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Preparation of $CuInSe_2$ Thin Films by using Various Methods (A Short Review)

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ABSTRACT

$CuInSe_2$ thin films are very important semiconductor material for solar cell applications because of chemical stability, direct band gap and high optical absorption coefficient. In this work, a review of $CuInSe_2$ films prepared using different deposition techniques such as electrodeposition, solvothermal, vacuum evaporation, hydrothermal and pulsed electrodeposition technique is presented. The review also includes the study of physical properties of these films which were derived using the characterization techniques such as field emission scanning electron microscopy, X-ray diffraction, Energy dispersive X-ray analysis, atomic force microscopy, UV-Visible spectrophotometer and Raman spectroscopy.

Keywords: Vacuum deposition, $CuInSe_2$ thin films, Electro deposition, Solar cells, Copper,

INTRODUCTION

Thin films with thickness ranging from a few nanometres to several micrometres[1-5] were synthesized by using different methods. Thin films have distinct advantages over bulk materials, such as they offer the potential for low cost processing with minimal material usage, and deposition could be carried out on various substrates[6-12]. Different processes for depositing thin films are broadly categorized into physical and chemical methods. Chemical methods are comparatively easier and cheaper than physical methods. Among the chemical methods there are vapor based and wet chemical (solution based) methods.

Wet chemical method is again cheaper than chemical vapor based methods. In this, the material is synthesized (using precursor chemicals) by various methods such as spray pyrolysis, electrodeposition, spin coating, anodization, hydrothermal, solvothermal, sol-gel, co-precipitation and combustion. Usually these methods involve a reaction process with or without the assistance of thermal assistance. The reactions are supposed to occur mostly at atmospheric pressures or at a vacuum level less than 0.1 mbar. If necessary inert gas atmosphere will be created by evacuating the working chamber by a rotary pump.

Compared to physical methods, it is easy to control deposition parameters in chemical methods. The route could be chosen depending on the requirement and final application of the material. Methods such as successive ionic layer adsorption and reaction (SILAR)[13-14], chemical bath deposition (CBD)[15-20], spray pyrolysis[21-23], electrodeposition, spin coating, and anodization are used for direct growth of microcrystalline films onto the substrate. Meanwhile methods such as hydrothermal, sol-gel, co-precipitation, and combustion are used to prepare nanoparticles of the material which has to be made in the form of ink/paste by mixing suitable solvent followed by thermal treatment. In this work, deposition of $CuInSe_2$ (CIS) films by using electrodeposition, solvothermal and hydrothermal methods was discussed. Characterization was performed by using various tools.

Literature survey

Solvothermal method

Solvothermal synthesis is a non-aqueous process in which the reaction between precursors occurs at higher pressure and at temperature [higher than the boiling of the solvent]. The reaction temperature is greater than 200°C in most of the cases. The phase and shape formation in $CuInSe_2$ thin films (CIS) through this process depends on the parameters such as type of solvent, capping agent, reaction temperature and duration. The shape of the particle changes with change in the reaction temperature. Nanoparticles of chalcopyrite CIS were obtained from solvothermal reaction when ethylenediamine was used as solvent and capping agent. Usually, the reaction takes place at 180 – 220°C and the average reaction time was 16 hours[24-28]. In the meantime, nanorods were obtained with soft solvothermal reaction at 120°C with ethylenediamine as solvent[29]. Microwave assisted solvothermal method with polyethylene glycol as solvent at above 200°C showed existence of multiple binary phases which requires high temperature annealing (~500°C)[30]. Table 1 shows the reaction temperature, time and the obtained shape of the nanoparticles. From the table 1, it is clear that, with the same solvent different morphology is obtained at different deposition durations and temperatures.

