



Copper Indium Disulfide Thin Films: Electrochemical Deposition and Properties

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Abstract

The electrochemical deposition method is an attractive technique to obtain a variety of thin films because of its advantages, such as low equipment cost and large-scale deposition. Different metal oxides, metal sulfide, and chalcogenide thin films have been deposited and successfully employed in various optoelectronic devices. Among these, chalcopyrite copper indium disulfide (CIS) thin films are widely useful for application in thin-film solar cells, photodetectors, light-sensing transistors, etc. The low material requirement for the fabrication of cells and low production cost makes it the top content for the manufacturing of optoelectronic devices. In a present review article, we have discussed the physical properties of CIS thin film deposited using the electrodeposition method. The preparative parameters and structural, optical, and electrical properties of the CIS thin films deposited using electrodeposition are discussed. Also, some strategies for the enhancement of the quality of CIS thin film are discussed.

Keywords: CuInS₂ (CIS); Electrodeposition; Chalcopyrite; Thin-films; Solar cell.

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1. Introduction

Now a day, chalcopyrite materials such as copper indium disulfide (CuInS₂ - CIS), Copper indium selenide (CuInSe₂ - CISE), and Copper indium gallium selenide (Cu(In, Ga)Se₂ - CIGS) are attracting significant attention in the scientific community due to the wide range of applications in optoelectronics (Fig. 1a). Among these, copper indium disulfide (CIS) is a widely studied thin material for solar cells, photodetector, and light-sensing transistors applications. The advantages such as a low raw material requirement for the fabrication of cells and low-cost production make CIS one of the top contents for the manufacturing of optoelectronic devices. The CISE and CIGS show a higher photo-conversion efficiency, but the higher toxicity of Se drives the researchers towards replacing Se with the less toxic CIS material.^[1] Therefore, CIS compound semiconductors have attracted

much attention because of their beneficial properties for various optoelectronic applications like solar cells, photoelectrochemical cells, photodetectors, and light-sensing transistors, etc.^[2-4] Copper indium disulfide (CIS) as a light absorber layer has shown the highest photoconversion efficiency among all the other I-III-IV₂ ternary chalcopyrite semiconductors.^[5] The CIS possesses a high absorption coefficient (10⁵ cm⁻¹), good thermal, environmental, and electrical stability, and optimum bandgap energy (E_g) of 1.5 eV for sunlight absorption.^[6] The best conversion efficiency of CIS solar cells was reported to be 12.5% on a cell scale.^[7] Different chemical deposition methods are reported for the deposition of CuInS₂ thin films, such as electrodeposition,^[8] SILAR^[9] chemical bath deposition (CBD),^[10] spray pyrolysis,^[11] etc. In the present review article, we have briefly discussed the electrochemical deposition method for the preparation of a CIS semiconductor thin film. Their preparative parameters and structural, morphological, and electrical properties are described. The data on preparative parameters -cost deposition method for various thin film materials. of CIS thin films from the previously published reports have been presented in tabular form.

1.1 Structure of CIS

CIS is one of the promising chalcogenide materials, which belongs to the I-III-VI₂ group. Fig. 1(b) shows a CIS unit cell,

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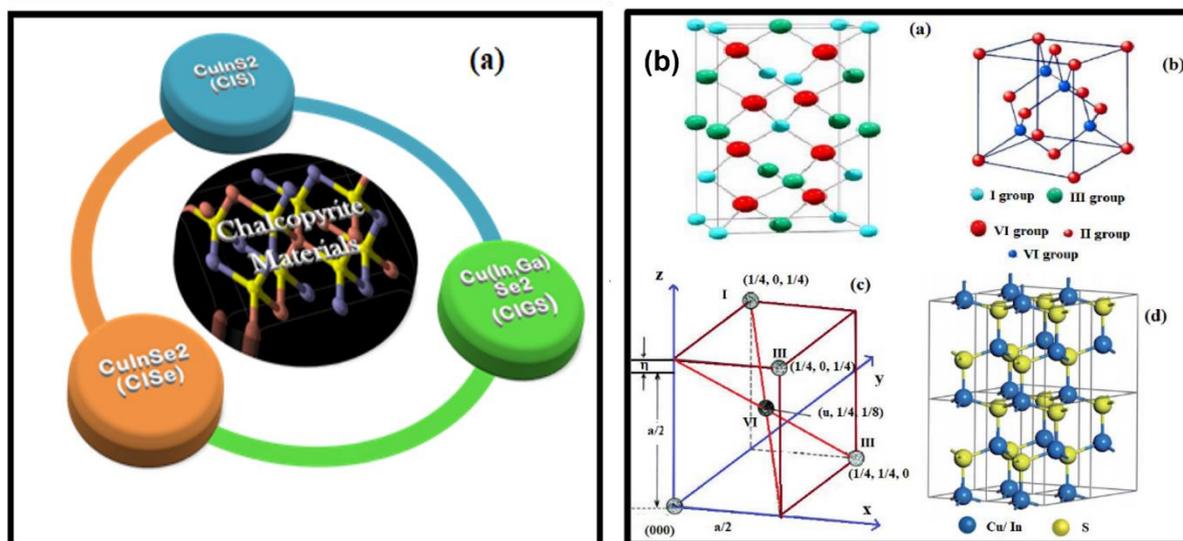


