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Pulsed Electrochemical Deposition of CuInSe_2 and Cu(In,Ga)Se_2 Semiconductor Thin Films

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Additional information is available at the end of the chapter

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Abstract

CuInSe_2 (CIS) and Cu(In,Ga)Se_2 (CIGS) semiconductors are the most studied absorber materials for thin films solar cells due to their direct bandgap and large absorption coefficient. The highly efficient CIGS devices are often fabricated using expensive vacuum based technologies; however, recently electrodeposition has been demonstrated to produce CIGS devices with high efficiencies and it is easily amenable for large area films of high quality with effective material use and high deposition rate. In this context, this chapter discusses the recent developments in CIS and CIGS technologies using electrodeposition. In addition, the fundamental features of electrodeposition such as direct current, pulse and pulse-reverse plating and their application in the fabrication of CIS and CIGS films are discussed. In conclusion, the chapter summarizes the utilization of pulse electrodeposition for fabrication of CIS and CIGS films while making a recommendation for exploring the group's unique pulse electroplating method.

Keywords: pulse electrodeposition, semiconductors, thin films, copper indium gallium selenide, photoelectrochemical cells, solar cells

1. Introduction

The present day's global energy production is mostly accomplished from the fossil fuels; however, the inherent problems associated with the use of fossil fuels such as their limited availability and the environmental issues force the mankind to look for alternative solutions for future energy supply. The need to develop renewable energy resources has come to the forefront of discussion. Photovoltaics (PV) is an emerging field and one of the choices for major means of future energy-harvesting. The efficiencies of PV conversion depend on the properties

of absorber layer, which is the heart of the solar cell. Silicon has been the foundation of the photovoltaics industry due to its well-known properties, high abundance and well-studied technological aspects of the growth. However, it requires expensive manufacturing technologies such as growing and sawing of ingots. Hence, current trend in photovoltaics requires the development of high performance inexpensive solar absorber materials that can serve in the long term as viable alternatives to the single crystal silicon technology. Among various technologies, CuInSe₂ based solar cells are the most studied and leading candidates to realize commercialization with efficiencies close to 23% [1].

2. Copper indium selenide (CIS) and copper indium gallium selenide (CIGS)

CIS is a ternary semiconductor belonging to the I-III-VI class, crystallizes to a chalcopyrite structure, possesses a direct bandgap of 1.04 eV and an absorption coefficient of $\approx 10^5 \text{ cm}^{-1}$ [2, 3]. The CIS-based solar cells exhibit excellent chemical stability, stability with time and doping versatility. Absorber layer is the key element of solar cells, which is produced mainly from the p-type semiconductor in thin films solar cells. The electrical properties of Cu ternary semiconductors are determined by native defects [4]. There are three possible electrically active defects namely, vacancies, interstitials and antisite defects [5–7]. It is these defects which determine the nature of the conductivity of CIS films whether n type or p type. Intrinsic copper vacancies (V_{Cu}) and copper on indium antisite defects (Cu_{In}) are the electrically active defects for a typical p-type CIS film. On the other hand, intrinsic selenium vacancies (V_{Se}) and indium on copper antisite defects (In_{Cu}) makes the CIS n-type. The material with Cu rich composition is not preferred mainly because of the formation of copper selenide (Cu_2Se). Cu_2Se being highly conductive, shorts out the junction. Adding more Indium than copper reduces the formation of Cu_2Se but it causes other defects like V_{Cu} and In_{Cu} which are compensating in nature [8]. Hence, the copper to indium ratio (Cu/In) is always maintained around unity. Samples with p-type conductivity are grown if the material is Cu-poor and is annealed under high Se vapor pressure, whereas Cu-rich material with Se deficiency tends to be n-type. CIS films when suitably manufactured tend to be p-type because of the low energy of formation of copper vacancies which give the material its conductivity [4, 7, 9]. CIS solar cells yielded relatively lower open circuit potentials due to its small bandgap. This limitation is overcome by adding controlled amounts of gallium to replace indium in the CIS structure [10]. The band gap of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ varies according to the equation [11].

$$E_g = 1.011 + 0.664x + 0.249x(1 - x) \quad (1)$$

Depending on the $[\text{Ga}]/[\text{In} + \text{Ga}]$ ratio, the bandgap of CIGS can be varied continuously between 1.02 and 1.68 eV [10, 12]. The addition of about 30% Ga in CIS increases the bandgap to 1.2 eV which has a closer match with the AM 1.5 solar spectrum [12, 13]. Addition of Ga not only increases the band gap but also has other beneficial effects such as improving the adhesion of the film to the Mo substrate, increased carrier concentration, etc. Though it is beneficial to add Ga to improve the properties of CIS, there is a limit to which it serves favorable.

Higher Ga content of 40% has a detrimental effect on the device performance, because it negatively impacts the transport properties of the CIGS absorber film. The current, high-efficiency devices are prepared with bandgaps in the range 1.20–1.25 eV, which corresponds to a Ga/(In + Ga) ratio between 25 and 30% [14–18].

The fabrication methods often are the big difference in industrializing a technology based on a materials system. To determine the most promising technique for the commercial manufacturing of modules, the foremost criteria are: (i) low cost, (ii) scalability, (iii) reproducibility and (iv) manufacturability. Several vacuum techniques including co-evaporation, sputtering, molecular beam epitaxy, pulsed laser deposition, etc., have been investigated for the formation of CIGS thin-films. The most successful technique for deposition of CIGS absorber layers for highest efficiency small area cells is the co-evaporation of elements from multiple sources where Se is offered in excess during the process [19]. Although thin-film CIGS solar cells with power conversion efficiencies over 23% have been demonstrated, the vacuum-based processes used therein pose cost and technological barriers in the production of PV modules. With this requirement in mind, development of low-cost methods to fabricate CIGS has become an intensively pursued goal and a variety of solution-based approaches have been demonstrated. Non-vacuum approaches, include electro or electroless-deposition, chemical bath deposition, particulate processes and coating involving molecular precursors are being explored. The efficiency gap between vacuum and non-vacuum deposited CIGS has been reduced in past years and processes from the above categories have now reported cells with efficiencies of 15–17%, thereby, showing promise for commercialization. Among these methods, electrochemical deposition is the most extensively explored technique for the deposition of CIGS absorber layers and has witnessed high efficiency devices [20–23], and will be discussed in detail in the following section.

3. Electrodeposition

The process of electro-reduction of precursor ions onto an electrode, substrate of interest, from an appropriate electrolyte by the utilization of electric current or potential between two electrodes is termed as electrodeposition. The properties of the deposit depends on several parameters including ionic concentrations, the electrodes used, the pH of the electrolyte, the temperature, the type of substrate, the stirring rate, the deposition voltage and the time of deposition. Electrodeposition is a promising approach to fabricate the absorber layers in thin films solar cells due to following advantages:

- It is a low cost solution based approach and avoids expensive vacuum technology
- High deposition rate on larger areas with lateral uniformity
- Use of low cost starting materials, e.g., low purity salts and solvents can be purified with application of small voltage before the electrodeposition
- Uses low temperature for deposition
- Deposition of films on a variety of shapes and forms of wires, tapes, coils, and cylinders

- Effective material use as high as 98% with minimum waste generation
- Control over the composition of individual elements by varying deposition parameters
- Extrinsic doping of semiconductors with appropriate elements by utilizing small concentrations of dopant precursor in electrodeposition bath
- Bandgap engineering either by varying the contents of individual elements in step-by-step approach or by using combinatorial approach

Owing to these advantages, electrodeposition satisfies all the necessary criteria for the research and development of PV solar cells. In addition, electrodeposition involves two fundamental approaches such as direct current and pulse plating wherein pulse plating further comprises pulse and pulse-reverse features. These features are unique in themselves that they provide additional process control variables and make electrodeposition an attractive tool for the deposition of semiconductors [24].