Table 1: Morphology of $CuInSe_2$ with respect to different deposition conditions

Synthesis temperature (°C)	Solvent	Time(h)	Morphology	Reference
180	Ethylenediamine, ethanol	2	Dispersive plates	[31]
180	Ethylenediamine, ethanol	12	Microspheres	[31]
180	Ethylenediamine, ethanol	48	Interconnected sheets	[31]
180	Ehylenediamine	18	Sheets	[27]
120	Ethylenediamine	18	Nanorods	[28]
200	Ethylenediamine	24	Irregular	[26]
200	Ethylenediamine	48	Mixture of sphere, rod and belt-like structures	[26]
180	Diethylamine	36	Spheres	[24]
180	Ethylenediamine	15	Whiskers	[24]
180	Ethanol	48	Spheres	[32]

Hydrothermal method

In hydrothermal synthesis, as the name implies, the precursors are subjected to the reaction in water. In this method, an autoclave is often used to create an atmosphere of increased pressure which in turn reduces the activation energy of the formation of final product. Hydrothermal process is known to be eco-friendlier than the solvothermal method since it uses water as solvent. Water is cheaper than other solvents and it can act as a catalyst for the formation of desired materials by tuning the temperature and the pressure. Also the water could be removed

very easily from the final product. Compared to solvothermal, hydrothermal reactions happen at low temperatures and low cost precursors are used.

In hydrothermal synthesis of $CuInSe_2$ thin films (CIS) at 150°C for 2 h, when ethylenediamine was used as capping agent, wurtzite structured CIS was formed. Also different morphologies were obtained for different molarities of ethylenediamine. At 10 mol ratio of the capping agent leads to cube like morphology while 5 mol ratio leads to the formation of rod like morphology[33]. Chalcopyrite nanocubes of CIS were obtained with hydrothermal synthesis at 180°C for 20 hours[34]. Jang and co-workers synthesized chalcopyrite CIS nanoparticle from metal precursors which is dissolved in acetic acid[35]. The reaction temperature of the autoclave was controlled from180°C to 220°C for 8 h to 16 hours. At lower concentrations of acetic acid (< 5 M), CIS phase coexisted with CISe phase. For the hydrothermal method, triethanolamine (TEA) is used mainly as the chelating agent[36, 37, 38]. Table 2 shows a review of deposition condition details of CIS using hydrothermal method and the resulting morphology. The morphology of sample strongly depended on the synthesis temperature, time, and chelating agent.

Table 2: Morphology of $CuInSe_2$ with respect to different hydrothermal deposition conditions

Synthesis temperature (°C)	Chelating agent	Time(h)	Morphology	Reference
150	Ethylenediamine	2	Spheres	[33]
180	--	20	Nanocubes	[34]
180	Acetic Acid	12	Spheres	[35]
220	Triethanolamine	6	Sheets	[36]
180	Triethanolamine	3	Sphere	[39]
180	Ethylenediamine	0.30	Rod	[40]

Electrodeposition technique

Electrodeposition is a method which also has been used widely in commercial sector. The elements to be deposited will be dissolved in a suitable electrolyte and the dissolved cations will be reduced with the help of applied bias so that they will form uniform coating on the working electrode (Fig.1). In addition, the complexing agent may be included to bring the reduction potentials of the individual elements closer. This low-temperature process is reasonably fast which helps in the deposition of large number of samples in a short period. Aqueous or non-aqueous solvents could be used as electrolyte. Here the applied bias should be greater than the reduction potential of the material to be deposited.

$CuInSe_2$ thin films (CIS) have been prepared extensively by electrodeposition. One-step and three-step electrodeposition are employed for the deposition of CIS. In one-step deposition the metal salts are dissolved in the electrolyte and compound will be deposited on the anode electrode in a single run. In three-step deposition, individual materials are deposited by one by one. Three-step process offers the feasibility to choose the applied bias, electrolyte and pH individually according to the reduction potential of the individual element. Meanwhile in one-step process, these parameters are selected which will be suitable for all the materials to be deposited.