Fig. 1 a) Chalcopyrite materials, b) CIS crystal structure. Reproduced with permission from.^[10] Copyright 2020 Engineered Science.

where copper, indium, and sulfur atoms are indicated in green, red, and yellow colors. The sulfur atoms present in the lattice are at the center of a tetrahedron with four cations at each corner. CIS has the molecular formula as ABX_2 , and it crystallizes in the I-42d space group.^[10] The crystal structure of CIS can change between three polymorph forms: chalcopyrite, sphalerite, and wurtzite, which differ in the order of Cu and concentration. The chalcopyrite cell structure is the most common structure for CIS material. It consists of eight atoms per unit cell with a non-symmorphic space group.^[12,13]

1.2 Optoelectronics properties of CIS thin film

CIS is a p-type semiconductor material,^[14-16] that exhibits a direct bandgap of around 1.3 to 1.5 eV which covers most of the visible region in the electromagnetic spectrum^[15-17] and significant absorption coefficient ($>10^5 \text{ cm}^{-1}$). These properties make CIS a suitable candidate for its application in most of the commonly used optoelectronic devices. Different properties of CIS material are summarized in Table 1.

Table 1. Optoelectronics properties of the CIS.

Optoelectronics Properties	Parameters	Ref.
Refractive index	3.32	[18]
The optical energy bandgap (E_g)	1.5 eV	[19-21]
Mobility (n-CIS) At $T = 300\text{K}$	$15 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$	[22]
Resistivity (n-CIS) At $T = 300\text{K}$	$1 \Omega\text{cm}$	[22]
Resistivity Carrier concentration	$11 \Omega\text{cm}$	[23]
Type of conductivity	p-type, n-type	[24]
Crystal structure	chalcopyrite	[25-28]

1.3 Synthesis methods of CIS thin film

CIS can be deposited as an n-type as well as a p-type thin film form by changing the elemental composition of the constituent material. The conductivity type of CIS thin films depends on

intrinsic defects, such as cation vacancies and anti-site defects.^[29] As mentioned above, the CIS thin films can be deposited using various technique methods. The physical deposition method requires high vacuum conditions, and the high cost is one of the significant issues related to vacuum deposition methods. Therefore, chemical deposition methods are one of the best solutions for this problem. The chemical deposition methods have attracted considerable interest because of their simplicity. It does not require sophisticated instrumentation for the deposition of CIS thin film. Low operating temperatures, large-area deposition, and flexibility in the selection of substrate are other advantages of the chemical method. The electrodeposition method is one of the simplest and low-cost methods for the deposition of CIS thin films. Fig. 2 shows the various chemical processes for the deposition of CIS thin films.

2. Electrodeposition of CIS thin film

Electrodeposition is a liquid-phase thin film deposition method based on an electrochemical reaction. It is nothing but a process of deposition of a thin layer of one material on the top surface of the different metal substrates via losing an electron to the ion in an electrolyte solution. One of the interesting features of this method is that we can easily deposit one-dimensional nanostructures, such as nanorods, nanowires, and nanotubes also it is possible to modify the surface properties of a material by using electrodeposition methods.^[30]

2.1 Experimental setup for electrodeposition

In electrodeposits method, the deposition takes place when an electric current flows through an electrochemical cell. The deposition setup consists of two conductive or semi-conducting electrodes immersed in an electrolyte. In most of the deposition, process three-electrode is used to deposit metal-semiconductor and oxide thin films. For a simple setup, at least two electrodes are required. One of the electrodes