3.1. Direct current (DC) Electrodeposition

Direct current electrodeposition is the conventional method wherein a constant current or potential is applied continuously during the deposition to coat the desired materials. **Figure 1** shows the schematic of the direct current applied and the typical growth process corresponding to it. DC technique effectively has two variables, namely, applied potential/current and time of deposition while the precursor concentration and electrolyte pH are the common variables. The morphology, composition and thickness of the deposit can be altered by varying these parameters. In DC, the continuous use of constant potential/current leads to deposition of films without any relaxation leading to the growth of existing nuclei instead of generating new nucleation sites thereby resulting in a rough and porous deposit. In addition, hydrogen evolution reaction (HER) competes along with the deposition of desired materials as often aqueous electrolytes are used. The HER not only influences the current efficiency of the technique but also the deposited film properties. Use of additives in conventional DC deposition has improved the morphology of the deposited films. Despite having several disadvantages, DC electrodeposition is still a leading technique for the production of single element deposits and binary alloys.

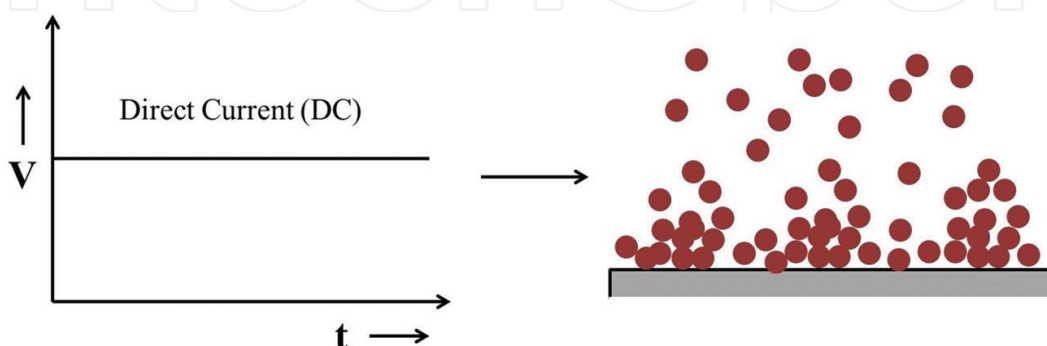


Figure 1. Schematic of direct current electrodeposition and expected growth process of the deposit.

3.2. Pulse electrodeposition

In pulse electrodeposition (PED), current/potential is applied in the form of modulated waves as shown in **Figure 2**. Compared to DC, PED offers additional process control variables like pulse on-time (t_{on}) and off-time (t_{off}). Often, the variation in t_{on} and t_{off} is expressed using a common parameter known as duty cycle, which is defined by the equation:

$$Duty\ Cycle\ (\%) = \frac{t_{on}}{t_{on} + t_{off}} \times 100 \quad (2)$$

The precise variation in duty cycle provides the control over electrochemical processes by affecting the diffusion layer, grain size and nucleation. Usually in electroplating a negatively charged layer is formed around the cathode which gets charged to a known thickness and prevents the ions from the bulk. In DC, this charged double layer prevents the passage of ions toward the cathode thereby affecting the features of the deposit and also causes the inhomogeneity in the concentration of ions in the electrolyte. However, in PED, the charged diffusion layer gets discharged and helps easier passage of the ions onto the cathode as the output is periodically turned off. Migration of ions to depleted areas in the bath during off-time makes the even distribution of ions for their easy availability during on-time. The presence of off time aids in the relaxation and the rearrangement of deposited atoms leading to the possibility of new nucleation sites during the subsequent deposition. This, in turn, not only improves the uniformity of deposition but also reduces the porosity and roughness of the deposit (see **Figure 2**). In addition, the entrapped hydrogen and impurities during the deposition diffuse out during the relaxation time. The additional process variables in PED ease the process of optimization for complex stoichiometric ternary/quaternary systems as the control over individual elemental composition is far better with the variation in duty cycle compared to DC technique.

3.3. Pulse reverse electrodeposition

Pulse reverse electrodeposition contains short anodic pulses alongside the cathodic as seen in PED (See **Figure 3**). This small anodic pulse is advantageous since it contributes to the electro-oxidation of the top layer from the deposited film thereby aids in smoothening of the deposit, removing the impurities as well as the entrapped hydrogen. The anodic pulse plays a major role in the deposition of systems like CIS and CIGS, wherein an undesired

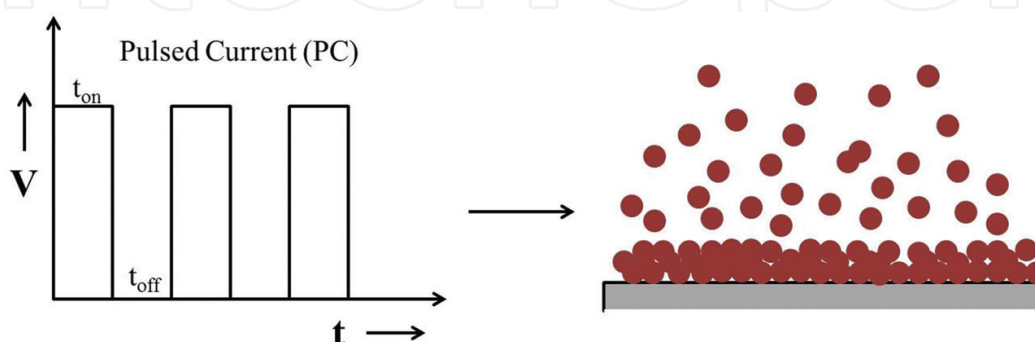


Figure 2. Schematic of pulse electrodeposition and expected growth process of the deposit.

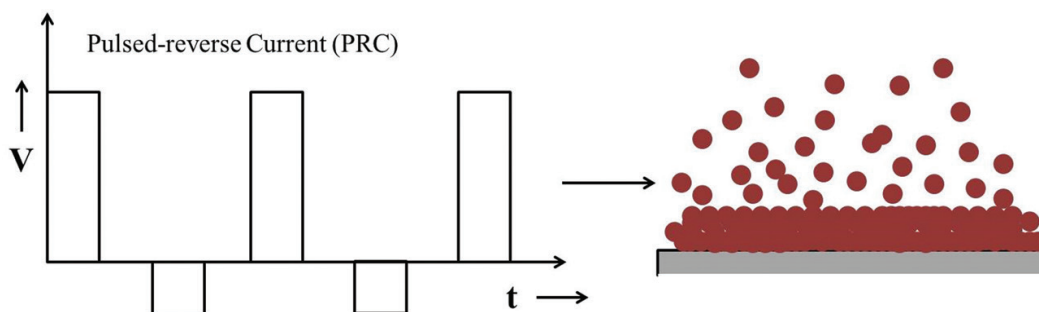


Figure 3. Schematic of pulse reverse electrodeposition and expected growth process of the deposit.