As far as the film properties are concerned, as-deposited films in one-step process are found to be crystalline with CIS phase while three-step process requires further heat treatment to get CIS phase[41-45]. The standard reduction potentials of Cu^{2+} and In^{3+} and Se^{4-} are +0.1 V, -0.58 V and 0.5 V versus saturated calomel electrode (SCE), respectively[46]. Hence, the deposition potential is found to vary between -0.6 and -0.9 V in these experiments so that all the elements will be reduced simultaneously. pH of the solution is maintained at ~ 2 in most of the electrodeposition process as mentioned in the Table 1. The reduction potentials of individual elements are found to be different at different pH values thereby affecting the deposition potentials. Lower pH values cause the dissolution of deposited metals and slow down the formation and absorption of metal hydroxide. In the meantime, higher pH values slow down the dissolution of the deposited metals[47]. Also In (indium) content in the film is low at higher pH because of the absorption of indium oxide in the electrolyte. Hence as a compromise between

the reduction potentials a pH~ 2 is used in most of the experiments.

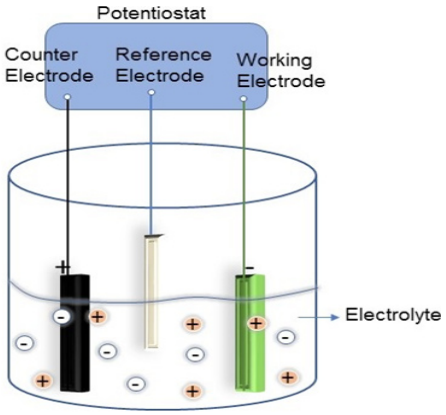

Fig. 1. Electrodeposition set-up

Table 3: Various deposition conditions have been reported by different researchers

pH	Deposition potential (V)	Annealing temperature (°C)	Reference
2	-0.8	250	[41]
1.2	-0.6	400	[47]
2.5	-0.8	400	[47]
1.5	-0.7	300	[48]
1.7	-0.6	400	[49]
2.5	-0.55	450	[50]
2	-0.8	250	[51]
1.5	-0.67	350	[52]
2	-0.7	350	[53]
2	-0.9	200	[54]

Secondary phases are quite normal in the as deposited films, which is removed by annealing. Annealing temperature varied from 250 to 450°C as indicated in Table 3. The shape of the grains in the CIS films formed by electrodeposition are found to have flower like structures[48-52].

Electrodeposition of CISe in aqueous and non-aqueous electrolytes

The standard equilibrium reduction potential of Cu, In and Se ions in the electromotive force series (EMF) series is +0.337/standard hydrogen electrode (SHE), −0.342/SHE and +0.741/SHE respectively. The challenge arises during electrodeposition of CISe is due to the active standard reduction potential of In (Indium) ions. Using complexing agents, the reduction potential of noble ions (Cu) can be shifted towards active ions (In), hence making the co-deposition of all the three ions easier. They also diminish hydrogen generation, avoid pinholes and improve the compactness of the as-deposited film. Other additives such as supporting electrolytes, surfactants, and brighteners are often used for improving the film quality.

The following section will briefly review the attempts made recently to co-deposit CISe films. Bhattacharya et al. were the first to report on the possibility to electrodeposit CISe thin films in a single step using triethanolamine (TEA) as complexing agent[55]. Since then, several works on electrodeposition of CISe using TEA have been reported as it can form strong metal-complexes with Cu^{2+} and $HSeO^{2-}$ ions and weak complexing with the In^{3+} ions. The most popularly used complexing agent in the early stages of CIS electrodeposition is thiocyanate ions (CNS-) due to its selectivity in the formation of ligands only with the Cu^{2+} ions[56, 57, 58]. Other alternative complexing agents such as citric acid, trisodium citrate[59, 60], tartrate ions[61], oxalic acid[62], glycine[63], potassium sodium tartrate[64] and EDTA[65] are also successfully utilized in the CISe electrodeposition. Apart from aqueous electrolytes, electrodeposition of CISe have been reported using non-aqueous electrolytes such as alcohol[66], ethylene glycol[67], DMF[68], DMSO[69] and ionic liquids (reline)[70]. The availability of wide electrochemical deposition window in non-aqueous electrolytes allows electrodeposition of In (III) and Ga (III) ions conveniently without the interference of hydrogen evolution reactions. Unlike aqueous electrolytes (where the metal ions solubility is limited by oxides/hydroxides precipitation), high solubility, and ligand concentrations can be achieved in water-free ionic liquids. Moreover, the high ligand concentrations ensure greater control on the metal speciation in the electrolyte[71]. Therefore, reline forms strong metal complexes with the ions, and hence, the necessity of using complexing agents is eliminated. Due to these reasons, non-aqueous electrolytes have gained significant attentions in the recent years.