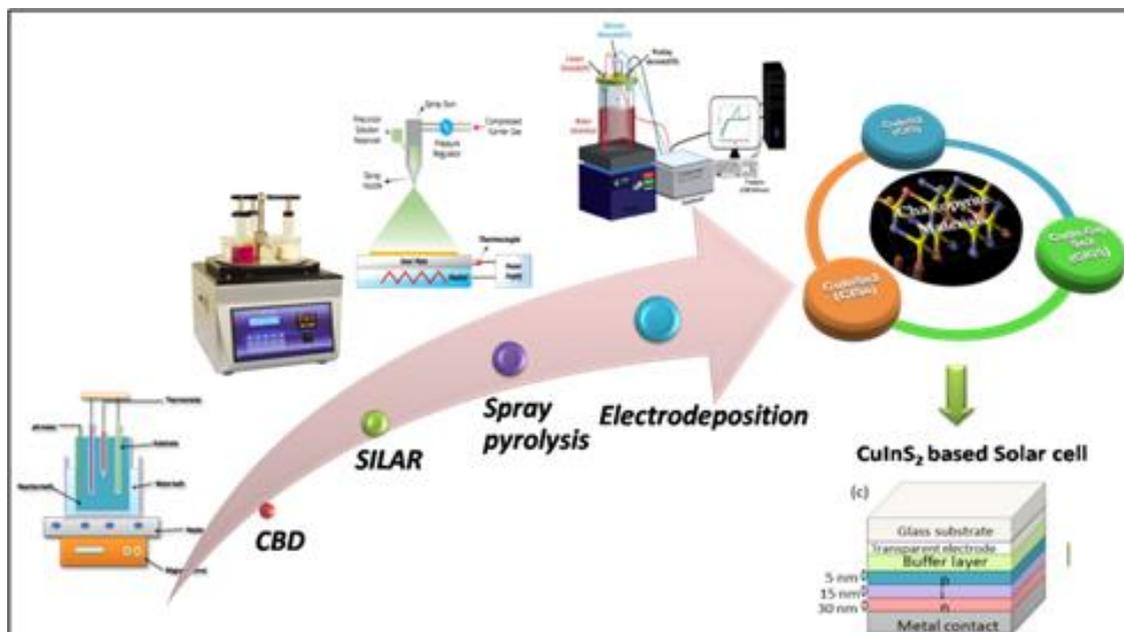


Fig. 2 Deposition of CIS thin-film by various chemical methods.

could be a working electrode or substrate, and the other should be a counter electrode. The counter-electrode (anode) is utilized to complete the electrical circuit and the working electrode (cathode) is the object where electrodeposition is intended. Electrolytes for electrodeposition are aqueous solutions generated by dissolving metal salts, generally comprising positive and negatively affected ions. Due to the transport of the charged species, via migration and diffusion, onto the polarised electrode surfaces, the current flows between the two conduction electrodes in the presence of an external voltage. The conduction mechanism must change from ionic to electronic on the surface of the electrodes. Three electrode systems require one more electrode in addition to the working electrode. The necessary apparatus for electrodeposition is shown in Fig. 3. Generally, various electrodes such as Ag/AgCl, Hg/HgCl, saturated calomel

electrode, and standard hydrogen electrode can be used.^[31] In the three-electrode system, the film growth occurs most often via a reduction reaction. Three electrode steps can also be used, with the third electrode serving as a reference electrode for controlling or measuring the electrochemical potential of the working electrode. If the potential of the working electrode is controlled, the resulting current may be measured. A deposition is always carried out at constant potential or constant flow. Nowadays CIS material is a widely studied material because of its unique and exciting optoelectronic properties. To date, a vast number of researchers have reported CIS thin film by various electrodeposition methods. Such as single-step electrodeposition, pulsed electrodeposition, co-electrodeposition, and sequential pulsed electrodeposition method.