secondary Cu-Se phase exists on the surface. With the appropriate control of the anodic pulse, excess copper and the undesired phases can be easily eliminated from the deposited films thereby, forming a phase-pure CIS/CIGS. Similar to PED deposition, the variation in pulse parameters is expressed using a common parameter known as duty cycle, which is defined by the equation:

$$\text{Duty Cycle (\%)} = \frac{t_c}{t_a + t_c} \times 100 \quad (3)$$

3.4. Electrodeposition of ternary/quaternary chalcopyrites

The goal of the electrodeposition (ED) is to assure an adherent, compact and a laterally uniform film with the desired stoichiometry. Lateral compositional uniformity is essential over large areas for commercialization of devices. The properties of the deposit solely depend on the control of individual parameters during ED such as electrode material, precursor concentration in electrolyte, applied potential/current and temperature. For single metallic systems like Cu or Zn these properties are well understood. However, deposition of CIGS contains multiple elements including a chalcogen making the ED process substantially complex. Despite that electrochemical deposition appears to be a promising technique for the low-cost solution preparation of CIGS semiconductors [25–27]. Indeed, electrochemical deposition has been widely investigated for CIGS deposition since the pioneering work by Bhattacharya et al. in 1983 [28]. Since then, more than 350 publications have been devoted to the electrochemical preparation of CIGS and several review papers have appeared [25, 29, 30], making electrodeposition the most intensely studied non-vacuum deposition method for CIGS. In light of this, this section reviews and summarizes the previously published work.

The first electrochemical approach to deposit polycrystalline CIS was reported by Bhattacharya in 1983, wherein Cu, In and Se were simultaneously deposited from an acidic solution [28]. Quickly after the first report, several approaches have been proposed for the synthesis of CIS thin films [31–33]. It is of general interest to perform a simultaneous codeposition of all three elements in achieving stoichiometric chalcopyrite CIS films. Such an approach was first initiated by Bhattacharya [28], which is by far the most investigated case as it involves only one electrochemical process, often termed as one-step electrodeposition. Typical electrochemical reactions involving the reduction of elements and formation of CIS/CIGS phase are detailed in [34].

One-step electrodeposition of CIS is usually carried out in an aqueous solution often containing chloride/sulfate precursors of Cu^{2+} or Cu^+ , In^{3+} , and $\text{SeO}_2/\text{H}_2\text{SeO}_3$. The deposition solution often contains a complexing agent in order to shift the reduction potentials of Cu and In closer together to improve the film quality. Complexing agents such as citric acid/citrate [35], ammonia [28], triethanolamine [28, 36], thiocyanate [37], etc., are used during the one-step electrodeposition of CIS thin-films. In addition, a supporting electrolyte such as chloride (LiCl [22, 34, 38, 39] or NaCl [40]) or sulfate (K_2SO_4 [41–43]) is added which results in an improved conductivity of the electrolyte leading to easier mobility of the precursor ions. Often amorphous or poorly crystalline CIS films were observed from electrodeposition which contains frequently degenerate Cu_{2-x}Se phases that are detrimental to the device performance [30, 37]. Also, Cu-rich films have generally larger grain sizes than stoichiometric or In-rich films. Due to these reasons, the electrodeposited CIS films often required to be annealed in a selenium atmosphere to correct for the stoichiometry and improve crystallinity.

Incorporation of Ga into the CIS thin-films, to improve the desired properties, was a challenging task for long time for the formation of quaternary CIGS thin-films. However, this bottleneck has been overcome in the recent past. Several researchers have reported the successful incorporation of Ga in the films up to desired range of amounts (6–8 at. %) for the preparation of high efficiency cells [22, 34]. Bhattacharya et al. were the first to report the insertion of Ga from a chloride bath, but to a very low content $\text{Ga/In} \approx 0.1$, wherein a superimposed alternating voltages has been used at 20 kHz [44]. But the breakthrough for the incorporation of Ga has been realized a little later when the group had used a pH buffer in the chloride bath, also known as Hydrion buffer ($\text{pH} = 3$) consisting of sulfamic acid and potassium hydrogen phthalate. The deposition potential was kept constant while the solution composition has been varied to realize the real possibility of incorporating Ga with the ratio Ga/In from 0.3 to 0.7. This process demonstrated the formation of CIGS films over a wide range of compositions suitable for efficient solar cells by one-step electrodeposition technique. CIGS layers generally deposited from the above mentioned electrodeposition technique often used an additional PVD step to achieve the required composition to form stoichiometric films [45, 46]. Bhattacharya et al. demonstrated a cell efficiency of 9.4% by using a similar PVD step to improve the composition of In and Ga in the as-deposited CIGS thin-films [39]. Valderrama et al. explored a similar electrodeposition technique followed by PVD step to achieve stoichiometric chalcopyrite CIGS films and additionally demonstrated the use of CIGS films to produce hydrogen by the use of photoelectrochemical testing of the films in H_2SO_4 [46]. Avoiding the formation of secondary phases was essentially a key point to achieve high quality CIGS thin-films and hence, higher efficiency. The formation of secondary phases was successfully prevented by the pretreatment of Mo substrate wherein a 1 min pre-deposition of CIGS was performed and a multi-potential deposition regime was employed to obtain crack-free CIGS layers [47].

In the similar context, addition of Ga seems to cause morphology related problems, often a concern during the electrodeposition of CIGS films. Fernandez et al. varied the concentration of precursor solution systematically and achieved a better control over composition and morphology of the CIGS films [39]. The presence of cracks in Ga-containing layers is often a serious problem [39, 47], though it can be reduced through the use of alcohol–aqueous solutions [48] or supporting electrolytes such as LiCl or Li_2SO_4 with gelatin as brightening additive [49]. Complexing

agents such as citric acid/citrate [50, 51], thiocyanate [52], sodium sulfamate [53], sulfosalicylic acid [54], etc., were often used to improve the composition and morphology of the CIGS films. These additives form complexes with the metal ions in the solution such as Cu, thereby resulting in controlled deposition rates and hence the morphology [55, 56]. Good quality CIGS thin films were also prepared from sulfate–citrate and chloride–citrate solutions [53, 57, 58] and control of the optical band gap by increasing the Ga content in the films was demonstrated [59].

To overcome the difficulty of In and Ga incorporation, alternative strategies to co-electrodeposition have been developed, often involving the deposition of stacked elemental layers or else deposition of alloys, followed by a selenization or sulphurization treatment to provide all of the chalcogen [21, 34]. Deposition of Cu-Ga [60] and Cu-In-Ga [52] alloys has been demonstrated, with the latter approach leading to 4% efficiency cells. Solopower explored the layer by layer electrodeposition to form stoichiometric CIGS thin-films [21]. The process also used several varieties of complexing agents, organic additives, etc., to correct the composition and improve the morphology of the films. In addition, current densities were varied during deposition and annealing temperatures were optimized to achieve high quality compact large grained stoichiometric chalcopyrite CIGS films. Devices and modules were fabricated using these films which had shown an efficiency of 15.36% on an area of 5.34 cm² and 13.4% on an area of 3.8 m². Most recently, electrodeposited CIGSSe devices have yielded conversion efficiencies upto 17.3% wherein electrodeposited Cu-In-Ga stack is rapid thermal treated in elemental selenium and sulfur atmosphere. Some of the recent notable reports with direct current electrodeposited CIGS solar cells are summarized in **Table 1**.