Challenges in obtaining compositional CISe thin films with pinhole free and with reduced surface non-uniformities

The influential parameters such as deposition potential, pH and bath composition etc., which can directly affect the film quality and composition have been discussed in the several cited literatures[72-75]. The stoichiometry and quality

of the as-deposited CISe thin films mainly depends upon the deposition potential and [Se^{4+}/Cu^{2+}] ions flux ratio. An extensive study on the influence of ion flux ratio on the stoichiometry and phase formations for binary Cu-Se and ternary Cu-In-Se systems were reported by Thouin *et al.,*[76, 77].

However, for obtaining seamless CISe thin films by electrodeposition, critical issues such as surface non-uniformities, pinholes and erosion or dissolution of CISe film during electroplating in highly concentrated baths yet need further attention. Only few studies have been carried to avoid surface non-uniformities and pinholes in the as-deposited CISe thin films. Chandran *et al.,*[78] reported that severe surface non-uniformities along with severe pitting over the CISe thin films when higher In^{3+} ion concentrations were used. Fig. 2 shows electrodeposited CISe using 10 mM of In^{3+} ions at a pH of 1.75 for 10 minutes. The as-deposited CISe film surface was highly In-rich and silvery by appearance. The presence of In- nano islands over the surface of the CISe films were confirmed by the image analysis as shown in Fig 2a. After pre-treatment process, the FE-SEM of PT–CISe revealed the presence of uniform particle morphology with reduced In-nano-islands (Fig. 2b)[78].

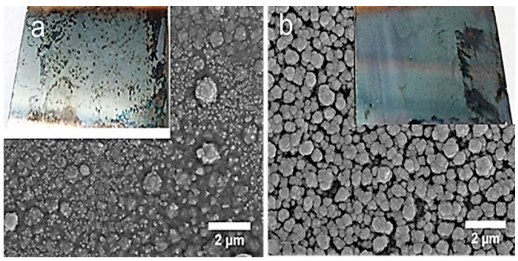

Fig. 2. FE-SEM of CISe electrodeposited at -0.65 V/SCE in citrate bath with (a) and without (b) pre-treatment and their corresponding photographic images (inset)[78]

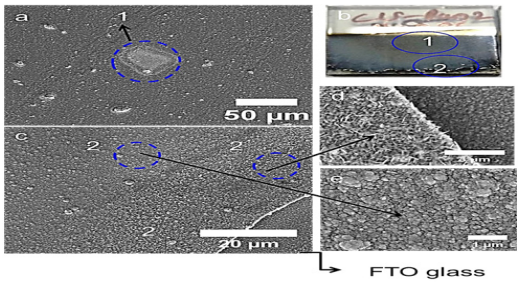

Fig. 3. (a) FE-SEM of surface non-uniformities in CISe thin films (-0.65 V/SCE), (b) photographic image (1- surface non-uniformities and 2- dissoluted zone), (c-d) FE-SEM of dissoluted zone and e) undissoluted zone (Original work)

Though employing optimal In^{3+} concentration and pre-treatment process can circumvent these issues, it was not possible to complete eliminate these surface non-uniformities completely. Fig. 3 shows the morphology of CISe deposited using less In^{3+} ion concentrations (5 mM). The compositional analysis revealed that the patches were majorly composed of Cu-poor CISe and rests of the other areas were Cu-rich. The plausible explanations for the appearance of such patches in CISe films can be due to the depletion or mass-controlled deposition of free Cu^{2+} ions along with fluctuating deposition of Cu-citrate complexes contributing to such Cu-poor patches in the CISe films. Such issues were minimized when high or optimal Cu^{2+} ion in the electrolyte & using fresh electrolytes for deposition. For prolonged deposition time (>15 min, pH=1.85), Chandran et al observed the dissolution of CISe thin films at the edges as shown in Fig.3 (b,c). In Fig.3(d), the microstructure of the dissoluted zone is provided and compared with undissoluted area (Fig.3e). The presence of platelet structures, a characteristic structure for CuxSe binary phase is evident for the dissoluting behavior of the CISe films, a similar mechanism taking place in binary Cu-Se system at higher cathodic potential[79,80]. Tentatively, they speculate that this dissolution might be due to the depletion of Cu^{2+} ions and along with high diffusion current contributed from the In^{3+} ions. These effects were minimized when suitable surfactants were used in the deposition. For an optimized bath, they were able to obtain a Cu-poor near stoichiometric CISe with silver gray appearance with reduced surface non-uniformities. In Fig. 4, the possible strategies for obtaining quality CISe thin films are proposed. These preliminary studies can shed light in the development towards the surface non-uniformity free CISe thin films which can contribute near to the improvement in the final efficiency of the devices.

