

Review

A Review of CIGS Thin Film Semiconductor Deposition via Sputtering and Thermal Evaporation for Solar Cell Applications

Karima Machkih, Rachid Oubaki and Mohammed Makha * 

Material Science, Energy and Nano-Engineering Department, University Mohammed VI Polytechnic UM6P, Lot 660 Hay Moulay Rachid, Benguerir 43150, Morocco

* Correspondence: mohammed.makha@um6p.ma



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Abstract: Over the last two decades, thin film solar cell technology has made notable progress, presenting a competitive alternative to silicon-based solar counterparts. CIGS ($\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$) solar cells, leveraging the tunable optoelectronic properties of the CIGS absorber layer, currently stand out with the highest power conversion efficiency among second-generation solar cells. Various deposition techniques, such as co-evaporation using Cu, In, Ga, and Se elemental sources, the sequential selenization/Sulfurization of sputtered metallic precursors (Cu, In, and Ga), or non-vacuum methods involving the application of specialized inks onto a substrate followed by annealing, can be employed to form CIGS films as light absorbers. While co-evaporation demonstrates exceptional qualities in CIGS thin film production, challenges persist in controlling composition and scaling up the technology. On the other hand, magnetron sputtering techniques show promise in addressing these issues, with ongoing research emphasizing the adoption of simplified and safe manufacturing processes while maintaining high-quality CIGS film production. This review delves into the evolution of CIGS thin films for solar applications, specifically examining their development through physical vapor deposition methods including thermal evaporation and magnetron sputtering. The first section elucidates the structure and characteristics of CIGS-based solar cells, followed by an exploration of the challenges associated with employing solution-based deposition techniques for CIGS fabrication. The second part of this review focuses on the intricacies of controlling the properties of CIGS-absorbing materials deposited via various processes and the subsequent impact on energy conversion performance. This analysis extends to a detailed examination of the deposition processes involved in co-evaporation and magnetron sputtering, encompassing one-stage, two-stage, three-stage, one-step, and two-step methodologies. At the end, this review discusses the prospective next-generation strategies aimed at improving the performance of CIGS-based solar cells. This paper provides an overview of the present research state of CIGS solar cells, with an emphasis on deposition techniques, allowing for a better understanding of the relationship between CIGS thin film properties and solar cell efficiency. Thus, a roadmap for selecting the most appropriate deposition technique is created. By analyzing existing research, this review can assist researchers in this field in identifying gaps, which can then be used as inspiration for future research.

Keywords: CIGS thin films; solar cells; physical vapor deposition; magnetron sputtering; thermal evaporation

1. Introduction

Electricity stands out as one of the most extensively utilized forms of energy, derived from a diverse range of sources [1,2]. The choice of energy source for electricity generation necessitates abundance and cleanliness to meet escalating demands while addressing environmental considerations. Among the renewable and boundless sources available, solar energy emerges as a prime contender for electrical energy production [3]. Photovoltaics, a technology centered around semiconductors, transforms solar energy into electricity. Despite ongoing advancements in the materials employed for photovoltaic technology, the

overarching objective persists in developing efficient technology at a cost-effective scale. Semiconductors designated for photovoltaic applications are typically classified into three types, delineated in Figure 1 [4].

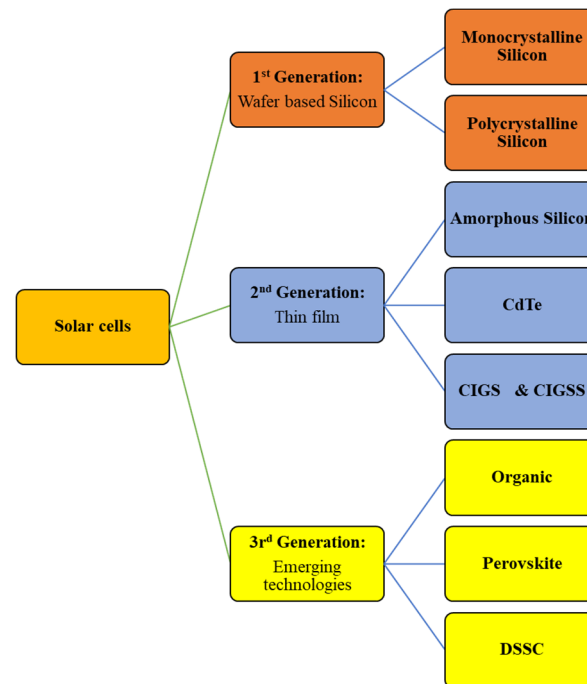


Figure 1. Photovoltaic cell generations.

The first generation of solar cells represents the oldest technology, utilizing silicon as the primary manufacturing material owing to its abundance. Silicon-based solar cell technologies, characterized by their high efficiency and long-term stability, hold a dominant position in the photovoltaic industry [5–8]. This technology can be classified into two sub-groups based on the method of silicon production. Monocrystalline silicon solar cells are made from single silicon crystals devoid of grain boundaries, achieving an efficiency exceeding 25% (NREL). However, the intricate production process results in higher costs, limiting the widespread adoption of this technology [9]. On the other hand, polycrystalline silicon solar cells consist of crystals with random orientation. Their simpler manufacturing method makes them more cost-effective compared to monocrystalline cells [9]. Nevertheless, they exhibit lower efficiency compared to monocrystalline, approximately 23% (NREL).

Second-generation solar cells, commonly referred to as thin film solar cells, emerged to meet the demand for reduced production costs, minimal material usage, and the advancement of flexible solar cell technologies [10]. Thin film technologies primarily involve the following:

- **Amorphous Silicon (a-Si):** Characterized by disorderedly organized silicon atoms, amorphous silicon differs from crystalline silicon. a-Si solar cells are more cost-effective than their crystalline counterparts due to the reduced silicon requirement. However, the fundamental limitation of this technology lies in its lower efficiency, attributed to material defects [11–13].
- **Cadmium Telluride (CdTe):** Stands out as a direct bandgap material with a higher absorption coefficient and greater chemical stability compared to a-Si. However, the main drawback of CdTe solar cells is the inclusion of cadmium (Cd), a heavy and hazardous metal [11].
- **Copper Indium Gallium Di-Selenide (CIGS):** A quaternary compound with a direct bandgap and a high absorption coefficient [11].

Additional types of thin films in the third generation encompass quantum dot [14], polymer [15], dye-sensitized [16], and concentrated solar cells [17]. It is important to note that these technologies are still in their early stages of development [11].

The objective of developing alternative solar cell technologies is to replace conventional silicon solar cells. In addition to high efficiency and low cost, several other factors must be considered when choosing the optimal alternative. These factors include stability, susceptibility to temperature variations, performance in low-light conditions, and environmental impact. Comparative assessments of alternative thin film solar cells by the National Renewable Energy Laboratory (NREL) indicate that CIGS-based solar cells emerge as the most efficient technology. Notably, CIGS offers an adjustable bandgap and exhibits a lower environmental impact. Moreover, it demonstrates enhanced resistance to shadows and performs more effectively at elevated temperatures than crystalline silicon [18]. Consequently, CIGS stands as a viable alternative to traditional silicon solar cells.

CIGS films required for thin film photovoltaic technology can be prepared through various methods, broadly categorized as vacuum-based methods involving deposition under vacuum conditions, primarily sputtering and co-evaporation and non-vacuum methods that do not rely on a vacuum [19]. The choice of deposition technique is a crucial step that significantly influences the performance of the device. The highest efficiency in CIGS solar cells has been attained through the use of vacuum technologies. Co-evaporation and sputtering stand out as the two most prevalent vacuum processes for CIGS deposition. These methods have recently gained popularity due to their compelling features, impacting cell efficiency and leading to the highest values among all deposition processes employed in CIGS manufacturing. In contrast, devices based on solution-deposited CIGS exhibit poorer performance and lag behind the vacuum-based approach [20,21].

This paper provides a comprehensive review of CIGS solar cell technology, with a focus on physical vapor deposition (PVD) techniques employed for depositing the CIGS absorbing layer. This exploration delves into the relationship between the elaboration process, the properties of CIGS, and the resulting performance of solar cells. Furthermore, the advantages, disadvantages, and challenges associated with magnetron sputtering and co-evaporation, two prominent PVD methods, are thoroughly examined. Additionally, this paper discusses methods aimed at enhancing the efficiency of CIGS-based solar cells manufactured through PVD techniques.

2. Properties of Chalcogenide Materials

In 1976, Kazmerski et al. [22] pioneered the development of the first thin film CISe_2/CdS solar cell, achieving a power conversion efficiency (PCE) of 5.7%. The distinctive features of the created junction resulted in CITE_2 exhibiting the highest PCE compared to other chalcopyrite materials such as CITE_2 and CIS_2 [23]. This superiority can be attributed to CISe_2 's lower lattice misfit with CdS at 1.2%, leading to reduced interfacial states [22,24]. However, it is worth noting that ternary CIS-based solar cells tend to have a lower open circuit voltage. The substitution of In for Ga was explored as a strategy to increase the band gap energy, subsequently enhancing the V_{oc} [25].