In addition to the synthesis of CIS and CIGS thin films by DC electrodeposition, PED technique has also been studied. Owing to the advantages of PED discussed in Section 3.2, it results in superior quality thin-films and enables one to avoid additional steps of deposition, post deposition treatments and the use of complexing agents. Kang et al. reported the preparation of CIS thin-films by pulse-reverse electrodeposition followed by selenization wherein stoichiometric CIS films with rough surface morphology exhibited an efficiency of 1.42% [61]. Li et al. employed a square wave modulated by a bell-like wave during the pulse plating for the fabrication of CIS thin-films. The study reported well adherent chalcopyrite CIS films with a uniform morphology [35]. A three-step pulse electrodeposition method was used for the fabrication of CIS thin-films reporting a mixture of phases such as Cu-Se, In-Se, CIS, etc., as confirmed from Raman and optical studies of the samples [62]. Valdes et al. employed different potentials during the pulses which resulted in chalcopyrite p-type CIS thin-films with different morphologies and compositions [63]. Murali et al. prepared CIS thin-films using pulse electrodeposition with varied duty cycle from 6 to 50% and reported the p-type phase pure CIS films with resistivities in the range of 1–10 ohm-cm [64]. Hu et al. employed the deposition of CIS films by pulse electrodeposition wherein multi potentials were used to control the composition of the films which resulted in improved deposition uniformity without any secondary phases [65]. Similar reports on the compositional control of CIS thin-films by the variation of pulse parameters have appeared in the recent past [66–69].

Fu et al., have explored different plating techniques including DC, pulse and pulse reverse electrodeposition for the fabrication of CIGS thin films and reported the elimination of undesired secondary phases like Cu_{2-x}Se to obtain single phase pure chalcopyrite CIGS thin films [70]. Liu et al., have employed the PED with the variation of duty cycle to remove the excess In and to avoid In-Se compounds during the deposition for the preparation of single phase CIGS

Absorber material	Substrate	Preparation method	Reported efficiency/ photocurrent (cell area in cm^2)	Remarks	Reference
CIGSe	Mo/glass	Cu-In-Ga oxide precursor followed by thermochemical reduction and selenization	12.4% (0.1)	A new approach by one-step electrochemical deposition of metal oxides followed by thermochemical reduction and selenization	[82]
CIGSe	Mo/glass	Stacked Cu/In/Ga followed by selenization	11.7 (0.4)	Step-by-step electrodeposition of Cu/In/Ga followed by selenization	[22]
CIGSe	Mo/glass	Stacked Cu/In/Ga layers followed by selenization	12.6 (0.1)	Impact of thickness is studied. 8.7% efficiency is achieved for an ultrathin 370 nm film of CIGS	[83]
CIGSe and CIGSSe	Mo/stainless steel foil	Four step electrodeposition of CIG layers followed by selenization	15.36% for CIGSe (5.4) 13.4% for CIGSSe (3824.6, submodule)	Development of roll-to-roll electrodeposited CIGS solar cells on flexible stainless steel substrates	[21]
CIGSe and CIGSSe	Mo/glass	Electrodeposited CuInGa layers annealed using Rapid thermal Processing under S and Se vapors	14.1% for CIGSe (0.5) 15.8% for CIGSSe (0.5)	Rapid thermal processing of electrodeposited CIG layers under S and Se atmosphere	[84]
CIGSSe	Mo/glass	Electrodeposited precursors followed by rapid thermal processing in S and Se atmosphere	10.6 (0.1) for CISSe 9.9 (0.1) for CIGSe	Sequentially electrodeposited copper indium precursors are annealed by RTP under S and Se atmosphere	[26]
CIGSSe	Mo/glass	Electrodeposited stacked Cu/In/Ga layers are annealed by RTP under S and Se atmosphere	13.8 (0.09)	All solution processed CIGSSe solar cells are made wherein i-ZnO/AZO window layer is deposited using solution based approach.	[85]
CIGSe	Mo/glass	Electrodeposited CIGSe layers followed by physical vapor deposition of In, Ga, Se and selenized	15.4% for ED CIGSe (0.4) 12.4% for EL CIGSe (0.4)	Physical vapor deposition of In, Ga and Se was performed on electrodeposited and electroless deposited CIGS layers for compositional adjustment	[23]

Absorber material	Substrate	Preparation method	Reported efficiency/ photocurrent (cell area in cm ²)	Remarks	Reference
CIGSe	Mo/glass	Three stage electrodeposition (CIGSe/Cu/In) process followed by annealing under Se atmosphere	10.9% (0.4)	Electrodeposited precursor layers are prepared in a three stage sequential route wherein Cu and In second and third layers are deposited on CIGSe layer	[38]
CIGSe CIGSe	Mo/glass	Electrodeposited CIGSe is annealed under selenium atmosphere and spray coated CIS nanoparticles followed by selenization	Photocurrent of 1 mA/cm ² for CIGSe and for CIGSe in ethyl viologen perchlorate electrolyte	CIGSe films were deposited from spray coating of nanoparticles and selenized while CIGSe were electrodeposited and selenized	[86]

Table 1. Notable reports on direct current electrodeposited CIS/CIGS with reported efficiencies.

thin films [58]. In one of the most successful efforts of fabrication of CIGS by pulse electrodeposition, Bi et al. have effectively utilized the parameters in electrodeposition to demonstrate CIGS solar cells with conversion efficiencies upto 10.39% [71] and 11.04% [72]. Cu-In-Ga metal precursors were electrodeposited by pulse current method wherein the charge density was chosen such that the desirable thickness of each layer is achieved. Electrodeposited metal stack was annealed in a three step process to achieve dense large grained CIGS layer which yielded high conversion efficiencies. **Table 2** summarizes the recent literature reported for CIGS thin films fabrication using pulse electrodeposition.

Materials	Substrate	Preparation method	Notable inference	Remarks	Reference
CIGSe	Mo/glass	Stacked Cu/In/Ga by DC and PC methods followed by selenization	11.04% efficiency for pulse plated CIGSe (0.34) 8.18% efficiency for direct current deposited CIGSe (0.34)	Direct current and pulsed current plating are explored for step by step Cu/In/Ga layers and pulse plated devices exhibited higher efficiency	[72]
CIGSe	Mo foil	DC, Pulse and pulse reverse plating of CIGS films followed by annealing in Ar	CIGS exhibited p-type and dark I-V curves are recorded	Use of pulse reverse potential eliminated the undesired CuSe phase	[70]
CIGSe	Mo/glass	Pulse reverse electrodeposition of CIGSe followed by selenization	Efficiency of 1.42% on 0.4 cm ² cell	Pulse reverse plating is employed to make CIGSe with device quality features	[61]
CIGSe	Mo foil	Pulse electrodeposition of CIGSe followed by annealing	PEC curves are recorded indicating photoactivity of CIGSe films	Variation in duty cycle is adopted and growth mechanism is studied	[58]