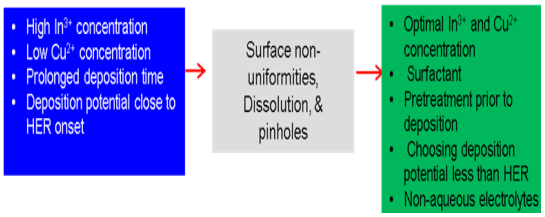

Fig. 4. Strategies to avoid surface non-uniformities and pinholes in CISe thin films

Thermal evaporation method

Thermal evaporation is referred as one

of the best processes after considering all aspects of fabrication and performance. It belongs to physical vapor deposition (PVD) category which uses vacuum technology for depositing a pure material to the desired surface. The materials to be deposited on substrate, (in this technique), can be atomic elements or molecules. The process encompasses warming the material to be deposited within a vacuum compartment to raise a vapor cloud inside the chamber. This vapor cloud navigates the compartment and sticks to substrate as a film[81]. This heating can be either filament evaporation or E-Beam evaporation as illustrated in Figure 5.

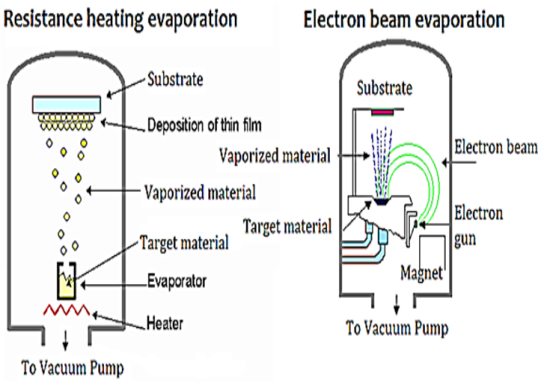

Fig. 5. Evaporation arrangements for Filament and E-Beam

The prime advantage of the vacuum evaporation is to deposit high-purity films from high-purity source material. Moreover, a solid in any form and purity can be utilized as source material and allows the usages of masks to deposit on the desired portion of the substrate. Furthermore, monitoring and control of the deposition are also relatively easy. On the other hand, the main disadvantage of evaporation process is the deposition of compounds and alloy are difficult to control. Moreover, large vacuum chambers are generally required to keep the substrate safe.

Among numerous materials for thin film solar cells, copper indium diselenide films (CIS) have been identified as one of the most encouraging contestant as it has comparatively a better and stable conversion efficiency of 21.7 %[82]. Due to its ideal adjustable band gap and high absorption, it has great electrical and optical characteristics. Furthermore, CIS adopts an easy and cost effective procedure to achieve large films at normal temperature[83,84,85]. Thermal evaporation technique has been used to produce $CuInSe_2$ films. Characterization has been performed (Table 4) by suing various tools such as X-ray diffraction (XRD), atomic force microscopy (AFM), Energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM) and UV-Visible spectrophotometer.