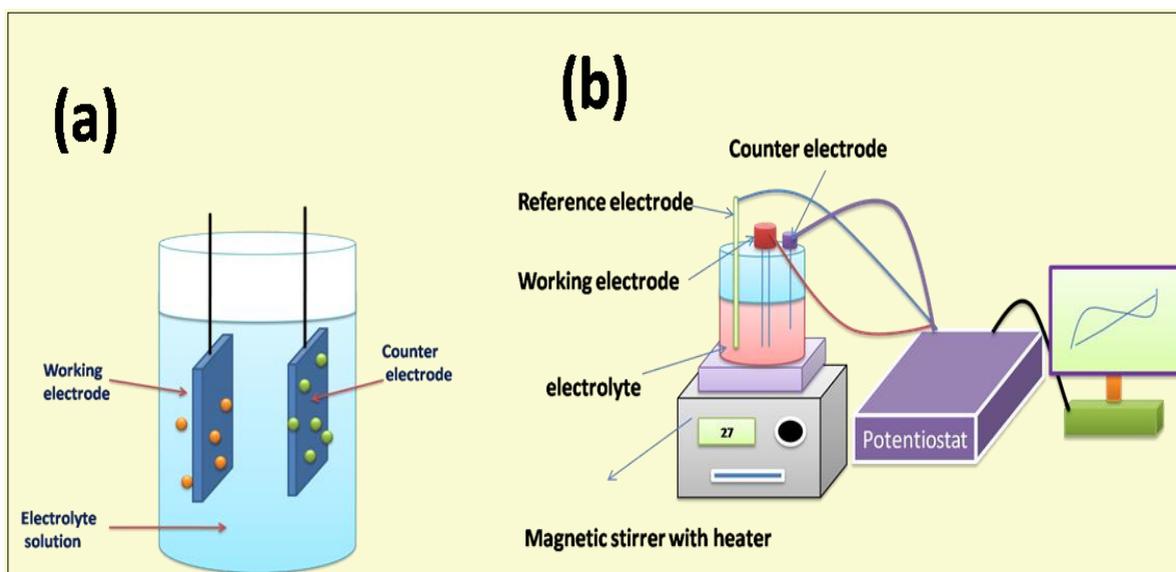


Fig. 3 Experimental setup for (a) two electrode electrodeposition systems and (b) three-electrode electrodeposition system.

2.2 Single-step electrodeposition of CIS thin film

Tang *et al.*^[32] were deposited n-type CIS thin films by one-step electrodeposition of Cu/In/S precursors followed by calcination in a mixture of N₂ and H₂ at 500 °C. The exciting thing in this study was the no use of toxic H₂S gas for sulfurization. Deposited CIS films were calcinated in a pure N₂ and a mixture of 8% H₂ and 92% N₂. The CIS film calcimined in pure N₂ resulted in the formation of CIS with In₂O₃ and Cu_xS impurities. In contrast, film calcinated in a mixture of H₂ and N₂ provided an extra pure CIS phase. Three electrode systems were used to deposit a CIS thin film. The molar ratio of Cu:In:S is adjusted by changing the volume ratio of the precursor solutions.

The effect of potassium hydrogen phthalate (C₈H₅KO₄) as an additive on CIS thin films has been successfully studied by using a novel one-step potentiostatic electrodeposition method.^[33] The XRD spectrum of the thin film deposited with C₈H₅KO₄ (23 mM) showed a peak at 27.80° which is a characteristic peak of chalcopyrite CIS structure. The SEM (Scanning Electron Microscopy) image reveals that the pure CIS thin film has a uniform surface with densely packed spherical clusters of smaller nanoparticles. The surface states of the CIS films transferred from the In-rich smooth surface to the Cu-rich rough surface with decreasing C₈H₅KO₄ quantity in the precursor solution. The complexation studies between C₈H₅KO₄ additive and Cu²⁺, In³⁺ cations reveal that most probable complexation happens between Cu²⁺ and C₈H₅KO₄⁻, whereas weaker complexing interaction of C₈H₅KO₄ with In³⁺ was reported. Guan *et al.*^[34] reported the effects of preparation conditions on the CIS films deposited by one-step electrodeposition. The deposited film shows an optical band gap of 1.53 -1.55 eV. With increasing, deposition potentials deposition current also increases. Particle film sulfurized at low S vapor concentrations shows superior crystallization. Optimized parameters for high-quality CIS thin films are -0.8 V, Cu²⁺/In³⁺ ratio 1.4, sulfur content 1 g, and sulfurization temperature 550 °C. Cheng *et al.*^[35] grow the CIS film by one-step electrodeposition. The effect of the [Cu]/[Cu + In] ratio in the solution bath on the growth of thin film and the physical properties of CIS film was studied systematically. All the deposited films have the CIS phase. As variation in [Cu]/[Cu + In] molar ratios, there is a change in the type of conductivity of the sample. When the molar ratio is less than 0.29, then the film is n-type conductive CIS. Vice versa when the molar ratio is higher than 0.33, then the film is p-type. The flat band potential of the p-type and n-type CIS is in the range of 1.08 to 1.22 V (vs Ag/AgCl) and 0.74 to 0.83 V (Vs Ag/AgCl) for n-type and p-type CIS film respectively.