Materials	Substrate	Preparation method	Notable inference	Remarks	Reference
CIGSe	Mo/glass	DC and pulse reverse plating of CIGS followed by selenization		Variation in duty cycle in pulse reverse plating yielded device quality CIGS films	[87]
CIGSe	Mo/glass	Step by step pulse electrodeposition of Cu/In/Ga films followed by selenization	10.39% (0.34)	Optimization of pulse conditions for each layer of Cu, In and Ga during pulse electrodeposition	[71]
CIGS	ITO	Pulse electrodeposition of CIGS followed by annealing	Photocurrents in μ A range are observed	Duty cycle has been optimized for device quality CIGS films	[88]
CISe	Mo foil	Pulse electrodeposition of CIS followed by annealing	PEC performance reported	A novel nanoflake morphology has been reported while obtaining stoichiometric CISe with optimization in duty cycle	[76]
CIGSe	Mo foil	DC and pulse plating of CIGSe films followed by annealing	PEC performance reported	DC and pulse plated CIGS films are compared. Optimization in pulse plating improves the morphology and crystallinity of CIGSe	[75]
CIGSe	Mo/glass	Two stage pulse electrodeposition of CuGaSe and In films followed by annealing	PEC performance reported	A sequential pulse electrodeposition approach is proposed so as to minimize the utilization of In concentration during electrodeposition of CIGSe films	[73]

Table 2. Summary of recent reports on pulse electrodeposited CIS/CIGS for application in thin films solar cells.

Despite having several advantages, pulse and pulse reverse electrodeposition techniques are underutilized for the fabrication of CIGS thin films. Considering the additional process variables these techniques offer, thin films photovoltaic community might consider exploring these processes for fabricating high quality CIGS films. Our group has explored these features while developing a simplified pulsed electrodeposition technique for the fabrication of CIGS thin films and is discussed below.

4. Pulsed electrodeposition of CIS and CIGS films: case studies

A new simplified pulse electrodeposition approach for the fabrication of CIS and CIGS films with compact and nanostructured morphologies was developed [73–76]. The approach utilizes a two electrode system by avoiding the conventional third reference electrode for the deposition of thin films. The commonly used expensive platinum counter electrode is substituted by

high purity graphite electrode thereby cutting down the cost. The technique by virtue of utilization of pulse plating avoids the use of any additives and complexing agents during electrodeposition while obtaining the stoichiometric films in a single step thereby eliminating multi-step deposition. The films are annealed under Ar atmosphere while avoiding the conventional selenium atmosphere making it an environmental friendly approach. In addition, a novel strategy has been developed to address the scarcity of Indium wherein In precursor has been effectively minimized compared to existing reports. Typical pulse electrodeposition set-up, applied pulse voltage wave form and the corresponding current density are depicted in **Figure 4**.

Since the approach avoids the use of reference electrode and employs a two-electrode system, prior to electrodeposition, cyclic voltammetry of the CIGS system using a two and three-electrode system are studied as shown in **Figure 5**. The reduction peak of CIGS is shifted from -0.8 to -1.1 V from three to two-electrode systems. Apparently, the potential shift is approximately same as the standard electrode potential of SCE vs. normal hydrogen electrode (NHE). However, experiments with different systems might be required to verify the same. The inference is utilized to adopt higher deposition potentials in the pulsed electrodeposition of CIS and CIGS films.

4.1. Study I: pulse electrodeposition of CuInSe_2 films

The pulse electrodeposition of CuInSe_2 (CIS) films is performed from a bath containing metallic chlorides of Cu, In and Ga while selenous acid is used as selenium precursor dissolved in pH 3 Hydriion buffer. The final pH of the bath is maintained around 2.0–2.5. Additives and complexing agents are completely avoided in this study. CIS films were electrodeposited using a deposition potential of -1.5 V while the variation in duty cycle has been studied. The applied pulse-voltage and the corresponding current density curves from **Figure 6** note that there is a small positive current density during the pulse off-time though no voltage is applied. This could be due to the presence of an electric double layer at cathode-electrolyte interface forming a capacitor of molecular dimension [58, 77]. The duty cycle for the application of pulses is varied in the range of 17–67% (varied off-time with fixed on-time). The PED technique employed in

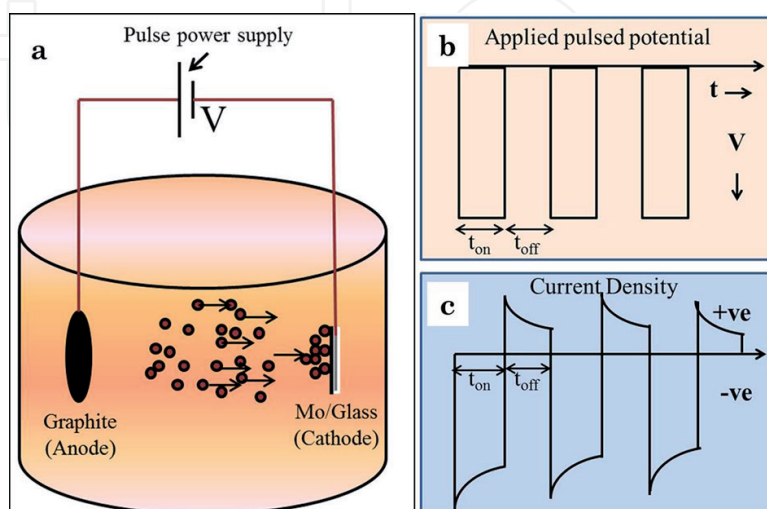


Figure 4. (a) Pulse electrodeposition set-up, (b) applied deposition voltage waveform and (c) corresponding current density employed for pulse electrodeposition of CIS and CIGS thin films.

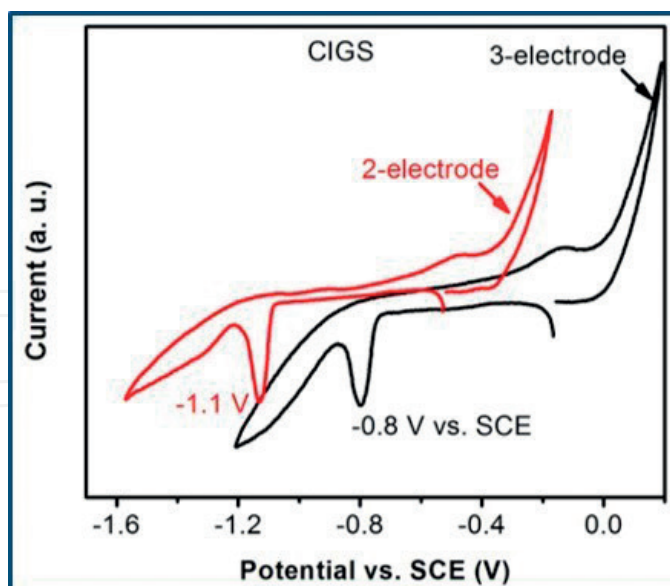


Figure 5. Cyclic voltammogram of Cu-In-Ga-Se system using a three-electrode and two-electrode configuration.

the present study did not result in any disruption and dissolution of the deposited film into the electrolyte, which generally happens with higher deposition voltages as previously reported [78]. The PED deposited CIS films are annealed at 550°C for 30 min under Ar atmosphere.