CIGS, with the chemical formula $\text{CuGa}_x\text{In}_{1-x}\text{Se}_2$, is a quaternary compound with a tetragonal chalcopyrite crystal structure. This structure originates from the duplication of the sphalerite structure, as illustrated in Figure 2 depicting the CIGS unit cell. Tetragonal distortion arises when the lattice ratio c/a deviates from 2, a phenomenon attributed to the formation of Cu-Se, In-Se, or Ga-Se bonds [26].

The crystal structure of CIGS was visualized using VESTA (Visualization for Electronic and Structural Analysis) software (version 3.5.8) [27]. CIGS, a compound comprising a solid solution of two components, CIS and CGS, underwent structural changes upon the introduction of Ga into the CIS component [26,28]. In the CIGS thin film, X-ray diffraction (XRD) peaks shifted to higher angles, indicating a reduction in the lattice parameter and, subsequently, a decrease in the cell parameters (a and c). This adjustment arose from the substitution of In, characterized by a larger ionic radius, for Ga, which possesses a smaller

ionic radius. However, a further increase in Ga concentration led to distortion in the CIGS cell [29].

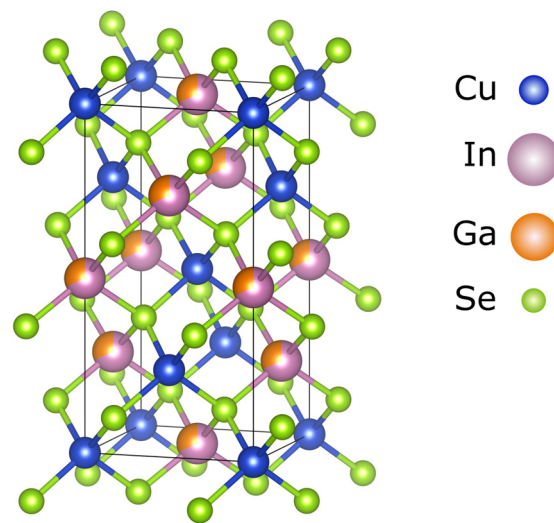


Figure 2. Tetragonal CIGS crystal structure.

Changing the Ga content has been demonstrated to exert a significant influence on the optical characteristics of CIGS. In order to align with the solar spectrum, the band gap can be adjusted, ranging from 1.04 for CIS to 1.7 for CGS [30]. The expression for the band gap as a function of Ga content is formulated as follows [31]:

$$E_g = (1 - x) E_{gCIS} + xE_{gCGS} - bx(1 - x) \quad (1)$$

In the provided equation, x refers to the atomic ratio of Ga/(Ga + In) (GGI) and b denotes the bending coefficient, ranking within the range of 0.15 to 0.24. The optimum band gap was identified to be approximately 1.14 eV [32], with higher absorption necessitating a band gap of 1.4 eV. It has been asserted that achieving high-efficiency CIGS solar cells is attainable with a GGI ratio ranging from 0.25 to 0.30, resulting in a band gap energy ranging from 1.10 eV to 1.20 eV [29,33].

Ga content has been found to impact the electrical characteristics of CIGS as well. The open-circuit voltage (V_{oc}) exhibited a linear increase until it reached a GGI ratio of approximately 0.3, beyond which it declined [32,34]. Given that V_{oc} is proportional to the bandgap [29,35], an increase in the bandgap (E_g) results in a corresponding rise in V_{oc} due to reduced recombination [36]. Conversely, the observed decline in V_{oc} at higher Ga concentrations ($GGI > 0.3$) is often attributed to significant defects associated with elevated Ga content [32,35,37,38]. The rise in Ga concentration is associated with a decrease in grain size, leading to an increase in both grain boundaries and void densities. These factors collectively serve as recombination sites [39]. It has been hypothesized that the escalation of the GGI ratio induces defect states in the mid-gap, functioning as recombination centers [32]. Additionally, the increase in Ga content in CIGS results in a linear decrease in short-circuit current density (J_{sc}) due to a reduction in the absorption coefficient, particularly at longer wavelengths. Consequently, this diminishes the external quantum efficiency (EQE) of solar cells, as illustrated in Figure 3 [29,34–36,40].

Solar conversion efficiency has been demonstrated to increase within a GGI ratio range of 0–0.3, peaking at around 0.3, after which, it starts to decline due to the reduction in external quantum efficiency (EQE). The specific recombination mechanism responsible for the EQE deterioration with a high Ga content remains inconclusive. Some studies attribute this decline to the creation of deep recombination levels within the bulk absorber [37], while others associate it with the presence of defects at the surface of the CIGS layer [25,41].

Additionally, the resistivity of CIGS films was observed to increase with rising Ga content for GGI ratios between 0.3 and 0.6, correlating with a decrease in Hall mobility [31].

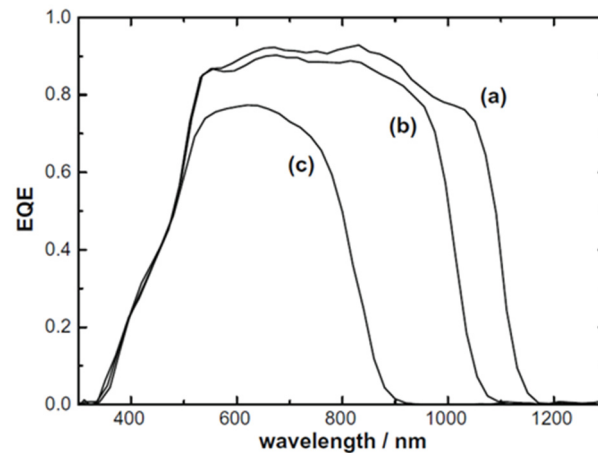


Figure 3. External quantum efficiency of CIGS solar cells with different Ga/(Ga + In) values of (a) 0.18, (b) 0.34, and (c) 0.78 [29] (copyright 2010, Elsevier).

3. Device Architecture of CIGS Solar Cells

Thin film solar cells are constructed by depositing thin layers of various materials on top of each other. Each layer serves a specific function contributing to the overall goal of efficiently absorbing light and effectively extracting free charge carriers. Figure 4 illustrates the typical structure of a CIGS device. The absorber layer plays a crucial role in a solar cell as it absorbs photons to generate electron–hole pairs. Therefore, the bandgap of this layer should be small enough to match the solar spectrum. If the energy gap (E_g) is high, the material becomes transparent to a wide wavelength range of the solar spectrum, whereas a low E_g layer is susceptible to more lattice vibrations due to the thermalization mechanism. The bandgap of CIGS can be adjusted by varying the Ga content, enabling the tuning of E_g to enhance efficiency [40]. Furthermore, a high absorption coefficient is essential to absorb light efficiently on thin layers. In the case of CIGS, a 2 μm thick layer proves sufficient to create solar cells with high efficiencies, owing to an absorption coefficient on the order of 10^5 cm^{-1} . CIGS is classified as a p-type semiconductor with a hole density ranging from 5×10^{15} to $1.47 \times 10^{20} \text{ cm}^{-3}$ [42].

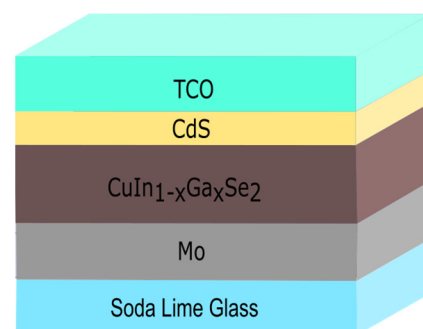


Figure 4. CIGS solar cell structure.

The free charge carriers generated within the absorber layer are directed toward the electrodes using the internal electric field established through the deposition of a buffer layer to form a PN junction. The buffer layer, crucial for this purpose, should exhibit over 80% transparency and possess a wide bandgap. CdS is a commonly employed material as a buffer layer in CIGS-based solar cells, primarily chosen for its high performance in cells with the inclusion of a CdS layer. With a bandgap of 2.4 eV [43], the deposited layer

typically has a thickness of around 50 nm [44]. However, concerns arise with the use of Cd due to its toxicity and optical losses.

The Mo layer serves as a common choice for the back contact in CIGS solar cells due to its low resistivity. Its thermal stability allows Mo to withstand the high processing temperatures of CIGS, which can reach up to 550 °C. Additionally, Mo's high reflectivity causes it to reflect light passing through the absorber layer, minimizing unabsorbed light [45]. The thickness of the Mo layer is optimized to facilitate the penetration of sodium from the glass substrate to the CIGS layer, leveraging the positive effect of Na on the absorber layer [46,47].