The electrochemical quartz crystal microbalance (EQCM) was used to study the growth of CIS films by one-step electrodeposition.^[36] A voltammogram study showed a cathodic peak at -0.3 V for 0.01 M CuSO₄ (pH -1.4) solution. Voltammogram and EQCM signal of 0.001 M CuSO₄ with 0.001 M In₂(SO₄)₃ at pH 1.1 showed a cathodic peak of copper at -0.3 V and anodic peaks of indium at - 0.8 V and - 0.15, -

0.65 V indicating the possibility of formation of indium oxides and indium sulfide, together with metallic Cu–In. It reported that the deposition of sulfur starts with - 0.4 V. Influence of deposition potential and concentration of precursors on properties of the structure of the CIS films studied. CIS film annealing at 200 °C in the nitrogen atmosphere shows the predominant CIS phase.

Iorio *et al.*^[37] reported the p-type and chalcopyrite phase of CIS thin film deposition. Such deposition text is place using a cost-effective and versatile one-step electrodeposition method. XRD spectra revealed the binding energies found for deposited CIS films are in good agreement with those of copper, indium, and sulfur. Surface morphology of without etched film agglomerated and after annealing, smooth homogeneous morphology was obtained. The average thickness of the film was 300 nm.

2.3 Frequency-regulated pulsed electrodeposition of CIS thin-film

Tang *et al.*^[38] deposited visible light active CIS nanoparticles on vertically aligned ZnO nanorod arrays on fluorine-doped tin oxide (FTO) substrate using electrodeposition. This electrodeposition is regulated by using an optimized frequency. Frequency tuning is used to control the diffusion and deposition of the secondary component (CIS) on the one-dimensional substrate (ZnO). Introducing a pulse in electrodeposition allows deposition throughout the substrate. Fig. 4 shows the schematic diagram of the mass transport and charge transport during the pulsed-electrodeposition of CIS nanoparticles on ZnO nanorods. High quality and uniform deposition of CIS nanoparticles are achieved on ZnO nanoarray by a pulse-regulated electrodeposition method (Fig. 4).

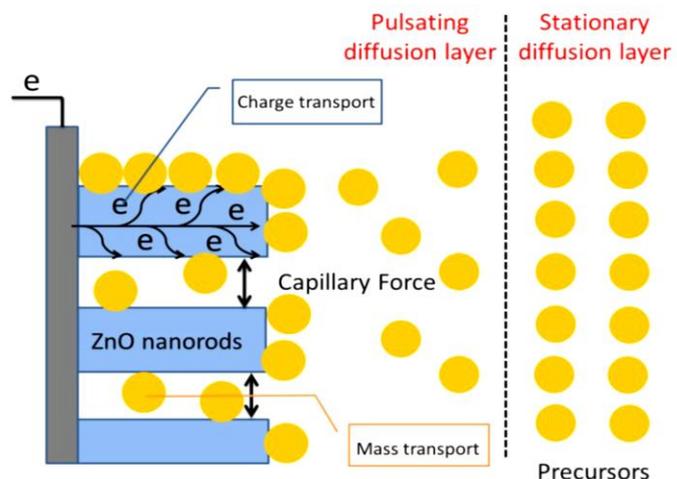


Fig. 4 Schematic diagram of the mass transport and charge transport during the pulsed electrodeposition of CIS nanoparticles on ZnO nanorods. Reproduced with permission from,^[38] Copyright 2015 The Royal Society of Chemistry.

2.4 Sequential electrodeposition of CIS thin-film

Wijesundera *et al.*^[21] carried out a sequential deposition of Cu

and In by electrodeposition to develop a CIS thin film on the Ti substrate. The X-ray diffraction spectra (XRD) for Cu/In = 0.40, 0.51, and 0.68 under saturated H₂S gas indicate transformation from the CuIn₁₁Si₁₇ phase to the CIS phase. SEM image showed a uniform and polycrystalline thin film with grain size in the range of 1–3 μm. From the optical study, a direct bandgap of 1.5 eV was observed. It also reported that the Mott-Schottky plot for Ti/n-CIS/p-ZnSe/is linear, indicating doping density is uniform and the space charge region is located within n- CIS film. A flat-band potential of 540 mV and a doping concentration of $4.3 \times 10^{17} \text{ cm}^{-3}$ is evident from the plot for the CIS film. A maximum of 540 mV open-circuit voltage was demonstrated from this heterostructure.

A sequential study of the electrodeposition of CIS was carried out.^[39] In the first stage, Cu-S films are deposited on a Ti substrate. In the second stage, the In-S system was examined, followed by the formation of CIS thin films from a ternary bath of the precursor solution. The deposition was carried out using CuSO₄ and In₂(SO₄)₃ and 400 mM Na₂S₂O₃ on the Ti electrode potentiostatically in the range -0.85-0.95 V. XRD patterns of the samples heat-treated showed the main CuInS₂ phase. However, in cases of Cu/In ratio = 12:8 and 10:10, diffraction peaks of indium oxide In₂O₃ were reported.