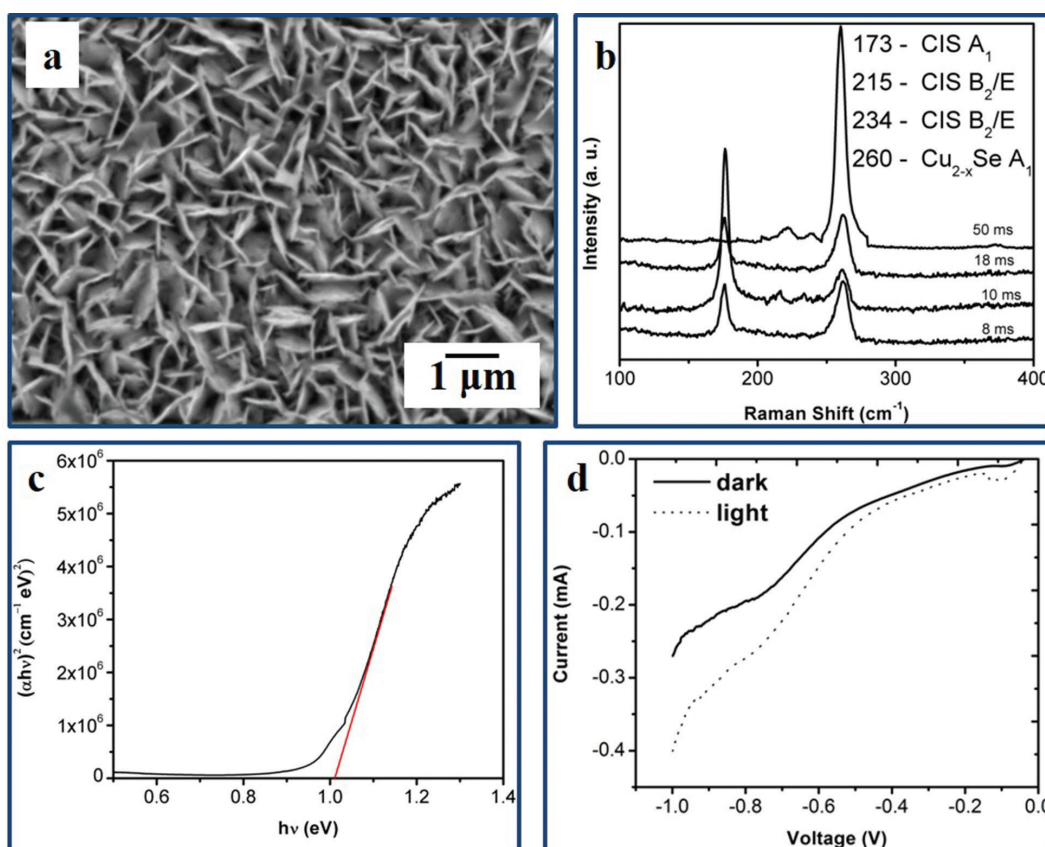


Figure 6. (a) Nanoflake morphology, (b) Raman spectra, (c) Tauc's plot and (d) photoelectrochemical I-V characteristics of pulse electrodeposited and annealed CIS films.

The compositional analysis indicated that with an increase in the pulse off time from about 5 to 50 ms during electrodeposition, the relative content of In in the film decreases from almost 40 to 2 at. %. This is due to the unintended positive current density observed in **Figure 4c**, which oxidizes the elements with least electronegativity from the deposited film leading to the dissolution of corresponding element into the electrolyte. A duty cycle of 50% has been considered optimal for obtaining stoichiometric CIS films. Morphological analysis reveal that the CIS films deposited with optimal conditions possess novel nanoflake-like architectures (see **Figure 6a**). Such morphology is expected to be advantageous since they possess high surface area of the film thereby causing improvement in absorption of light and photoresponse. This is also expected to be advantageous at the device stage since it facilitates increase in the p-n junction interface area of the solar cell which directly influences its performance. Additionally, flake like crystallite structure is favorable to increase current carrier concentration, electron transmission and thus induce the generation of photocurrent [79]. Another interesting aspect from this study is the effective reduction in the secondary phases during the electrodeposition of CIS/CIGS films. The variation in duty cycle explored in the present study yielded the films with reduced copper selenide phase for optimal conditions. Raman spectra of the electrodeposited and annealed CIS films are shown in **Figure 6b**. The spectra contain well-defined peaks at wavenumbers of 172, 215, 234 and 260 cm^{-1} and are attributed to the A_1 , B_2 and E modes of CIS films and the peak at 260 cm^{-1} is attributed to the A_1 mode of Cu_{2-x}Se . As the spectra reveal the optimized condition with relative Cu/In ratio close to 1, shows least intense peak for copper selenide thereby affirming its reduction. Bandgap of CIS films as obtained from optical absorption spectroscopy is 1.02 eV (from **Figure 6c**), which matches well with the theoretical value of 1.04 eV for stoichiometric chalcopyrite CIS films [80]. Photoelectrochemical performance of CIS films as shown in **Figure 6d** confirms the photoactivity and p-type conductivity.

4.2. Study II: comparison of direct current and pulse electrodeposited CIGS films

CIGS thin films are deposited using direct current (DC) and pulsed current (PC) methods from a bath of metal chlorides and selenous acid in pH 3 Hydrion buffer devoid of additives and complexing agents. **Figure 7a** and **b** shows the surface morphologies of DC and PC plated CIGS films. DC deposited CIGS films exhibited porous and rough morphology with finer spherical particles while dense uniform films with coarser spherical particles are observed for PC deposited CIGS. PC method can produce relatively more homogeneous surface with good adhesion to the substrate because the rate-determining step of the deposition process is controlled by a mass-transfer process. Relaxation during the pulse off-time in the PC electrodeposition not only allows the diffusion of ad atoms but also facilitates the formation of new nucleation sites thereby leading to the homogeneous and compact morphology unlike the DC deposition wherein building-up of material takes place at same nucleation sites leading to the roughness of the film. The stoichiometry of the DC and PC electrodeposited CIGS films is determined, from EDS, to be $\text{Cu}_{1.10}\text{In}_{0.54}\text{Ga}_{0.23}\text{Se}_{2.13}$ and $\text{Cu}_{0.98}\text{In}_{0.73}\text{Ga}_{0.25}\text{Se}_{2.03}$, respectively, indicating copper rich composition in DC CIGS films.

Figure 7c shows the XRD patterns of annealed DC and PC electroplated CIGS films, which show the preferred orientation corresponding to (112) and other peaks to (211), (220), (312)