The nature of the CIGS/back contact interface is another critical consideration in selecting the back-contact material. Orgassa et al. [48] revealed that Mo remains almost inert during the deposition of CIGS, unlike Cr, Mn, Ti, and V, which react with Se during CIGS deposition. In many studies, MoSe₂ has been identified on the CIGS/Mo interface, with reports indicating that the MoSe₂ layer enhances the ohmic contact between CIGS and Mo [49–52].

A transparent and conducting oxide (TCO) is used as a front electrode to collect charges while facilitating light transmission to the absorber layer. Tin-doped indium oxide (ITO) is the conventional TCO used in thin film solar cells; however, the scarcity of indium and its high demand contribute to price fluctuations. Fluorine-doped tin oxide (FTO) and aluminum-doped zinc oxide (ZnO:Al) emerge as viable alternatives due to their abundance and cost-effectiveness. ZnO:Al has a band gap ranging from 3.36 to 3.45 eV and electric conductivity in the range of $(0.56\text{--}1.64) \times 10^3 \Omega^{-1}\cdot\text{cm}^{-1}$ [53]. An issue arises during annealing treatment, where aluminum diffuses into the CIGS layer through CdS, raising the gap energy of CIGS. To counteract this diffusion, the deposition of i-ZnO is employed as a mask layer.

Glass, polymer, and metal foils are used as substrates for fabricating both rigid and flexible solar cells. The quality of thin films is highly sensitive to the state of the substrate surface, necessitating a thorough cleaning process. The processing temperature must also adhere to the substrate's temperature limits. Soda-lime glass is a widely used substrate due to its chemical inertness, thermal stability, low cost, and the presence of sodium, an element that enhances the electrical properties of CIGS. The production of high-performance solar cells often involves processing CIGS at elevated temperatures (approximately 550 °C). Consequently, sodium diffuses from the substrate to CIGS through the Mo layer, thereby improving the p-type conductivity of the absorber layer.

4. Challenges with the Deposition of CIGS Thin Films Using Solution-Based Processes

Solution processing has the potential to enhance the market share of CIGS solar cells owing to its cost-effectiveness, roll-to-roll manufacturing capability, and high throughput [54]. The development of CIGS films through solution-based processes can be accomplished by either growing CIGS directly onto the substrate surface using techniques such as chemical bath deposition or electrodeposition or by coating the surface using liquid precursors through methods like dip-coating, spin-coating, spray pyrolysis, and screen printing.

The electrodeposition technique has proven to be effective in the fabrication of efficient CIGS-based solar cells [55]. CIGS coatings can be produced by simultaneously electrodepositing the metal elements (one-step) or depositing them sequentially (two- or three-step). Subsequently, the films undergo selenization and/or sulfurization at elevated temperatures to achieve the chalcopyrite structure. Despite the advantages of low investment and operational costs, along with high material utilization, electrodeposition poses challenges in terms of controlling purity, homogeneity, compactness, pinholes, and stoichiometry.

Electrochemistry significantly influences the properties of the deposited film, and the differing standard reduction potentials of the metal elements make precise composition control challenging. The low standard potential of Ga results in the generation of hydrogen gas in the aqueous solution, impeding the deposition of Ga. To address this issue, the

pulse current electrodeposition technique has been employed to reduce the evolution of hydrogen, resulting in a smooth and compact layer with an efficiency of 11.04% [56].

The selenization process following the electrodeposition of CIGS leads to a reduction in the surface gap, primarily caused by the accumulation of Ga near the CIGS/Mo interface, thereby limiting the V_{OC} [54]. To address this, Gao et al. [57] deposited an In_2S_3 layer by spin-coating prior to CdS deposition to increase the surface band gap. Optimizing the thickness of the In_2S_3 layer resulted in a device with a power conversion efficiency (PCE) of 12.88%, while the efficiency of the uncoated CIGS was 10.03%. Additionally, in a recent study, Gao et al. [58] introduced a Cu-rich CIGS layer before depositing the CIGS film. This approach led to higher crystal quality and reduced trap defects, enhancing the generation and transfer of charge carriers, ultimately resulting in a device with an efficiency of 16.05%.

Zhang et al. [59] achieved the fabrication of CIGS solar cells with an efficiency of 17.3% using a spin-coating technique. These devices utilized a Ga notch profile, effectively enhancing the collection of photogenerated charge carriers. Instead of employing conventional sputtered ZnO, ZnO nanoparticles were deposited, leading to improved transmittance of the window layer and enhanced interface quality. It is worth mentioning that this process required 14 deposition cycles with baking at 280–340 °C, followed by an annealing treatment at 500–600 °C.

In the pursuit of highly efficient, solution-based CIGS solar cells, Zhang et al. utilized hydrazine (N_2H_4) and dimethyl sulfoxide (DMSO) as solvents [59]. Hydrazine, despite its advantage of decomposing without leaving impurities, is highly toxic and explosive, prompting ongoing research for nonhydrazine routes [20]. Additionally, metal species such as In^{3+} exhibit low solubility in DMSO, necessitating additional heating [60].

One of the challenges in the production of CIGS films using solution-based processes lies in achieving the growth of a pure and pinhole-free CIGS layer. Numerous sources of impurities, such as solvents and stabilizers, can introduce carbon, oxygen, and nitrogen into the deposited layer. Consequently, the performance of CIGS solar cells can decline due to the deterioration of electrical properties. For example, Ahn et al. [61] utilized ethyl-cellulose as a binder material, which remained as a thick layer between Mo and CIS, leading to an increase in series resistance (Figure 5). Additionally, pinholes can form after the removal of solvents from the coating. Despite the advantages offered by solution-based processing, there still exists a substantial efficiency gap between vacuum and solution-based devices.

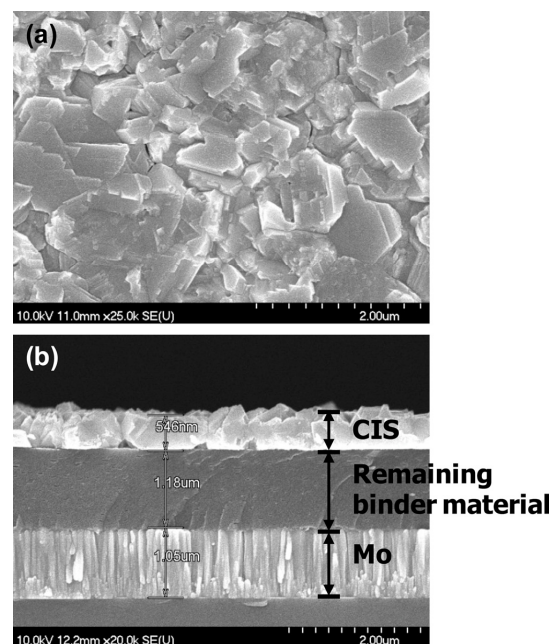


Figure 5. (a) Top view and (b) cross-sectional SEM micrographs of film selenized at 530 °C for 30 min with Se vapor effused at 150 °C [61] (copyright 2010, The American Chemical Society).

5. Physical Vapor Deposition Methods Used for the Preparation of CIGS Thin Films

5.1. Working Principle of the Deposition Techniques

Thermal evaporation is a straightforward process within the physical vapor deposition technique. In this method, a source material is heated until its particles vaporize. The resulting vapor expands in the vacuum chamber and condenses on the substrate, which typically has a lower temperature than the source material. Figure 6 depicts a schematic diagram of a co-evaporation system.

There are two main types of thermal evaporation based on the method used to heat the material for deposition [62]:

- **Resistive Heating:** This method employs a resistively heated source to evaporate the targeted material. The source is typically constructed from refractory metals such as tungsten, molybdenum, and tantalum, which possess high melting points.
- **Electron Beam Evaporation:** In this technique, a material is evaporated by focusing an intense electron beam on it. Electron beam evaporation addresses challenges associated with resistive heating, including contamination and the difficulty of evaporating materials with high melting points.

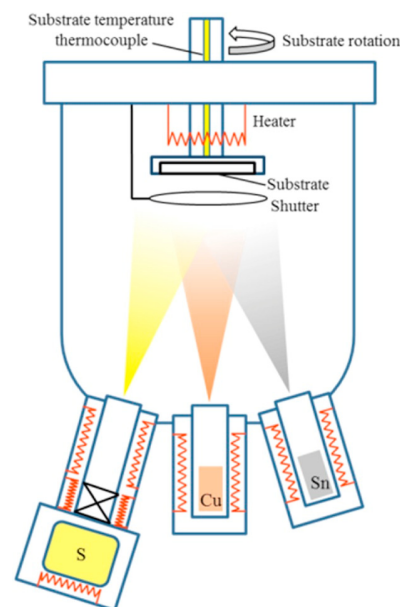


Figure 6. Schematic diagram of a co-evaporation system [63] (copyright 2017, Springer).

