

## Review Article

# Progress in Polycrystalline Thin-Film Cu(In,Ga)Se<sub>2</sub> Solar Cells

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Received 7 January 2010; Revised 21 May 2010; Accepted 30 June 2010

Academic Editor: Gaetano Di Marco

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For some time, the chalcopyrite semiconductor CuInSe<sub>2</sub> and its alloy with Ga and/or S [Cu(InGa)Se<sub>2</sub> or Cu(InGa)(Se,S)<sub>2</sub>], commonly referred as CIGS, have been leading thin-film material candidates for incorporation in high-efficiency photovoltaic devices. CuInSe<sub>2</sub>-based solar cells have shown long-term stability and the highest conversion efficiencies among all thin-film solar cells, reaching 20%. A variety of methods have been reported to prepare CIGS thin film. Efficiency of solar cells depends upon the various deposition methods as they control optoelectronic properties of the layers and interfaces. CIGS thin film grown on glass or flexible (metal foil, polyimide) substrates require p-type absorber layers of optimum optoelectronic properties and n-type wideband gap partner layers to form the p-n junction. Transparent conducting oxide and specific metal layers are used for front and back contacts. Progress made in the field of CIGS solar cell in recent years has been reviewed.

## 1. Introduction

Current trends suggest solar energy will play an important role in future energy production [1]. Silicon has been and remains the traditional solar cell material of choice. Although silicon is a highly abundant material, it requires an energy intensive process to purify and crystallize. Furthermore, installations of silicon cells require heavy glass protection plates, which reduce residential applications [2].

Recently, commercial interest is beginning to shift towards thin-film cells [3]. Material, manufacturing time, and weight savings are driving the increase in thin-film cells. Cu(In,Ga)Se<sub>2</sub> (CIGS) is one of the most promising semiconductors for the absorber-layer of thin-film solar cells [4]. The conversion efficiency of such cells on glass substrates is approaching 20% [5]. Chalcopyrite-based solar modules are uniquely combining advantages of thin-film technology with the efficiency and stability of conventional crystalline silicon cells. Copper indium gallium selenide (CIGS) solar cells have the highest production among thin film technologies. Advances in preparation and efficiency have allowed these cells to be produced rapidly and are approaching market values for carbon-based energy production [6].

The first report on chalcopyrite-based solar cell was published in 1974 [7]. The cell was prepared from a p-type CuInSe<sub>2</sub> (CISe) single crystal onto which a CdS film was evaporated in vacuum. This combination of a p-type chalcopyrite absorber and a wide-gap n-type window layer still is the basic concept upon which current cell designs are based. The typical design, first described in 1985 [8] is shown in Figure 1 and a typical cross-section CIGS device structure is shown in Figure 2. The CuInSe<sub>2</sub> crystal was replaced by a polycrystalline thin film of the more general composition Cu(In,Ga)(S,Se)<sub>2</sub>.

Many groups across the world have developed CIGS solar cells with efficiencies in the range of 15–19%, depending on different growth procedures. Glass is the most commonly used substrate, but now efforts are being made to develop flexible solar cells on polyimide [9–17] and metal foils [2, 18–29]. Highest efficiencies of 14.1% and 17.6% have been reported for CIGS cells on polyimide [30] and metal foils [31], respectively. Recently a slight increase in efficiency of 14.7% and 17.7% has been reported for CIGS cells on polyimide and metal foils [32], respectively.

CIGS solar cells also attract considerable interest for space applications due to their two main advantages. It offers