Table 4: There are some highlighted results as reported by many researchers

References	Highlighted results
Shah and co-workers, 2009[86]	XRD data confirmed single phase of $CuInSe_2$ when the temperature was 423 K and above. Band gap values (1.01 to 1.06 eV), activation energy (82-42 meV), and electrical resistivity values (0.15-20 ohmcm), strongly depended on the deposition temperature.
Ray and co-workers, 2009[87]	EDAX spectra showed that near stoichiometric composition for all the samples deposited at various substrate temperatures (423-573 K). As the substrate temperature increases, the grain size was also increased according to atomic force microscopy images.
Prabahar and co-workers, 2010[88]	Thin films of various thicknesses (405, 565, 745 nm) have been prepared according to SEM analysis. The SEM images revealed that grain size is mainly depended on Cu:In ratio.
Hasan co-workers [89]	The optical transmittance spectra confirmed that the films annealed at 350°C for 15 min have been observed to have better qualities if compared to 200, 250 and 400°C (do not show any well-defined absorption region). From the obtained band gap values (0.967, 0.975, 0.978 eV), we can observe that band gap is inversely proportional to the Cu/In ratios (0.958, 0.632, 0.579).
Mahesh co-workers[90]	Copper indium diselendie films prepared on glass substrate (under vacuum 10-5 Torr) indicated a uniform and homogeneity distribution of crystallites. XRD data showed that annealed films are polycrystalline in nature.
Parihar and co-workers, 2011[91]	Current-voltage analysis showed better ideality factor values in annealed films (with increased film thickness). The Schottky diodes displayed the existence of barrier inhomogeneity at the M-S interface.
Senthil and co-workers, 1999[92]	Electronic hopping plays a great role as shown in conduction studies. The value of dielectric constant (10.8 at 5MHz and room temperature), ac (0.12 eV) and dc (0.27 eV) activation energies has been reported.

Pulse electrodeposition

Pulse and pulse-reverse plating are the advanced features of electrodeposition possessing additional variables which can control aspects like composition and morphology of the electrodeposit. Pulse deposition involves parameters like cathodic potential/current, pulse on-time, pulse off-time and deposition and pulse-reverse plating additionally has a reverse anodic potential/current with anodic pulse on-time and off-time. Parameters and features of pulse and pulse-reverse electrodeposition are schematically represented in Fig. 6. Appropriate modulation of these parameters helps in improved control over composition of individual elements. In addition, diffusion of entrapped gases, rearrangement of ad-atoms, etc. takes place during pulse off-time thereby leading to homogeneous compact deposition with reduced porosity[93].

Pulse plating essentially plays a key role in the deposition of ternary systems wherein achieving desired composition is crucial in final performance of the absorber layer. For instance, pulse off-time (relaxation time) during pulse electrodeposition can be suitably varied to obtain desirable composition of In in $CuInSe_2$ (CIS) films[94]. On the other hand, pulse-reverse electrodeposition, by virtue of possessing an additional anodic potential step helps in removal of impurities, surface dispersed undesired phases, etc. while also facilitating the advantages of pulse plating. Despite possessing additional process parameters and added advantages, pulse and pulse-reverse plating techniques are less explored for the fabrication of CIS films.