Sputtering is a form of physical vapor deposition (PVD) wherein atoms are ejected from a solid material, known as the target, due to momentum transfer from energetic particles, typically argon (Ar) particles. Figure 7 illustrates a schematic diagram of a sputtering deposition system. Aside from its role in depositing material, sputtering is also employed for cleaning the surfaces of solid materials [64].

The sputtering process occurs in three steps:

- An ion, often an argon ion (Ar), accelerates toward a negatively charged target.
- The accelerated ion hits the target material, leading to a series of atomic collisions.
- As a consequence of these collisions, one or more atoms from the target are ejected and become free in the form of ions or neutral particles.

The efficiency of a sputtering process is quantified by the sputtering yield, which is defined as the number of atoms or molecules ejected from a target surface per incident ion. The sputtering yield is influenced by factors such as the masses and atomic numbers of the target and sputtering gas, atomic surface binding energy, and the kinetic energy of the bombarding particles [65].

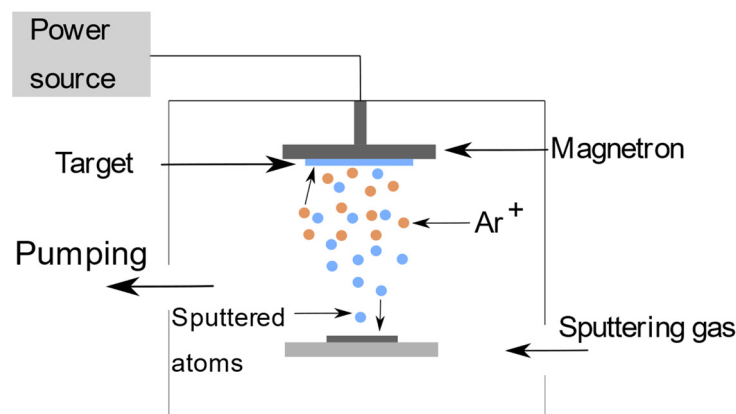


Figure 7. Schematic diagram of sputtering deposition system.

Compound films can be deposited in two different modes. Non-reactive mode involves sputtering a compound target or multiple targets—either compound or elemental—using an inert gas. In this mode, sputtering occurs without the presence of a reactive gas. In reactive mode, sputtering takes place in the presence of a reactive gas along with the inert gas (usually argon, Ar) and a chemical reaction occurs between the target material and the reactive gas. Commonly used reactive gases include oxygen and nitrogen [66].

Despite the numerous advantages of traditional sputtering for thin film synthesis, this process has a few limitations, including low deposition rates, substrate heating, and low ionization efficiency. These drawbacks stem from the fact that secondary electrons emitted during the sputtering process are accelerated far away from the target, as the target is negatively charged. This movement is constrained by a magnetic field that confines electrons in the vicinity of the target. The development of a new process based on the use of a magnetic field addresses these limitations and is known as “magnetron sputtering” [67].

In magnetron sputtering, a magnetic field is generated using permanent magnets. Within the magnetic field lines, electrons move in a spiral pattern. As these electrons move, they collide with argon atoms, generating more ions than in traditional sputtering. This higher ion density leads to an increased deposition rate. Importantly, because the plasma is confined near the target, magnetron sputtering minimizes harm to the substrate and reduces surface heating [66]. The sputtering process can utilize different power sources to ignite plasma. Two common forms include direct current magnetron sputtering (DcMS) and radio frequency magnetron sputtering (RfMS). In DcMS, typically used for the deposition of conductive materials, a continuous current is provided to generate energetic particles that sustain the sputtering process. In RfMS, an alternating current is used to prevent charge accumulation on the target. This power source is versatile and can be applied for both conductive and non-conductive targets [68].

High-power impulse magnetron sputtering (HiPIMS) is another method for powering magnetrons utilizing a very high peak power density (measured in kW/cm²) over a relatively short duration at a low duty cycle (on/off time ratio) [69–72]. The distinctive feature of HiPIMS is its high pulse power, resulting in substantial ionization of the target species. This enhanced ionization contributes to improving the properties of the growing film. It is important to note that despite the same power input, the sputtering rate in HiPIMS is lower compared to DC magnetron sputtering [69–71].

5.2. Deposition of CIGS Films by Thermal Co-Evaporation

CIGS deposition using this process involves the evaporation of separate elemental sources, a method known as the co-evaporation process. The control of elemental fluxes over time enables versatile deposition, and the precise adjustment of these fluxes can result in high-performance devices. Various approaches have been employed in the manufacturing of CIGS coatings using this method. The one-step process involves the simultaneous evaporation of all elements, while in the two and three-step processes, the metal precursors

are deposited in two and three steps, respectively. The three-stage process has proven to be the most successful in producing state-of-the-art devices.

5.2.1. Three-Stage Deposition

Figure 8a shows the profiles of substrate temperature and fluxes of CIGS elements in a standard three-stage process. In the first step, In and Ga are co-evaporated in the presence of Se flux on Mo/glass substrates. Subsequently, Cu and Se are deposited, and, finally, these layers are subjected to a flux of In, Ga, and Se in the third step. The last step is crucial for consuming the excess of Cu_{2-x}Se to prevent a reduction in power conversion efficiency (PCE) due to the high conductivity of Cu-Se phases. Gabor et al. [72] fine-tuned the Se flux in the first step to achieve a composition of $(\text{In}_x, \text{Ga}_{1-x})_2\text{Se}$. This optimization resulted in a PCE of 15.9%, attributed to the reduced roughness of CIGS films and the Ga gradient along the depth (notch structure), leading to lower interface defects. Table 1 summarizes the electrical performance of CIGS solar cells, including the methods used for the elaboration of CIGS films.

Contreras et al. [73] reported the elaboration of an 18.8% efficient device with the $\text{ZnO}/\text{CdS}/\text{Cu}(\text{In}, \text{Ga})\text{Se}_2/\text{Mo}$ structure, achieving a 1.1% increase in efficiency compared to the previous three-stage process [74]. This improvement was primarily attributed to the reduction in the absorbance of the window layer. The presence of a back surface field, arising from the graded Ga profile within the CIGS layer, facilitated longer diffusion of minority carriers, leading to a further increase in short circuit current (I_{sc}). Despite the lower band gap of 1.12 eV compared to the 17.7% efficient device (1.14 eV), the V_{oc} increased from 0.674 V to 0.678 eV, attributed to the reduction of recombination within the space charge region. Repins et al. [75] modified the process by excluding Ga, resulting in an enhanced PCE of 19.9%. The cell exhibited a high fill factor (FF) of 81.2%, attributed to the reduction of charge carrier recombination. The authors proposed that this improvement was due to a reduction of the band gap in a portion of the space charge region (SCR).

It is believed that (220)/(204)-oriented CIGS allows for the production of high-performance devices [73]. Chaisitsak et al. [76] emphasized the importance of controlling the Se/metal flux in the first step to influence the preferred orientation. Crystals with the (220)/(204) orientation are favored at high Se/metal flux, leading to an improved device performance from 15.5% to 17% by shifting the preferential orientation from (112) to (220)/(204). The latter orientation is thought to enhance Cd diffusion, resulting in the formation of a homo-junction. Kim et al. [77] found that CIGS films oriented along the (220)/(240) plane exhibit lower levels of defects compared to (112) oriented samples. However, increasing the substrate temperature from 400 °C to 440 °C induced a change in crystal orientation toward the (112) plane, leading to an enhancement of PCE from 12.1% to 13.6%. This improvement was mainly attributed to the creation of a double-graded band gap. Photon energy mappings of CIGS revealed higher nonradiative recombination centers at the (112)-oriented absorber compared to the (220)/(204)-oriented one [78].

Achieving high crystallinity in CIGS through the three-stage process typically requires elevated temperatures, around 560 °C. Li et al. [79] proposed a modified three-step process with a lower temperature of 470 °C, incorporating an additional Cu-rich phase after the second step, as illustrated in Figure 8. Figure 9 shows the JV curve at different Cu contents. The introduction of an appropriate additional Cu content of 6 at. % improved crystallinity and grain size. It was observed that the preferential orientation of CIGS shifted toward (220)/(204) with the added Cu content, resulting in a 2% increase in efficiency compared to the standard three-stage process [79].