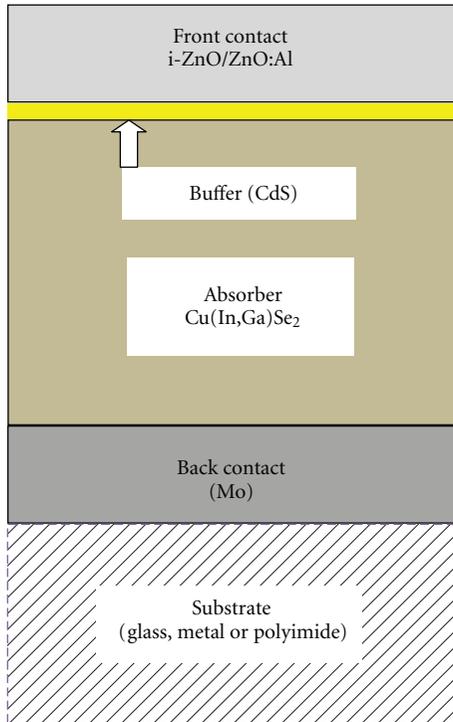


FIGURE 1: Schematic cross-section of a chalcopyrite-based thin-film solar cell. Typical materials for the individual parts of the cell are given in brackets.

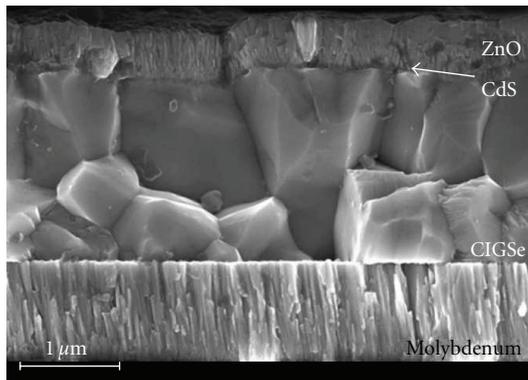


FIGURE 2: Scanning electron micrograph of the cross-section of a typical chalcopyrite solar cell with  $\text{Cu(In,Ga)Se}_2$  (CIGSe) absorber (substrate now shown). Taken from [34].

specific power up to 919 W/Kg, the highest for any solar cell [23]. CIGS cells are also superior to GaAs cells in radiation hardness [33]. Moreover, the flexibility of these cells allows for novel storage and deployment options [23].

There are several reviews available dealing with different aspects of CIGS solar cells [35–39]. The emphasis of the present paper is placed on the progress made in different aspects of CIGS solar cells in the recent times.

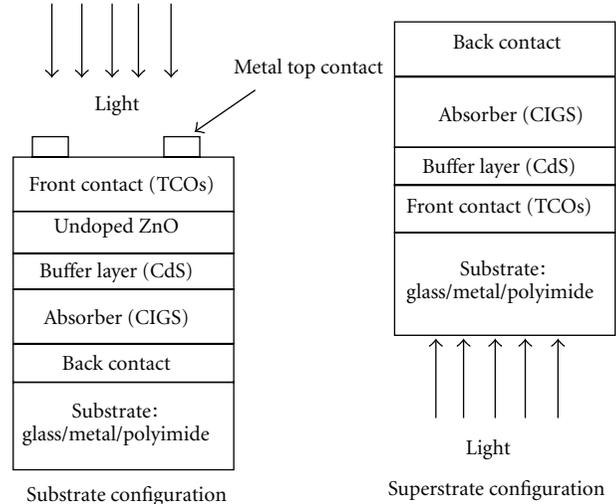


FIGURE 3: Schematic cross-section of “substrate” and “superstrate” configuration of CIGS solar cell.

## 2. CIGS Cell Configuration

The Cu-chalcopyrites exhibit the highest efficiencies among the thin-film solar cells with a record lab-scale efficiency reaching nearly 20% [5]. Most commonly CIGS solar cells are grown in substrate configuration (see Figure 3). This configuration gives the highest efficiency owing to favourable process conditions and material compatibility. Cell preparation starts with the deposition of back contact, usually Mo, on glass, followed by the p-type CIGS absorber, CdS or other weakly n-type buffer layer, undoped ZnO, n-type transparent conductor (usually doped ZnO or  $\text{In}_2\text{O}_3$ ), metal grid, and antireflection coating. It requires an additional encapsulation layer and/or glass to protect the cell surface.