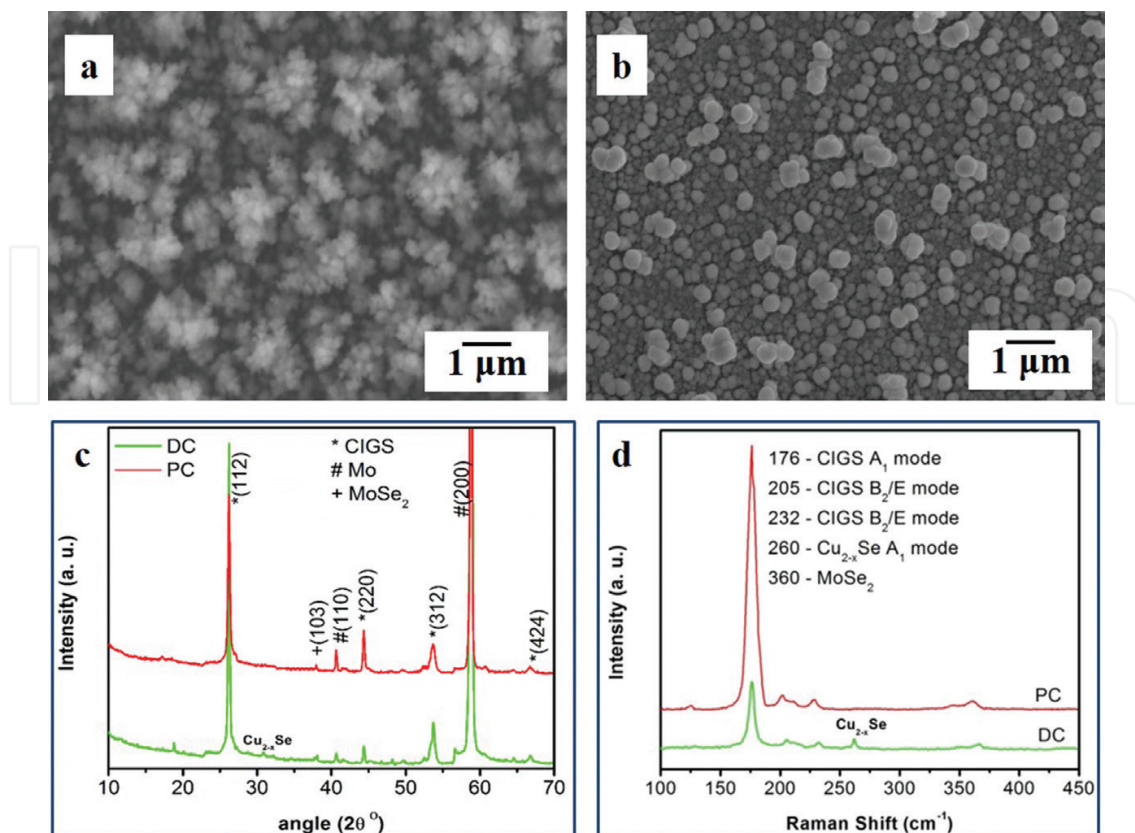


Figure 7. (a) and (b) surface morphologies, (c) XRD patterns and (d) Raman spectra of direct current and pulse electrodeposited CIGS films.

and (424) for CIGS are observed thereby confirming the presence of chalcopyrite CIGS phase. Additionally, Mo substrate and MoSe₂ peaks are observed [81]. XRD pattern also reveals the presence of copper selenide in DC electroplated CIGS while it is absent in PC plated films indicating the phase-pure CIGS formation by PC approach. **Figure 7d** shows the Raman spectra of the DC and PC electrodeposited CIGS thin films and contain A₁, B₂ and E modes of the CIGS at 176, 205 and 232 cm⁻¹, respectively. In addition, a less intense peak corresponding to A₁ mode of Cu_{2-x}Se at 260 cm⁻¹ is found in case of DC electrodeposited CIGS thin film. The copper rich composition in DC plated CIGS films facilitated the formation of the Cu_{2-x}Se phase, which is generally dispersed on the surface [84, 87]. PC electrodeposition with suitable optimization of parameters aided control over the composition of elements and eliminated Cu_{2-x}Se phase. The bandgap of direct current and pulse plated CIGS films is obtained from Tauc's plots as shown in **Figure 8a**, which are determined to be 1.21 and 1.29 eV, respectively. The photoelectrochemical J-V characteristics of annealed DC and PC electrodeposited CIGS thin films studied in 0.5 M Na₂SO₄ are shown in **Figure 8b**. Increase in cathodic current with potential confirms the p-type conductivity. Also, the PC plated CIGS films show lower dark current and higher photocurrent compared to DC plated films, which could be attributed to the dense morphology with stoichiometric chalcopyrite CIGS without secondary phases. **Figure 8b** shows the amperometric J-t curve confirming the photoactivity of CIGS under chopped illumination.

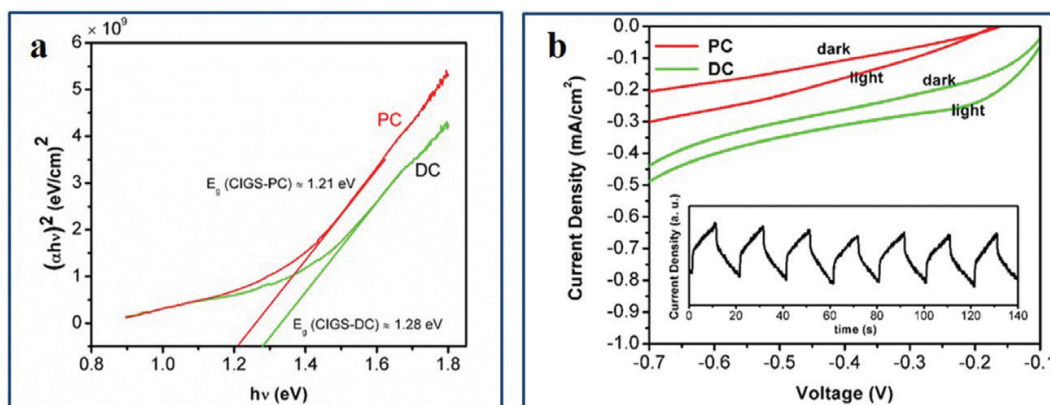


Figure 8. (a) Tauc's plots and (b) photoelectrochemical J-V characteristics of direct current and pulse electrodeposited CIGS films.

4.3. Study III: sequential pulsed electrodeposition of CIGS thin-films

The sequential technique has been proposed to essentially minimize In precursor to address the scarcity of In. The usage of In in the growing electronic and optoelectronic industries is very high in the form of materials such as indium doped tin oxide (ITO), CIS, CIGS, InP, InN, InGaAs, InAlAs, etc., making it one of the most scarce elements in the near future. In this context, a novel sequential PC approach is explored for the fabrication of CIGS thin-films. Deposition of Cu-Ga-Se films is carried out by optimizing the deposition voltage in the first stage followed by subsequent deposition of In in the second stage. The sequentially deposited Cu-Ga-Se/In thin-films are annealed in Ar atmosphere and characterized.

The optimized CuGaSe/In annealed films are noted to have a compact morphology (**Figure 9a**), which is well-suited for application as solar absorber layers, since it facilitates easier diffusion of minority charge carriers and reduces recombination. XRD and Raman analyses confirm the presence of chalcopyrite CIGS films without any undesired phases as shown in **Figure 9b** and **c**. In addition to the micro-Raman analysis of CIGS films, Raman mapping of the optimized films is performed to further verify their phase-purity. **Figure 9d** shows the Raman mapping wherein red refers to the dominant CIGS, green to Cu_{2-x}Se and blue to In_2Se_3 phase. The map of annealed films contains only CIGS phase, thereby indicating the absence of any secondary phases. It also affirms the fact that the elements undergo interdiffusion during the annealing and form the desired chalcopyrite CIGS phase.