Increasing the deposition rate is one approach to enhancing the throughput of three-stage CIGS solar cells. In a study, the deposition rate was elevated from 35 nm/min to 500 nm/min in the second step, resulting in more compact films with reduced voids [80]. These voids are typically associated with the transformation of Cu-Se phases to CIGS. A deposition rate of 600 nm/min in the third step led to the formation of small grains at the film's surface and altered the Ga grading profile. Despite the high rates in the second

step causing a 10% reduction in efficiency relative to films produced at a deposition rate of 35 nm/min, overall efficiency was maintained [80]. However, high rates in the first and third steps with insufficient Se supply induced blister defects and Cu-rich large-tube-like structures, respectively.

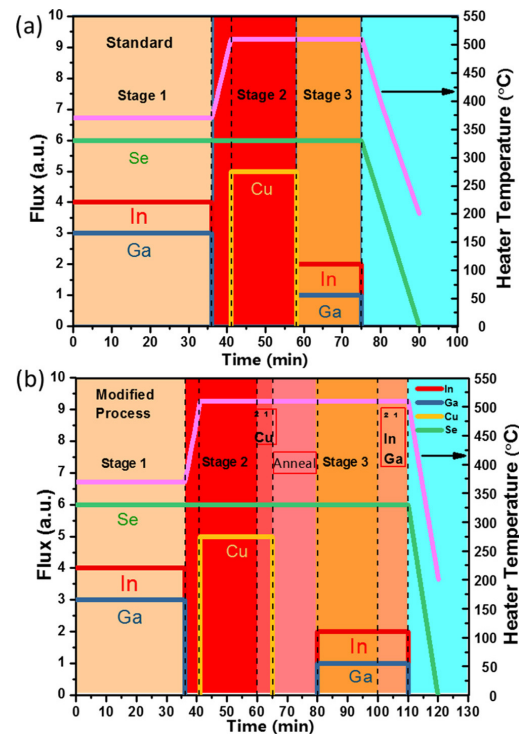


Figure 8. Fluxes and substrate temperatures for Cu, In, Ga, and Se of the (a) standard and (b) modified three-step co-evaporation process for CIGS film deposition [79] (copyright 2020, American Chemical Society).

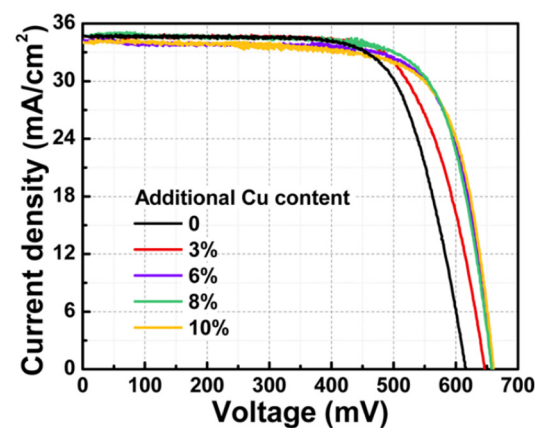


Figure 9. Measured 1 sun device performances of the CIGS solar cells with different additional Cu contents after the second stage of the three-stage co-evaporation process [79] (copyright 2020, American Chemical Society).

In addition to the co-evaporation of CIGS, optimizing the alkali post-deposition treatment (PDT) resulted in a power conversion efficiency (PCE) of 21.7% [81], an improvement of 0.9% compared to a reference device [33], attributed to an increase in short-circuit current density (J_{sc}). External quantum efficiency (EQE) measurements revealed an increase beyond 1000 nm and below 520 nm (Figure 10). The improvement in EQE at short wavelengths was linked to a reduction in CdS thickness, while a modified gallium, indium, and selenium (GGI) factor along the thickness direction contributed to the EQE enhancement in

the infrared region. The deposition process resulted in an effective double-graded band profile characterized by a lower band gap (1.13 eV) and a steep slope near the back contact (Figure 10). The front steep slope did not compromise performance, possibly due to defect passivation via PDT [81]. The introduction of heavier alkali elements such as rubidium (Rb) and cesium (Cs) further improved cell performance beyond 22% [82].

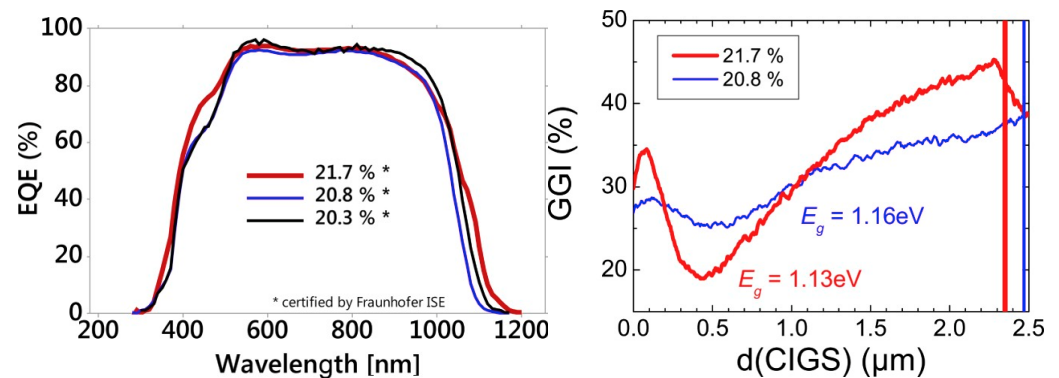


Figure 10. External quantum efficiency (EQE) and GGI grading of the 21.7% and the 20.8% devices [81] (copyright 2015, Wiley-VCH Verlag).

The three-stage process offers flexibility and can be adjusted in various ways to achieve the desired composition and bandgap. However, achieving fine control over the composition is not straightforward and may impact the reproducibility of the process.

5.2.2. Two-Stage Deposition

The incorporation of a Cu-rich step in the co-evaporation process is vital for improving grain growth. This is facilitated by the two-stage process, implemented in three different ways. In one approach, an $(\text{In, Ga})_2\text{Se}_3$ precursor is deposited at a substrate temperature of 350 °C, followed by the supply of Cu and Se elements [83]. In another configuration, Cu, In, Ga, and Se are deposited in the Cu-rich step, after which, the Cu flux is turned off. This configuration is also known as the CURO process [33]. In the Boeing-like process, Cu, In, Ga, and Se are supplied first, followed by a decrease in the Cu flux. This is also referred to as the bi-layer process [84,85]. T. Wada et al. [86] investigated the impact of temperature on CIGS properties. The deposition of the precursor in the first step was carried out at 350 °C, while the temperature of the second step varied in the range of 350–500 °C. The distribution of In and Ga was not uniform across the film, and this non-uniformity became less pronounced as the temperature rose. Films deposited at temperatures over 350 °C exhibited a conversion efficiency of more than 11%, while the film deposited at 350 °C lacked photovoltaic properties due to the formation of a conductive Cu_{2-x}Se layer at the surface. With the increase in the GGI ratio at the surface, the band gap near the PN junction also increased with rising temperature.

In the same study, the team examined the impact of post-annealing on the CIGS absorber layer deposited by the two-step process at various temperatures (room temperature, 100 °C, 200 °C, and 350 °C). The film deposited at room temperature exhibited separated layers of In-Ga-Se and Cu-Se. Interdiffusion between the layers was initiated at 100 °C, and chalcopyrite CIGS formation became evident at 350 °C. After annealing at 530 °C, all deposited films displayed a chalcopyrite CIGS structure without a second phase. However, due to significant volume variation caused by Se re-evaporation, the film deposited at room temperature delaminated during post-annealing. The highest efficiency, approximately 15.5%, was recorded for films deposited at 350 °C. Chia-Hua Huang et al. [87] achieved a lower efficiency of 13.2% using the Boeing-like process, which was also lower than the efficiency achieved in the single-step process investigated in the same study. Despite the larger grain size in the two-step process compared to the single step, the latter resulted in

higher efficiency, indicating that grain size is not the sole factor affecting the efficiency of CIGS solar cells.

5.2.3. Single-Stage Deposition

Single-stage co-evaporation is a process in which the four elemental sources (Cu, In, Ga, and Se) are evaporated simultaneously from evaporation sources. The deposition of CIGS in one step makes it easier to control, faster for deposition, and less costly than the three-step co-evaporation process. Cu-poor CIGS thin films have been successfully synthesized using the single-step co-evaporation method [87–89].

Wang et al. [88] investigated the effect of temperature on the properties of CIGS thin films. The deposited films were 1.5–2 μm thick, with CGI and GGI ratios of 0.85 and 0.3, respectively. The structural and electrical properties were studied in the temperature range of 350–550 °C. The CIGS films were (112)-oriented when the temperature was below 400 °C, while they became randomly oriented above this value. For thin films produced at temperatures less than 450 °C, an (In, Ga)₂Se₃ phase was observed. Above this temperature, the second phase disappeared.