The structure of a CIGS solar cell is quite complex because it contains several compounds as stacked films that may react with each other. Fortunately, all detrimental interface reactions are either thermodynamically or kinetically inhibited at ambient temperature [40]. The cover glass used in substrate configuration is not required for the cells grown in the superstrate configuration (see Figure 3). CIS-based superstrate solar cells were investigated by Duchemin et al. [41] using spray pyrolysis deposition, but efficiencies did not exceed 5%. The main reason for this low efficiency in CdS/CIGS superstrate cells is the undesirable interdiffusion of Cd into CIS (or CIGS) during the elevated temperatures required for absorber deposition on CdS buffer layers [42]. To overcome this problem of interdiffusion more stable buffer materials and low-temperature deposition processes such as electrodeposition (ED), low-substrate temperature coevaporation and screen printing were investigated. Nakada and Mise [43] achieved a breakthrough by replacing CdS with undoped ZnO and coevaporating  $\text{Na}_x\text{Se}$  during CIGS deposition. With the additional introduction of composition grading in absorber layer, 12.8% efficiency cells were developed [43].

TABLE 1: Superstrate Cells.

Efficiency	TCO	Buffer	Absorber	Reference
( $V_{oc} > 800$ mV) 3%	ZnO	None	CuGaSe <sub>2</sub>	Klenk et al. [48]
2.8%	ITO	In <sub>2</sub> Se <sub>3</sub>	CuInSe <sub>2</sub>	Kampmann [49]
6.6%	ITO	CdS	CuInSe <sub>2</sub>	Yoshida and Birkmire [50]
6.7%	ZnO	CdS	CuInSe <sub>2</sub>	Negami et al. [51]
8.1%	ZnO	CdS	CuInSe <sub>2</sub>	Nakada et al [52]
11.2%	ZnO	None	Cu(In,Ga)Se <sub>2</sub>	Haug et al. [47]
12.8%	ZnO	None	Cu(In,Ga)Se <sub>2</sub>	Nakada and Mise [43]

This coevaporation of Na<sub>x</sub>Se for incorporation of sodium in CIGS is essential for high-efficiency cells, as the ZnO front contact acts as diffusion barrier for Na from the glass substrate and leads to a low net carrier density in CIGS and cells with low open-circuit voltage ( $V_{OC}$ ) and fill factor (FF) [44]. (*The influence of Na on CIGS optoelectronic properties is discussed in Section 6*) Investigations of the interface between the ZnO buffer layer and CIGS revealed the presence of a thin layer of Ga<sub>2</sub>O<sub>3</sub> which acts as barrier against photocurrent transport [43, 45, 46]. However, Na-free superstrate solar cells with efficiencies up to 11.2% was obtained, but a strong light-soaking treatment was necessary [47].

Preparing a blocking contact in superstrate structure has been difficult. Only small-area cells have been demonstrated so far and even those show limited performance (see Table 1). It is interesting to note that approaches not using buffer layers have resulted in higher efficiency than those using CdS buffers prepared by various methods.

Another interesting application for superstrate solar cells are tandem solar cells. These solar cells employ two separate solar cell structures for a more efficient conversion of the illumination. Superstrate solar cells are then required as top cell for the short wavelength part of the solar irradiation. Tandem solar cell will not be the part of present discussion. The details can be referred to in the following articles [53–56].

### 3. Back Contact

Molybdenum (Mo) is the most common metal used as a back contact for CIGS solar cells. Several metals, Pt, Au, Ag, Cu, and Mo, have been investigated for using as an electrical contact of CIS- and CIGS-based solar cells [57–59]. Mo emerged as the dominant choice for back contact due to its relative stability at the processing temperature, resistance to alloying with Cu and In, and its low contact resistance to CIGS. The typical value of resistivity of Mo is nearly  $5 \times 10^{-5} \Omega \text{ cm}$  or less. The preferred contact resistivity value is  $\leq 0.3 \Omega \text{ cm}$ . Results have been reported in several papers [57, 60, 61] concerning the influence of the mechanical and electrical properties of the Mo films on the performance of the photovoltaic devices. Molybdenum is typically deposited by e-gun evaporation [61, 62] or sputtering [63–65] on soda-lime glass which ideally provides