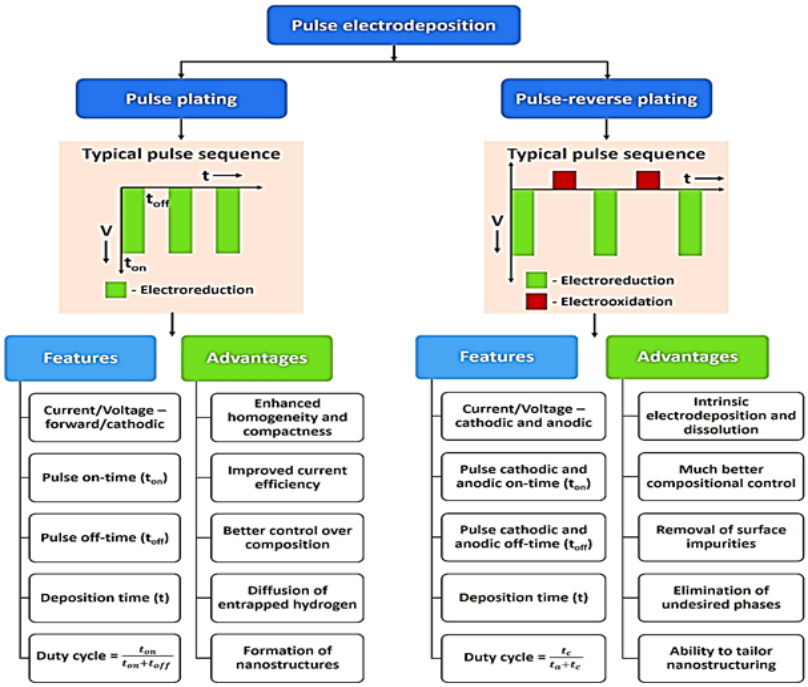

Fig. 6. Schematic illustration of types, features and advantages of pulse electrodeposition

Various reports on pulse electrodeposition of CIS are summarised in Table 1.1.42% efficient CIS solar cells are prepared by Kang *et al.,* wherein CIS absorber layers are fabricated using pulse-reverse electrodeposition technique with a subsequent selenization process[95]. Caballero-Briones *et al.,* employed pulse electrodeposition for the preparation of CIS films and inferred that the films contain binary and ternary phases as observed from the Raman spectroscopy analysis[96]. Uniformly adhered CIS films with tetragonal chalcopyrite structure were fabricated using pulse plating technique wherein a bell-like modified square wave form is employed for deposition[97]. Valdes et al reported the fabrication of chalcopyrite CIS films with different composition and morphologies by adopting a variable potential pulse sequence[98,99]. Multi potential pulse electrodeposition was employed by Hu et al to fabricate single phase chalcopyrite CIS

films and the different potentials in the study contributed to regulate the composition and homogeneity of the deposition[100]. The relative content of In was modulated appropriately by modifying the duty cycle during the pulse electrodeposition of CIS films and the study also unveiled a novel flake-like nanostructured morphology which aided in improved photoelectrochemical performance[101]. Based on various studies, it is indeed clear that pulse electrodeposition adds the extra advantage in modulating the composition of individual elements and obtaining the stoichiometric CIS with chalcopyrite phase which is crucial in ternary compounds and eases the process of optimization for absorber layers[102-105].

Table 5: Summary of reports on pulse electrodeposition of $CuInSe_2$ thin films

Material	Method	Description	Performance	Reference
$CuInSe_2$	Pulse reverse electrodeposition and selenization	Stoichiometric copper poor CIS films by appropriate use of anodic potential	1.42 % efficient CIS solar cells	Kang and co-workers, 2009[95]
$CuInSe_2$	Three step pulsed electrodeposition	Number of pulses, pulse duration and concentration are varied to obtain CIS films and as-deposited films are characterized	A photocurrent of 3.73 µA at -0.2 V	Caballero and co-workers, 2011[96]
$CuInSe_2$	Pulsed electrodeposition with multi potentials followed by annealing	Use of multi potential to obtain control over atomic ratios in CIS films	-	Hu and co-workers, 2011,[100]
$CuInSe_2$	Pulsed electrodeposition and annealing	Optimization of In content by varying duty cycle. Chalcopyrite CIS films with nanostructured flake-like morphology	Photoactivity of CIS is confirmed from photoelectrochemical characterization	Mandati and co-workers, 2013[101]
$CuInSe_2$	Pulse plating followed by annealing	Systematic study of CIS with varied duty cycle	Photoresponse from semiconductor-liquid junction	Mandati, 2015[106]
$CuInSe_2$	Sequential potential pulses during electrodeposition	Improvement in microstructure and elimination of secondary phases with varied pulse duration and precursor concentration	Photoresponse and confirmation of p-type conductivity	Palacios-Padrós, and co-workers, 2010[107]

CONCLUSION

This short review has provided some of the progresses in the preparation of ternary $CuInSe_2$ thin films by using solvothermal, hydrothermal, electrodeposition, vacuum evaporation and pulsed electrodeposition method. The advantage and disadvantage of each technique has been briefly described. Critical issues pertaining to the surface non-uniformities and strategies to avoid the issues have been proposed. Currently, power conversion efficiency more than 10% could be observed for the $CuInSe_2$ films.

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