Jia-wei et al. [89] and Huang et al. [87] studied CIGS thin films deposited at 490 °C and 570 °C, respectively. In both studies, XRD analysis revealed the absence of any secondary phase, confirming the claim of Wang et al. [88] that at temperatures below 450 °C, the reaction of Cu, In, Ga, and Se is not complete due to low thermal energy. The temperature of 450 °C was found to be the threshold for grain size variation. At $T < 450$ °C, the grain size remained the same (<1 μm), and when the temperature exceeded this threshold, the grain size increased.

The surface morphology observed in ref. [89] showed triangular grains with some voids. The same microstructure was found by Wang et al. [88] at low temperatures. As the temperature increased, the microstructure became compact and dense [87,88]. The presence of an (In,Ga)₂Se₃ phase at low temperatures resulted in high resistivity and low carrier concentration. The increase in temperature led to a complete reaction between Cu, In, Ga, and Se elements and thus improved the electrical properties. The highest conversion efficiency in the range of the temperatures studied of 12.1% was achieved at 550 °C [88]. At 570 °C, Huang et al. [87] reported an efficiency of 14.4%.

5.3. Deposition of CIGS Films by Sputtering Methods

Magnetron sputtering has gained significant attention for depositing CIGS thin films using vacuum methods. This technique offers several advantages, including high deposition rate, control of composition and crystallinity, and enhanced adhesion [44]. These advantages make magnetron sputtering a promising technique for the production of CIGS thin films in the context of solar cell applications. Moreover, the technique offers scalability for cost-effective large-scale manufacturing compared to the three-step co-evaporation process [90]. Direct current magnetron sputtering (DcMS), pulsed DcMS, radio frequency magnetron sputtering (RFMS), and HiPIMS techniques were used for the deposition of CIGS. These films were deposited using a non-reactive quaternary target [83] or in reactive mode using a sputtered CuInGa target and evaporated H₂S [90] or Se reactive gases [85].

5.3.1. Two-Step Deposition

Figure 11 illustrates the steps involved in the two-step deposition process for CIGS films. This sequential deposition approach entails initially depositing the metal elements, followed by the selenization process to generate the CIGS film. Sung et al. [91] implemented this method by sputtering Cu_{0.8}Ga_{0.2} and In targets to deposit a CuGa/In/Se stack in the first step, subsequently evaporating a Se target in the second step. Subsequently, annealing was carried out at varying temperatures without the presence of any Se gas precursor. Films formed at temperatures below 510 °C exhibited multiple phases, such as Cu₁₁In₉, Cu₂Se, and In₂Se₃, with Ga-rich small grains near the substrate surface due to the low

diffusivity of Ga. The achievement of a single chalcopyrite phase with uniform growth was realized through selenization at temperatures exceeding 510 °C.

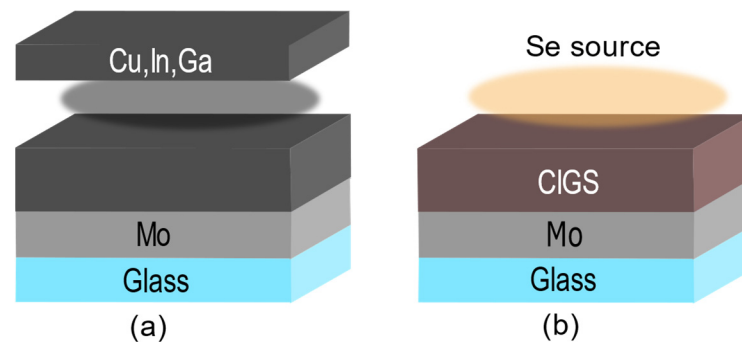


Figure 11. Steps of the sequential deposition process of CIGS, (a) the sputtering of the metal elements, and (b) the selenization step using a Se vapor or H_2Se gas.

Liang et al. [92] deposited the metal elements in the order of In/Cu/CuGa, utilizing DcMS and pulsed DcMS to sputter In and Cu/CuGa targets, respectively. The selenization step was carried out in the presence of H_2Se gas. Suppressing Ga agglomeration near the back contact was achieved by elevating the selenization temperature from 450 °C to 575 °C, resulting in a V_{oc} increase of 0.079 V, as shown in Figure 12, attributed to the blue shift of the band gap. Additionally, enhanced crystallinity and larger grains at higher temperatures, as depicted in Figure 13, increased shunt resistance, ultimately yielding a solar device with an efficiency of 15.09%.

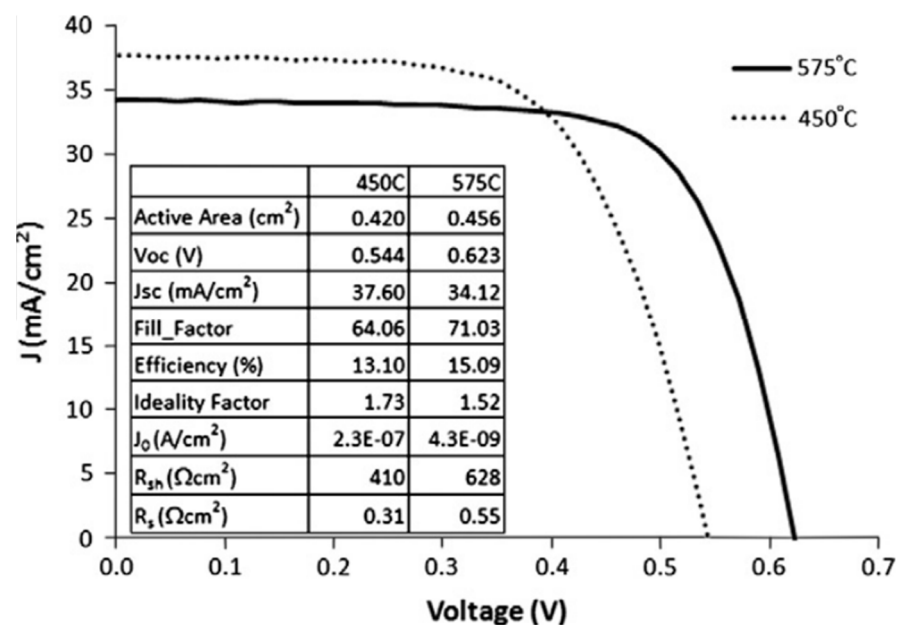


Figure 12. Results on a device with the best performance for $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ ($x = 0.3$) selenized at 450 °C and 575 °C [92] (copyright 2012, Elsevier Ltd.).

Huang et al. [87] initiated the deposition process by sequentially depositing CuGa and In. In the second step, they conducted selenization using various Se vapor flow rates. Films deposited under a high flow rate of Se exhibited improved surface morphology with denser grains. Olejníček et al. [93] observed that the HiPIMS process had minimal impact on CIGS properties, while the selenization atmosphere played a more significant role. Initially, an 800 nm layer of CIG alloy was deposited from a ternary target with the composition $\text{Cu}_{0.45}\text{In}_{0.4}\text{Ga}_{0.15}$. Subsequently, selenization was carried out under vacuum or Ar, employing different profile temperatures to achieve a 2 μm thick CIGS layer. The Ga substitution

level was found to decrease during selenization under vacuum, suggesting that if CIS and CGS phases are formed separately, the interdiffusion between the two phases is low due to the lower temperature (500 °C) reached and the loss of excess Se when evaporated under vacuum at high temperatures. Su et al. [94] fabricated CIG films using a ternary target at various power densities and then transformed them into CIGS by selenization of the metallic precursors using Se vapor. They noted that the surface roughness of CIGS depended on the roughness of the initially deposited CIG films. Achieving a flat and dense CIGS film was possible by reducing the power density to 0.2 W/cm².

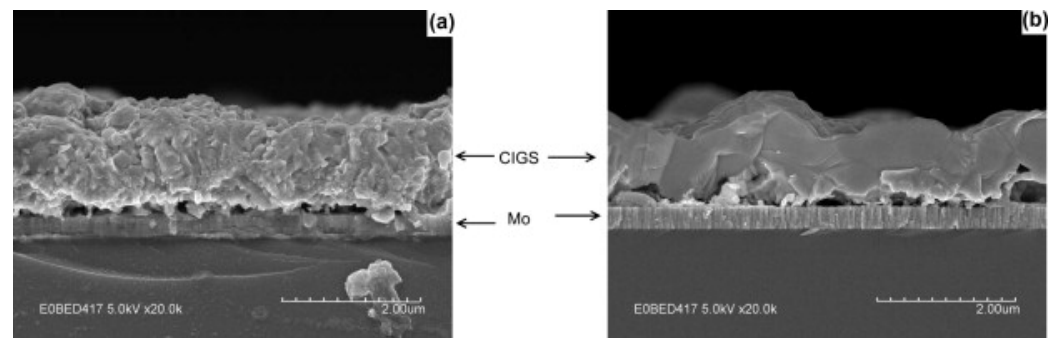


Figure 13. Cross-section SEM of CIGS films selenized at (a) 450 °C and (b) 575 °C [92] (copyright 2012, Elsevier Ltd.).