an inexpensive, inert, and mechanical durable substrate at temperatures below 500–600°C. Intrinsic stresses in molybdenum films depend on the experimental deposition parameters [61–66], inducing significant changes in the structural and electrical properties. Films with compressive stresses have near bulk like values of the electrical resistivity and a dense microstructure, but films under tensile stresses exhibit altered physical properties and a more open porous structure [61–64]. Gross stress may be determined by visual inspection in that highly compressed films tend to buckle up, frequently in zigzag patterns, whereas films under extreme tensile stress develop a system of stress lines that look scratches. Orgassa et al. [67] fabricated CIGS solar cells with different back-contact materials, emphasizing the role of the back contact as an optical reflector. Early results by Russell et al. [68] and Jaegaermann et al. [69] suggested that Mo back contacts for CIS form a Schottky-type barrier with a barrier height of 0.8 eV for the intimate p-doped CIS/Mo contact. The work of Shafarman et al. [70], who analyzed the Mo/CIS interface separately from the cell, shows the contact to be ohmic.

The influence of MoSe<sub>2</sub> on the ohmic contact behaviour at the CIGS/Mo interface makes MoSe<sub>2</sub> formation an important issue. Fundamental work by Raud and Nicolet [71] on Mo/Se, Mo/In, and Mo/Cu diffusion couples showed Se to react with Mo, forming MoSe<sub>2</sub> in very small amounts after annealing at 600°C. Kohara et al. [72] have also shown the formation of nearly ideal ohmic contact between Mo and CIGS that occurs via an intermediate MoSe<sub>2</sub> layer. Jones et al. [73] investigated the interface properties of d.c.-sputtered Mo on CIS layers, deposited by coevaporation, and concluded that MoSe<sub>2</sub> does not form below 500°C and it might be an artifact of the sputtering process. Similar results have been obtained by Schmid et al. [74] they detected Mo–O and Mo–O–Se compounds, while selenizing the Mo-coated substrate prior to the CIS deposition at 600°C. They concluded that there should be a Schottky-type barrier at the CIS–Mo/MoO<sub>2</sub> interface. Wada et al. [75] have also suggested that CIGS/Mo heterocontact including a MoSe<sub>2</sub> layer is not Schottky type, but a favorable ohmic type contact. Nishiwaki et al. [76, 77] have also studied the formation of MoSe<sub>2</sub> layer at the CIGS/Mo interface during “3-stage” process.

Wada et al. [78] reported the formation of a MoSe<sub>2</sub> layer at the Mo/CIGS interface during the second stage of the three-stage process, yet only under (In,Ga)-rich growth and

for substrate temperatures higher than 550°C. They found Na to enhance the formation of MoSe<sub>2</sub>. Assmann et al. [79] have also shown the presence of MoSe<sub>2</sub> at the Mo/CIGS interface; they conclude that mechanical stable MoSe<sub>2</sub> at the interface gives good adhesion. Recently, Shimizu et al. [80] have studied the variation of Mo thickness from 0.2 μm to 0.07 μm on the properties of CIGS solar cells. They conclude that there is a tradeoff between the decreased sodium diffusion for thicker Mo layers and decreased fill factor for thin layers. The optimum Mo thickness suggested was 0.2 μm. They have also found that water vapour introduced during CIGS growth improve the overall photovoltaic properties.

MoSe<sub>2</sub> layers were confirmed also in CuGaSe<sub>2</sub>-based solar cells by Würz et al. [81]. Contrary to the above results, Ballif et al. [82] could not detect any intermediate compound within the Mo/CIGS interface. Mo back contact for flexible polyimide is also been investigated by Zhang et al. [83].

The properties of molybdenum thin films evaporated onto large area (30 cm × 30 cm) soda-lime glass substrates at different deposition rates have been investigated by Guillén and Herrero [84]. During the formation of films, Na ion diffuse from the soda lime glass substrate through the Mo back contact into the absorber layer. The diffusion of Na into absorber film depends on the deposition conditions of the Mo back contact [85–87]. Nowadays, Mo growth by sputtering or e-beam evaporation is the most commonly used back contact for CIGS solar cells.