2.5 Co-electrodeposition of CIS thin-film

Yuan *et al.*^[40] deposited CuInS thin films by electrochemical co-deposition of the Cu-In alloy layer, followed by sulphurization. In this study, Triethanolamine is used as a complexing agent to suppress the reduction of Cu²⁺. The CIS film deposited at a sulfurization temperature of 400 °C and deposition potential of 1000 mV shows good crystallinity. As the prepared film shows aggregated morphology and further sulfurization, it shows flake-type morphology.

3 Influence of processing parameters

3.1 Sulfurization

Lu *et al.*^[41] studied the influence of processing parameters on the deposition of CIS film. The film deposited at 400 °C shows a high surface quality and large grain size. The 10.5 h at 50 °C and 23 h at 30 °C is the suitable growth aging time for the deposition of the chalcopyrite film. Sulfurization of electrodeposited Cu–In alloy was carried out at 550 °C for 30 min in 100% H₂S gas.

Usually, electrodeposited Cu-In precursors are annealed in costly and toxic H₂S gas. Still, nonuniform CIS film has been obtained. Because of that, it is a need for the fabrication of uniform CIS film without the usage of toxic H₂S. Few researchers annealed electrodeposited Cu-In precursors without the usage of toxic H₂S gas. Tang *et al.*^[32] deposited a deposited n-type CIS thin films followed by calcination in a mixture of N₂ and H₂ at 500 °C. The exciting thing about this is no need for toxic H₂S gas for sulfurization. Deposited CIS films calcinated in a pure N₂ and a mixture of 8% H₂ and 92% N₂. The CIS film calcined in pure N₂ resulted in the formation

of CIS with In₂O₃ and Cu_xS impurities. At the same time, film calcinated in a mixture of H₂ and N₂ provided an extra pure CIS phase. Similarly, Rodriguez *et al.*^[42] reported a one-step electrodeposition method to obtain (CIS) film. They did not use Toxic H₂S gas during annealing. The deposited films were annealed in a 95% N₂ + 5% H₂ atmosphere for one h at 400 °C.

Yeh *et al.*^[43] revealed the influence of various electrodeposition and sulfurization parameters on CIS film deposition. As the annealing temperature increased from 500 °C to 600 °C, the CuS peaks suppressed simultaneously In₂S₃ peaks become strengthen, increase in grain cluster sizes and the growth of CIS. The heat treatment was included in the fabrication process of CIS film to suppress the formation of the CuS phases. A suitable quantity of sulfur powder and a specific annealing temperature could suppress the CuS phases. Hence well-crystallized CIS film obtains.

CIS films were electrodeposited using CuSO₄, In₂(SO₄)₃, and Na₂S₂O₃ by electrodeposition.^[39] As-deposited films were amorphous. They confirmed that after annealing at 573 K, the CIS phase was observed. Prepared films were nonstoichiometric with a tetragonal chalcopyrite-type structure.

3.2 In/Cu ratio

Cheng *et al.*^[35] reported that as an increase in [Cu]/[Cu + In] molar ratio in the solution bath, the samples transform from the In-rich CIS phase to the Cu-rich CIS phase. As variation in [Cu]/[Cu + In] molar ratios, there is a change in the type of conductivity of the sample. When the molar ratio is less than 0.29, then the film is n-type conductive CIS. Vice versa when the molar ratio is higher than 0.33, then the film is p-type. Nakamura *et al.*^[44] studied various In/Cu ratios during the deposition of CIS thin-film systematically. Improvement in the crystallinity of the film as a decline In/Cu ratio. They confirmed that after annealing the crystallinity of CIS film enhanced. A larger grain size was observed for Cu-rich film than for In-rich film. Zangari *et al.*^[45] reported that as increasing Cu/In ratio carrier density increased; however, the photoelectrochemical response of the CIS films was not directly related to Cu/In ratio. Martinez *et al.*^[46] reported that when the rate of [Cu²⁺]/[In³⁺] = 1, then the conductivity was of the n-type, however, if [Cu²⁺]/[In³⁺] is more than 1, the conductivity was p-type.

Storkel *et al.*^[47] used a novel method to remove the unwanted CuS in Cu-rich prepared CIS/CdS/ZnO photovoltaic cells by a combined chemical/electrochemical procedure. In the process as-grown, CuS-covered CuInS₂ samples were studied in the alkaline electrolyte (0.1 M K₂SO₄, pH-10) for two different potentials of -0.95 and -0.8 V versus SCE. The current versus time plot for CuS covered CIS in the electrolyte. An approximately 2 μm thick sheet of CuS was reported to be removed by this technique. Table 2 shows the preparative parameters for the deposition of CIS thin film deposited using the electrodeposition method.