Sputtering from separate targets resulted in CIGS films with rough surfaces, especially when depositing In-rich or Cu-rich phases [95]. The deposition of In on CuGa led to In agglomeration, resulting in rough surfaces [92]. However, when utilizing a quaternary CIGS target for sputtering and subsequently performing selenization through a two-step temperature process, a high-quality CIGS layer was produced, leading to a photovoltaic conversion efficiency of 7.95% [96].

Sulfurization following the selenization process has been employed to form Cu(In,Ga)(Se,S)₂ after sputtering the CIG film. The introduction of sulfur serves to increase the bandgap energy. The motivation for sulfurization lies in enhancing the bandgap near the buffer layer [97]. In contrast to Ga, which affects the conduction band, sulfur acts on both bands, enabling the tuning of the bandgap profile. A front surface rich in sulfur in CIGSSe reduces the valence band edge, impeding the diffusion of holes toward the buffer layer. Meanwhile, the back surface, being Ga-rich, elevates the conduction band edge, preventing the diffusion of electrons toward the rear contact. By employing this approach, along with a high-transparency TCO, a broader notch within the graded bandgap, and potassium (K) treatment, an enhanced efficiency of 22.3% was achieved, which was attributed to the increased capture and absorption of infrared (IR) radiation.

5.3.2. Single-Step Deposition

The one-step process is a straightforward method involving the deposition of CIGS using a single quaternary target, as seen in Figure 14, eliminating the need for additional selenization. Consequently, the use of the toxic H₂Se gas for selenization at higher temperatures can be circumvented. This process provides the simplest means of controlling the composition of the deposited film by adjusting the composition of the target. In a study by Chen et al. [98], the target composition was modified to be Se-rich (52.92 at. %) to address the issue of Se vacancies in the deposited film, resulting in an enhanced PCE of 10.14%. The accumulation of Ga near the Mo rear contact was a common occurrence after selenization [99]. This Ga buildup often led to a decrease in V_{oc} due to the formation of a Ga-deficient region near the CdS/CIGS interface. The use of a quaternary target was employed to mitigate this issue [100].

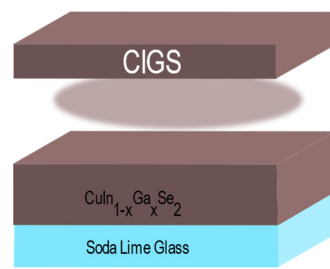


Figure 14. One-step sputtering of CIGS films using a quaternary target.

The morphology of as-deposited one-step CIGS layers reveals fine grain sizes with low crystallinity. An annealing step is essential to enhance the properties of CIGS films. In a study by Shi et al. [96], a two-step annealing treatment in a Se atmosphere was employed for the one-step RFMS-deposited CIGS. The deposition at room temperature resulted in the presence of InSe and Cu-rich phases (Cu_2Se , Cu_3Se_2). However, after annealing treatments at 230 °C and then 500 °C, only the CIGS phase remained [96]. An increase in annealing temperatures from 525 to 550 °C led to a reduction in Se content from 50.6% to 50.2%, causing a significant decrease in J_{sc} (Figure 15) due to the recombination of charge carriers at the Se vacancies [101]. The presence of these vacancies was confirmed by the observation of a photoluminescence peak at 1.05 eV when the annealing temperature exceeded 525 °C (Figure 16).

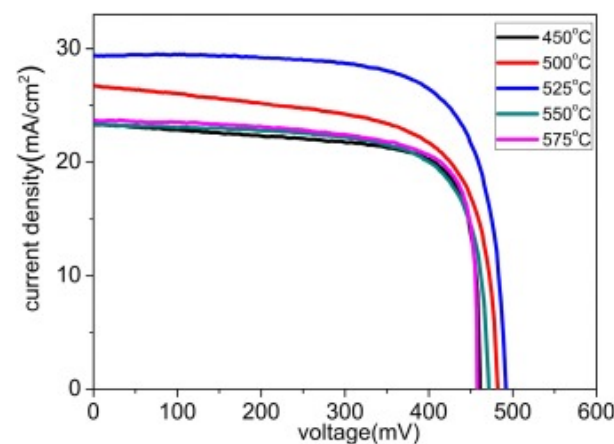


Figure 15. Current–voltage curves of CIGS solar cells with absorbers annealed at different temperatures [101] (copyright 2017, Elsevier).

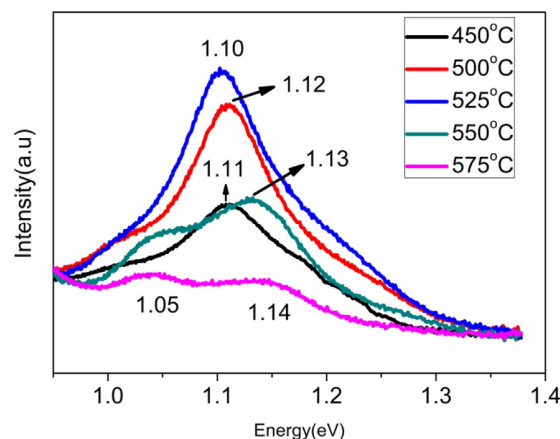


Figure 16. Photoluminescence of CIGS solar cells with absorbers annealed at different temperatures [101] (copyright 2017, Elsevier BV).

Ouyang et al. [102] explored a wide range of annealing temperatures in a Se-containing atmosphere. The CuSe phase disappeared at temperatures exceeding 270 °C, while the Cu_{2-x}Se₂ and ordered vacancy compound (OVC) phases were consumed by the recrystallization of CIGS at temperatures above 410 °C. The films deposited at 550 °C exhibited a compact and homogeneous structure, resulting in a device with an efficiency of 13.5%. The formation of the ordered vacancy compound (OVC) layer at the CIGS/CdS interface reduced the interface recombination of charge carriers due to its wide bandgap. Consequently, an efficiency of 16.7% was achieved with a 1.4 µm thick CIGS layer deposited by DcMS from a quaternary target, followed by annealing at 550 °C under an Ar + H₂Se atmosphere [100]. The annealing atmosphere of CIGS deposited from a quaternary target influences the quality of the layer. Liu et al. [103] reported a decrease in Se content in the CIGS layer when annealing was performed under vacuum. Annealing in a Se atmosphere is crucial to compensate for Se loss.

Halbe et al. [104] made the first attempt to use HiPIMS for the production of CIGS thin films. The CIGS layer was deposited by sputtering a CIG alloy using a compound target in the presence of Se vapor at 560 °C. The 1 µm thick CIGS film elaborated by HiPIMS resulted in a device efficiency of 11.2%, while the PCE measured for the DcMS deposited CIGS was 10.2%. The high efficiency observed with HiPIMS was attributed to the large grain size along the thickness direction and the high density of the film. Further improvement to 13.1% was achieved by decreasing the grain size through the control of the CIG/Se deposition rate ratio, leading to a substantial increase in shunt resistance.

In our prior work, CIGS thin films were deposited using both DcMS and HiPIMS methods from a single quaternary CIGS target [105]. The resulting films exhibited a CIGS chalcopyrite phase with enhanced crystallinity as sputtering power increased. Notably, the chemical composition of the deposited films deviated from the target composition; HiPIMS-deposited films were relatively richer in Se but deficient in In, Cu, and Ga. This was attributed to the back-attraction effect on sputtered ions. The CIGS films deposited by DcMS were Se-poor and Cu-rich, while HiPIMS samples were Se-rich and Cu-poor, suggesting the potential of HiPIMS to produce CIGS films for photovoltaic application [105].

Table 1. Photovoltaic parameters of CIGS solar cells.