Kim et al. [88] have tried Na-doped Mo/Mo bilayer on Alumina substrate and have shown improvement in photovoltaic properties. Nakada [89] has tried transparent conducting oxide as back contact. The TCO back contact deteriorated at high absorber deposition temperature. The formation of Ga<sub>2</sub>O<sub>3</sub> was also reported at the CIGS/ITO and CIGS/ZnO:Al interfaces.

#### 4. CIGS Absorber Layer—Deposition Methods

I–III–VI<sub>2</sub> semiconductors, such as CIS or CIGS are often simply referred to as chalcopyrites because of their crystal structure. These materials are easily prepared in a wide range of compositions and the corresponding phase diagrams are well investigated [90–92]. For the preparation of solar cells, only slightly Cu-deficient compositions of p-type conductivity are suited [93, 94]. The details of material properties will not be discussed here.

A wide variety of thin-film deposition methods has been used to deposit Cu(In,Ga)Se<sub>2</sub> thin films. To determine the most promising technique for the commercial manufacture of modules, the overriding criteria are that the deposition can be completed at low cost while maintaining high deposition or processing rate with high yield and reproducibility. Compositional uniformity over large areas is critical for high yield. Device considerations dictate that the Cu(In,Ga)Se<sub>2</sub> layer should be at least 1 μm thick and that the relative compositions of the constituents are kept within the bounds determined by the phase diagram.

The most promising deposition methods for the commercial manufacture of modules can be divided into two

general approaches that have both been used to demonstrate high device efficiencies and in pilot scale manufacturing. The first approach is vacuum coevaporation in which all the constituents, Cu, In, Ga, and Se, can be simultaneously delivered to a substrate heated at 400°C to 600°C and the Cu(In,Ga)Se<sub>2</sub> film is formed in a single growth process. The second approach is a two-step process that separates the delivery of the metals from the reaction to form device-quality films. Typically the Cu, Ga, and In are deposited using low-cost and low-temperature methods that facilitate uniform composition. Then, the films are annealed in a Se atmosphere, also at 400°C to 600°C. The reaction and anneal step often takes longer time than formation of films by coevaporation due to diffusion kinetics, but is amenable to batch processing.

**4.1. Coevaporation.** The most successful technique for deposition of CIGS absorber layers for highest-efficiency cells is the simultaneous evaporation [95] of the constituent elements from multiple sources in single processes where Se is offered in excess during the whole deposition process. The process uses line-of-sight delivery of the Cu, In, Ga, and Se from Knudsen-type effusion cells or open boat sources to the heated substrate. While a variation of the In-to-Ga ratio during the deposition process leads to only minor changes in the growth kinetics, variation of the Cu content strongly affects the film growth.

The sticking coefficients of Cu, In, and Ga are very high, so the film composition and growth rate are determined simply by the flux distribution and effusion rate from each source. Different deposition variations, using elemental fluxes deliberately varied over time, have been explored using coevaporation. Four different sequences that have been used to fabricate devices with efficiencies greater than 16% are shown in Figure 4.

The first process (Figure 4(a)) is the simplest stationary process in which all fluxes as well as substrate temperature is constant throughout the deposition process [96]. Advanced preparation sequences include a Cu-rich stage during the growth process and end up with an In-rich overall composition in order to combine the large grains of the Cu-rich stage with the otherwise more favourable electronic properties of In-rich composition. The use of this kind of procedure is called “*Boeing or bilayer process*” (Figure 4(b)) originates from the work of Mickelsen and Chen [97, 98].