Table 2. Preparative parameters for the deposition of CIS thin film by Electrodeposition method.

Sr. No	Precursors	SBT(Substrate)/ DT (deposition temperature)/ ST (substrate temperature)/ CE (Counter electrode)	Remark	Reference
1	0.01M cupric acetate 25 mM InCl ₂ , 0.1M sodium acetate	SBT- Ti DT-55 °C ST-550 °C CE-Pt plate	The transformation from CuIn ₁₁ S ₁₇ phase to CIS phase as Cu/In atomic ratio increases. The film shows good morphology. The direct band edge = 1.5 eV. A flat band potential of 540 mV and a doping concentration of $4.3 \times 10^{17} \text{ cm}^{-3}$ is evident from the Mott–Schottky plot for the CIS film.	[21]
2	30 mM CuCl ₂ (99.9%, 30 mM of InCl ₃ and 300 mM of Na ₂ S ₂ O ₃	SBT- FTO ST-500 °C CE-Pt foil	CIS thin films showed n-type conductivity. The XRD showed a tetragonal chalcopyrite structure. Sulfurization is carried out which is free from toxic H ₂ S gas. The CIS film calcinated in a mixture of H ₂ and N ₂ provided an extra pure phase of CIS.	[32]
3	12.5 mM CuCl ₂ , 10mM InCl ₃ , 40 mM Na ₂ S ₂ O ₃ , 100 mM LiCl and 0.23 mM C ₈ H ₅ KO ₄ . HCL (pH-2.5)	SBT-Ni DT-30 ST-350 °C CE-Pt	The XRD shoed chalcopyrite structure. Pure CIS thin film has a relatively uniform surface that consists of densely packed spherical clusters of smaller nanoparticles. The Cu(C ₈ H ₅ O ₄) ⁺ and In(C ₈ H ₅ O ₄) ²⁺ complexes formed from the binding of Cu ₂ ⁺ , In ³⁺ ions, and –COO– group in the C ₈ H ₅ O ₄	[33]
4	12 mM copper (II) chloride, 6.7-10 mM indium chloride, 25 mM sodium thiosulfate, 0.5 mM potassium chloride, and 0.1 M citric acid. C ₆ H ₈ O ₇ -complexing agent, KCl aqueous solution -supporting electrolyteNH ₄ OH ₆ .	SBT-ITO-coated glass substrates DT-RT ST-400-550 °C under Ar atmosphere CE-platinum plate	All films showed p-type conductivity. The optical band gaps were estimated to be between 1.53–1.55 eV. The deposition current increases with increasing deposition potentials. Film sulfurized at low S vapor concentrations shows superior crystallization Optimized Parameters –0.8 V, Cu ²⁺ /In ³⁺ ratio 1.4, sulfur content 1 g, and sulfurization temperature 550 °C	[34]
5	CuCl ₂ 0.01 mol, InCl ₃ , 0.50 mol, Na ₂ SO ₃ and 0.2 mol, Na ₃ C ₃ H ₅ O(COO) ₃ , Sodium citrate. HCL and NaOH (pH 8)	SBT-FTO DT-30 °C ST-450 °C CE-Pt	The CIS film showed a chalcopyrite phase, with a bandgap of 1.43 eV and the conductivity observed was p-type.	[37]
6	10 mM CuCl ₂ and 100 mM Na ₂ S ₂ O ₃	SBT-ZnO/FTO ST- 500 °C CE- Pt foil	Sequential pulsed-electrodeposition method high quality and uniform deposition of CIS nanoparticles achieved	[38]
7	CuCl ₂ ·2H ₂ O, InCl ₃ ·4H ₂ O, Na ₂ S ₂ O ₃ ·5H ₂ O and LiCl, H ₂ So ₄ and Tartaric acid	SBT-Ti ST-40 CE-Pt	The electrical conductivity measurement study reveals that if the ratio $[\text{Cu}^{2+}]/[\text{In}^{3+}] = 1$, the conductivity is of the n-type, however, if $[\text{Cu}^{2+}]/[\text{In}^{3+}]$ is more than 1.5 the conductivity is p-type. The charge carrier density, flat-band potential, carrier concentration, and bandgap of p-CIS were observed to be 0.45 V, $3.14 \times 10^{16} \text{ cm}^{-3}$, 1.55 eV respectively.	[39]
8	5 mM CuCl ₂ and five mM InCl ₃ , using TEA as the complexing agent (0.2 M) and sodium citrate (0.010 M) as the buffering agent	SBT-ITO DT-30 °C ST-400 °C Under N ₂ atmosphere CE-Pt foil	Well, the crystalline chalcopyrite structure of CIS film was observed after sulfurization at 400 °C temperature. The Co-deposition potential was 800 - 1100 mV. The optical bandgap was estimated to be 1.49 eV. After sulfurization, the aggregates particles turn into flakes	[40]