Device Structure	Deposition of CIGS	PCE (%)	FF (%)	Voc (mV)	Jsc (mA/cm ²)	Device Area (cm ²)	Ref.
MgF ₂ /ZnO/CdS/CIGS/Mo		20.8	79.1	757	34.8	0.5	[33]
ZnO/CdS/CIGS/Mo	Pulse current electrodeposition	11.04	63.40	505	34.47	0.34	[56]
MgF ₂ /ZnO/CdS/CIGS/Mo		15.9	76.6	649	31.88	0.437	[72]
MgF ₂ /ZnO/CdS/Cu(In,Ga)Se ₂ /Mo	Three-stage	18.8	78.6	678	35.2		[73]
MgF ₂ /ZnO/CdS/Cu(In,Ga)Se ₂ /CuGaSe ₂ /Mo	Two-stage	17.7	77.2	674	34.0	0.414	[74]
MgF ₂ /ZnO/CdS/Cu(In,Ga)Se ₂ /Mo		19.9	81.2	690	35.5	0.419	[75]
ZnO/CdS/CIGS/Mo		17.6	0.79	671	33.20		[76]
ITO/ZnO/CdS/CIGS/Mo/PI		13.6	67.23	620	32.75	0.5	[78]
ZnO/CdS/CIGS/Mo		16.9	74.3	658	34.6	0.5	[79]
MgF ₂ /ZnO/CdS/CIGS/Mo	Multi-stage	21.7	79.3	746	36.6		[81]
MgF ₂ /ZnO/CdS/CIGS/Mo		22.6	80.6	741	37.8	0.5	[82]
ZnO/CdS/CIGS/Mo		10.14	63.0	505	32.3	0.4	[98]
MgF ₂ /ZnO/CdS/CIGS/Mo	One-step	16.7	70.6	614	38.6	0.86	[100]
ZnO/CdS/CIGS/Mo	Two-step	13.5	70	530	36.5	0.86	[102]
ZnO/CdS/CIGS/Mo		10.2	67.0	533	28.0	0.43	[104]
		11.2	67.9	520	31.0	0.43	
		13.1	69.9	563	33.0		

6. Current Status, Challenges, and Future Prospects

CIGS thin film solar cells outperform commercial solar cells, mainly traditional silicon wafer solar cells, due to the numerous advantages. These include comparable efficiency, light weightiness, suitability for curved surfaces, tunable properties through composition adjustments, lower environmental impact, and cost-effectiveness due to the usage of less material. Despite the numerous benefits mentioned, this technology has some limitations, such as its reliance on indium, a rare metal that can potentially increase production costs; moisture damage when used in humid environments, necessitating adequate protection; and a decrease in cell efficiency when transitioning from lab-scale to large-scale production. Hence, the choice of deposition process is critical in resolving some of these difficulties, particularly the loss in efficiency.

The exploration of non-vacuum processes for the synthesis of CIGS solar cells has garnered considerable attention, primarily due to their potential for low production costs and efficient material utilization, resulting in less material wastage compared to vacuum processes. Additionally, these methods are well-suited to applications on flexible substrates in low-temperature conditions. However, the application of solution-based methods for CIGS production at lower temperatures has been associated with challenges, leading to the development of solar cells with lower efficiency [106]. Issues such as the use of toxic solutions, poor adhesion, non-uniform film deposition, and the incorporation of impurities contribute to the lower conversion efficiency of CIGS solar cells produced via wet methods when compared to vacuum processes [106]. Despite these challenges, the exploration of non-vacuum methods continues to be a focal point for researchers seeking cost-effective and flexible approaches to CIGS solar cell synthesis.

CIGS thin films deposited using vacuum techniques demonstrate better quality due to more favorable synthesis conditions, enabling the growth of pure and homogeneous thin films. Sputtering techniques, in particular, have contributed to further enhancing CIGS efficiency. The ability to control the final properties of the films makes sputtering suitable for large-scale deposition. Achieving higher film purity is possible by working at very low base pressures and utilizing high-purity targets. The deposition parameters, including sputtering power, working pressure, and bias voltage, can be adjusted to control grain size, crystallinity, and surface roughness. High-power impulse magnetron sputtering (HiPIMS) stands out as a promising technique for CIGS deposition, resulting in dense, large-grained, and smooth thin films [107]. These features are crucial for the development of efficient solar cells. CIGS thin films obtained using HiPIMS have demonstrated higher efficiency compared to those produced by direct current magnetron sputtering (DCMS), primarily due to improved morphology [104]. Moreover, HiPIMS is suitable for CIGS deposition on flexible substrates as it produces high-energy species that contribute to improved properties without the need for high-temperature conditions.

Even though vacuum techniques offer numerous advantages for CIGS synthesis, they are not without limitations. One significant drawback is the high cost of equipment and increased energy consumption associated with operating under vacuum conditions, leading to higher production costs compared to solution processes [108]. Additionally, the slow processing speed, particularly in large-scale applications, is a challenge when using vacuum conditions. The low deposition rate in techniques like HiPIMS further contributes to the overall limitation of the process [109]. The line-of-sight nature of physical vapor deposition (PVD) processes poses a challenge in achieving very uniform coatings, a crucial requirement for CIGS thin films. This challenge can be addressed by implementing a moving substrate in front of a fixed target.

It is essential to note that while CIGS properties play a significant role in determining solar cell efficiency, other factors such as substrate type and the properties of all other layers in the solar cell must be carefully considered for overall improved efficiency.

- Various types of substrates have been employed for CIGS solar cells, each offering distinct advantages. Soda–lime glass (SLG) stands out as the most commonly used substrate due to its alkali diffusion properties and suitability for relatively high-

temperature CIGS solar cell production [110]. Flexible substrates have also gained attention, offering the advantage of the low-temperature deposition of CIGS thin films. Polyimide substrates, for example, have achieved an efficiency of 18.7% [111]. In cases where high-temperature processing is required, ceramics can serve as flexible substrates, providing an alternative to rigid SLG [110].

- The Mo thin film has demonstrated its effectiveness as a suitable back contact for CIGS solar cells. However, the challenge lies in simultaneously achieving both good adhesion and low resistivity in this material [111]. To address this, a bilayer approach is often employed instead of a single layer. The first layer is designed for high adhesion, while the second layer serves as a low-resistivity thin film [112]. The selenization process, leading to the formation of a MoSe₂ layer, has been found to enhance the adhesion of the CIGS thin film on Mo, preventing interface recombination [113]. The thickness of the MoSe₂ layer is a crucial factor influencing its impact on the Mo/CIGS interface properties [50], although controlling its thickness during the selenization step can be challenging [110]. To address this, an alternative approach is to deposit all cell layers using sputtering with an interlayer of MoSe₂, providing greater control over the process.
- The most commonly used buffer layer for CIGS solar cells is CdS. However, CdS has a relatively low band gap of about 2.4 eV, which can result in the absorption of light, particularly in short wavelengths [114]. To address this issue and replace the toxic cadmium with more environmentally friendly elements, various alternatives have been explored. These alternatives include ZnO [115], ZnSe [116], Zn(O,S) [117], ZnMgO [118], ZnSnO [119], and In₂S₃ [120].
- Indium scarcity and high demand might contribute to an increase in the cost of CIGS solar cells. CZTS-based solar cells were developed to substitute Zn for In; however, their power conversion efficiencies are still very low to compete with CIGS counterparts. The substitution of more In for Ga is another way to reduce In usage, which also comes with the advantage of a larger band gap, allowing its use as a top cell in tandem devices. An alternative approach consists of reducing the thickness of the absorber layer so that it is lower than 400 nm [121]. Recent numerical models predict the possibility of reaching efficiencies as high as 21% for these ultra-thin solar cells [122]. This would reduce the material use and increase the production throughput.
- The “tandem solar cell” approach involves combining two or more junctions in a solar cell. In this configuration, the top junction is designed to absorb high-energy photons, while the bottom junction is responsible for absorbing low-energy photons [123]. One promising tandem solar cell configuration is the perovskite/CIGS tandem solar cell, which has demonstrated an efficiency exceeding 24% according to the National Renewable Energy Laboratory (NREL). This tandem configuration leverages the strengths of both perovskite and CIGS materials to enhance overall solar cell performance.

7. Conclusions

In this review, we delved into the characteristics of CIGS thin films, the various fabrication processes, and the performance of CIGS-based solar cells. A detailed comparison was drawn between different physical vapor deposition techniques, specifically, evaporation and magnetron sputtering. This review explored the impact of fabrication methods and deposition conditions on the properties of CIGS films. Solar cells produced through the three-step process showcased impressive performance; however, challenges persist in scaling up this intricate process.

While solution-based processes have shown promise, they often result in lower-quality CIGS films, prompting the need for further research into non-toxic preparation routes. Magnetron sputtering techniques, with their higher deposition rates and superior uniformity across large surfaces, offer a compelling alternative. The potential simplicity, compositional control, and safety benefits of one-step sputtering make it an intriguing approach. However, it is worth noting that the efficiencies of devices fabricated using one-step sputtered

CIGS are currently lower compared to those fabricated using evaporation and two-step sputtering techniques. Although CIGS has been successfully deposited using direct current magnetron sputtering (DcMS) and radio frequency magnetron sputtering (RfMS), research on one-step sputtering employing high-power impulse magnetron sputtering (HiPIMS) is an area that warrants further exploration.

The use of one-step sputtering (HiPIMS) is intended to overcome the impurity and uniformity issues. Furthermore, the dense and compact microstructure provided by the high-energy species makes this technique promising, offering the potential to increase durability and cell efficiency. Tandem solar cells can also increase efficiency. Therefore, future research must focus on determining the ideal combination for CIGS solar cells to reach maximum efficiency while reducing total manufacturing costs.

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