This bilayer process yields larger grain sizes compared to the constant rate (single stage) process. This is attributed to the formation of a Cu<sub>x</sub>Se phase during the Cu-rich first stage, which improves the mobility of group III atoms during growth [99–101]. Another possibility is the inverted process where first (In,Ga)<sub>2</sub>Se<sub>3</sub> is deposited at a lower temperature (typically ~300°C). Then Cu and Se are evaporated at an elevated temperature until an overall composition close to stoichiometry is reached [102–104]. This process leads to smoother film morphology than bilayer process. The so-called “*three-stage process*” introduced by Gabor et al. [103] from NREL is shown in Figure 4(c).

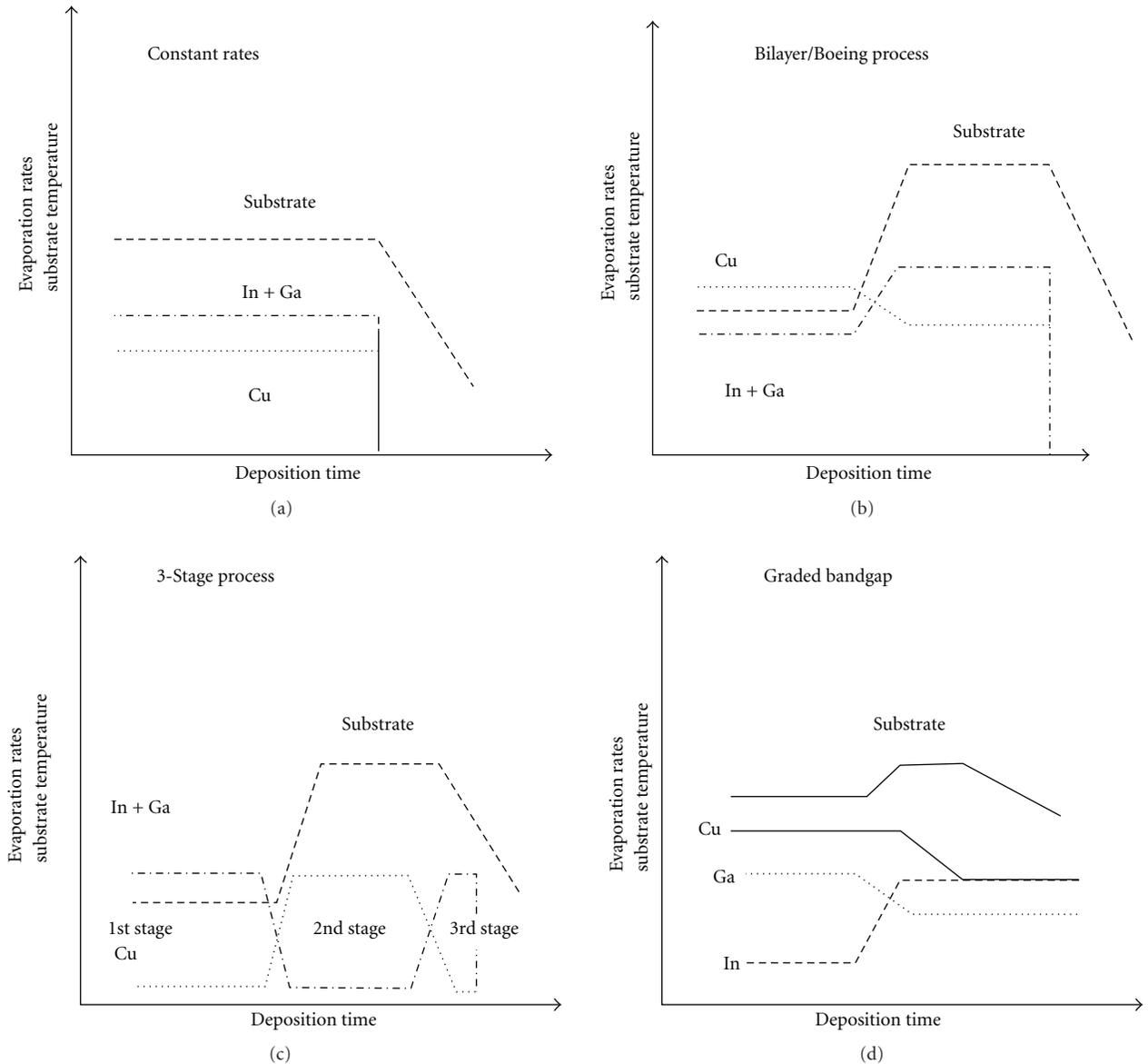


FIGURE 4: Schematic illustration of different coevaporation process. In all cases, a constant Se flux is also supplied.

