost effective method for the fabrication of thin-film solar cells. It is hoped that this literature review will help readers in their understanding of the current topics and issues that fall under the topic of CIGS solar cells and assist in future research.

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