Continued

Sr. No	Precursors	SBT(Substrate)/ DT (deposition temperature)/ ST (substrate temperature)/ CE (Counter electrode)	Remark	Reference
9	0.01M cupric acetate, 0.01M InCl ₂ , 0.1 M sodium acetate And 100% H ₂ S	SBT-Ti DT-50 °C ST-550 °C CE-Pt	Polycrystalline nature and the chalcopyrite structure of CIS thin film. The 10.5 h at 50 °C and 23 h at 30 °C is the suitable growth aging time for the deposition of the chalcopyrite film. The film deposited at 400 °C shows the high surface quality and large grain size.	[41]
10	CuSO ₄ and In ₂ (SO ₄) ₃ and 400 mM Na ₂ S ₂ O ₃ .i HCL, (pH - 3.22 - 1.74)	SBT-Ti 500 °C CE-carbon rod	The XRD study showed the amorphous nature of the film. After heat treatment, the CIS phase was observed along with the indium oxide In ₂ O ₃ peak. For pH around 1.5, a single phase of CIS formed and no peaks of indium oxide. Peaks of the CIS phase broadened with an increase of In ³⁺ ion concentration in the deposition solution	[44]
11	2.5 mM CuSO ₄ , 5 mM In ₂ (SO ₄) ₃ , 50 mM Na ₂ S ₂ O ₃ , 5 mM Na ₂ - EDTA and 100 mM Li ₂ SO ₄ The pH was adjusted to 3 using H ₂ SO ₄	SBT - ITO DT-RT ST-550 °C under sulfur	The sample grown at deposition potential of -1.0 V and annealed at 550 °C has major phase In ₂ S ₂ . P-type conductivity. Show photo enhancement effect	[48]
12	50 mM CuSO ₄ , 150 mM trisodium citrate, and 242 mM citric acid. The pH was adjusted to 2.4 using H ₂ SO ₄ .	SBT-MO DT-24 °C ST-560 °C Under H ₂ S CE-Pt-sheet	SEM image showed large grains with a porous appearance. The XRD showed chalcopyrite structure, and p-type photo responses were reported	[49]

4. Conclusion

The present review outlines the preparative parameters and the physical properties of the CIS absorber layer deposited via electrodeposition methods with extracts from published investigations by numerous researchers. Overall, the synthesis section highlights the synthesis parameters as well as the composition, morphology, and properties of the CIS absorber layer. High quality and uniform deposition of CIS film are achieved by a pulse-regulated electrodeposition method. The applied frequency during the electrodeposition of CIS film was one of the essential parameters. It was controlling the two critical coating mechanisms over one-dimensional nanostructures like nanorod nanofiber *etc.* The CIS film calcinated in a mixture of H₂ and N₂ provided an extra pure phase of CIS since there is no need to use toxic H₂S gas for sulfurization. The CIS deposition has been reported at different temperatures of the precursor solution and different substrate temperatures.

However, reports on room temperature deposition of CIS thin-film are limited. The room temperature deposition leads to amorphous, known-stoichiometric film composition. For low-temperature deposition, knowledge of proper

optimization of preparative parameters and an understanding of suitable solution chemistry is required. The crystalline nature can enhance by annealing the sample at a different temperature. The sulfur deficiency was found in many of the electrodeposited samples. Segregation of binary Cu-S compounds, especially CuS (covellite) occurs at the surface. It is necessary to remove this phase before further processing. Combined chemical/electrochemical procedure methods can be employed to remove these unwanted phases.

In many cases, Cu-rich films showed more electrical conductivity than In-rich samples. In electrodeposition as Cu/In ratio increases, there is a decrease in the crystallite size of the CIS thin film. Improvement in the crystallinity of the film as a decline In/Cu ratio. As variation in [Cu]/[Cu + In] molar rates, there is a change in the type of conductivity of the sample. When the molar ratio is less than 0.29, then the film is n-type conductive CIS. Vice versa when the molar ratio is higher than 0.33, then the film is p-type. A larger grain size was observed for Cu-rich film than for In-rich film. The film sulfurized at low sulfur vapor concentrations shows superior crystallization.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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