TEM analysis is used to confirm the inter-diffusion of In and to infer the CIGS phase formation. The TEM image of CIGS particles is shown in **Figure 10a**. The selected area diffraction (SAED) pattern and TEM-EDS analyses are included as an inset in **Figure 10a**. SAED shows the orientations corresponding to (112), (220), (312) and (400) of CIGS, which corroborate the observation from XRD. TEM-EDS analysis shown in **Figure 10a** confirm the presence of Cu, In Ga and Se affirming the interdiffusion of In (deposited in stage II) during annealing. **Figure 10b** shows the Mott-Schottky ($1/C^2$ vs. V) plot of CIGS thin-films in 0.5 M H_2SO_4 at a frequency of 10 kHz in the dark. The slope of the MS plots is negative, thereby confirming that the CIGS film is p-type. The flat band potential was found to be -0.15 V (vs. SCE) by extrapolating

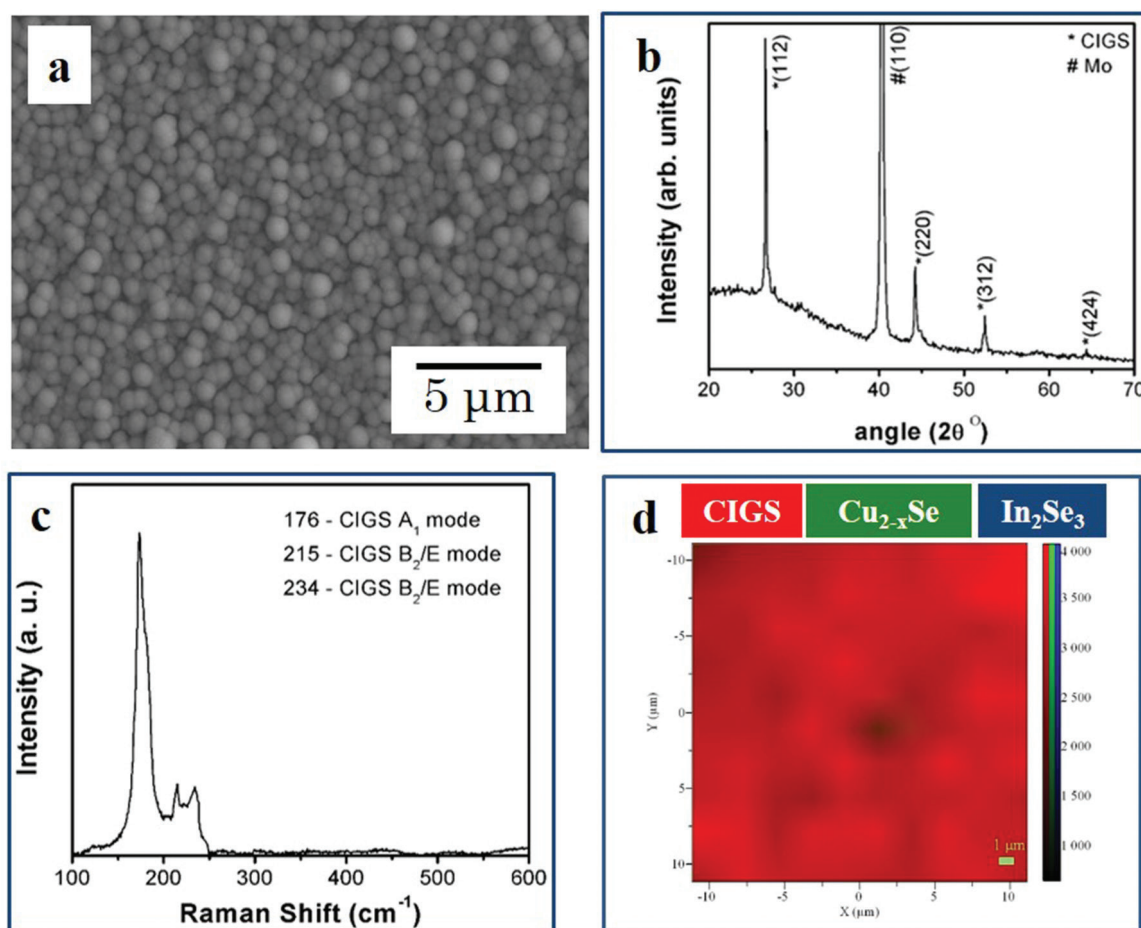


Figure 9. (a) Surface morphology, (b) XRD pattern, (c) Raman spectrum and (d) surface Raman mapping of sequentially pulse electrodeposited CIGS films.

the linear section to x-axis. In addition, $N_a \approx 2.6 \times 10^{16} \text{ cm}^{-3}$, calculated using the slope of the curve. The flat-band potential and acceptor density determined herein are close to the values reported previously [46]. **Figure 10c** shows the amperometric current-time (I-t) curve of CIGS films obtained at -0.4 V by chopped light, which demonstrates the nature of photoactivity of

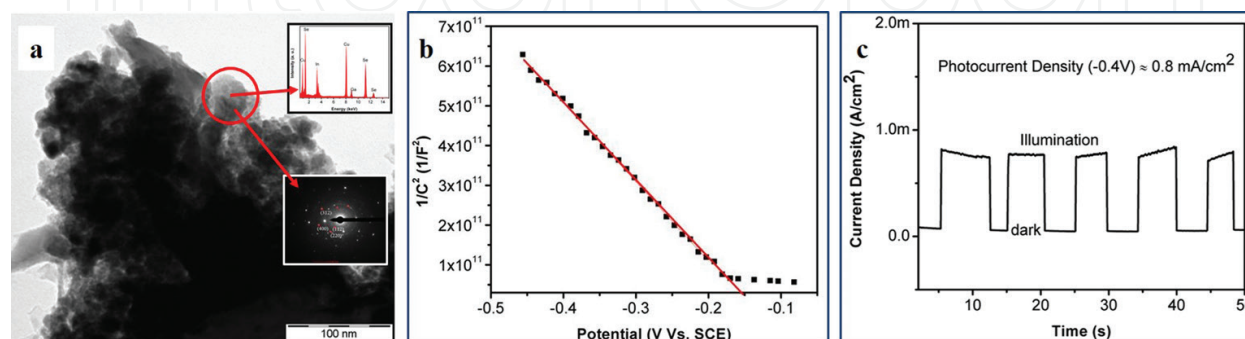


Figure 10. (a) TEM image (inset: TEM-EDS, SAED pattern), (b) Mott-Schottky analysis and (c) amperometric J-t curve of sequentially pulse electrodeposited CIGS films.

CIGS films with a photocurrent density of $\approx 0.8 \text{ mA/cm}^2$. The improved photoresponse of CIGS films indicate their potential for application in thin-film solar cells and photoelectrochemical hydrogen generation.

5. Conclusions

Electrodeposition is a versatile technique for the growth of semiconductor thin films on large areas with a very low capital investment. Considering the state of energy requirement, it is pertinent to explore this low cost technique for production of copper indium selenide (CIS) and copper indium gallium selenide (CIGS) semiconductor films which are the potential candidates for application in solar photovoltaics. The features of electrodeposition with its advanced techniques are discussed in detail while also reviewing the utilization of these for the fabrication of CIS and CIGS thin films. A state-of-the-art summary has been presented on the direct current and pulse electrodeposition of CIS and CIGS thin films detailing various approaches explored while obtaining high efficient CIGS devices. In addition, a new low cost environmental friendly pulse electrodeposition technique has been proposed for the fabrication of CIS and CIGS thin films. In conclusion, the chapter puts forward the idea to photovoltaic community to explore the economic pulse electrodeposition technique for the fabrication of high quality CIGS semiconductor thin films for application in thin films solar cells.

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