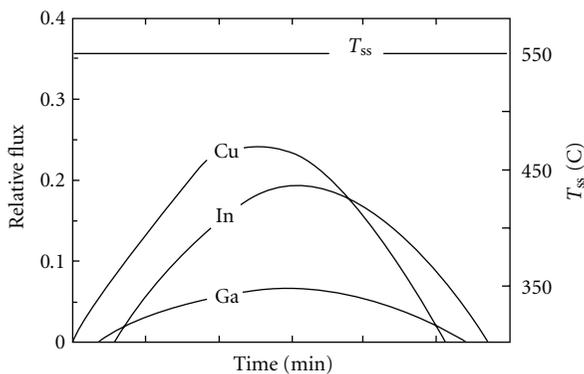


FIGURE 5: Flux distributions of different elements for in-line system. A constant Se flux is also supplied (from [35]).

This method leads, up to now, to the most efficient solar cells. The smoother surface obtained with three-stage process reduces the junction area and thereby is expected to reduce the number of defects at the junction and also facilitates the uniform conformal deposition of a thin buffer layer and prevents ion damage in CIGS during sputter deposition of ZnO/ZnO:Al. Variations of the Ga/In ratio during deposition (Figure 4(d)) allow the design of graded band-gap structures [105].

In one of the other process (shown in Figure 5) is an in-line process in which the flux distribution results from the substrate moving sequentially over the Cu, Ga, and In sources. This was first simulated in a stationary evaporation system [106] and demonstrated by Hanket et al. [107] and has subsequently been implemented by several groups in pilot manufacturing systems.

#### 4.2. Sequential Approach—Selenization of Precursor Material.

The interest in sequential processes is sparked by its suitability for large-area film deposition with good control of the composition and film thickness. Such processes consist of the deposition of a precursor material, followed by thermal annealing in controlled reactive or inert atmosphere for optimum compound formation via the chalcogenization reaction. This is commonly referred as selenization of stacked metal or alloy layers. The metals and alloys can be deposited by variety of methods which involve vacuum or no vacuum. The most common of vacuum process is sputtering [108–114] and thermal evaporation [113, 115–131]. The two step process has many variations in both the precursor deposition and the Se reaction step.

**4.2.1. Vacuum-Based Approach.** This general approach was first demonstrated by Grindle et al. [132] who sputtered Cu/In layers and reacted them in hydrogen sulfide to form  $\text{CuInS}_2$ . This was first adapted to  $\text{CuInSe}_2$  by Chu et al. [121]. The highest-efficiency  $\text{Cu(InGa)Se}_2$  cell reported using the reaction in  $\text{H}_2\text{Se}$  is 16.2%, on the basis of the active area [133], but there have been less effort at optimizing laboratory-scale cell efficiencies than with coevaporated  $\text{Cu(InGa)Se}_2$ . Using the two-step selenization/sulfurization approach, some groups have reported CIGSS-solar cells with  $V_{\text{OC}}$  and efficiency above 600 mV [134] and 14%, respectively, [135]. Lately, an efficiency of 13% [136] has been achieved on  $30 \times 30$  cm large modules. Recently 14.3% has been reported on  $30 \times 30$  cm large modules [137] and 14.7% on  $10 \times 10$  cm minimodules [138]. In both cases, sulphur as well as selenium is used for absorber preparation.

The precursor films are typically reacted in either  $\text{H}_2\text{Se}$  or Se vapor at  $400^\circ\text{C}$  to  $500^\circ\text{C}$  for 30 to 60 min to form the best device quality material. Poor adhesion [139] and formation of a  $\text{MoSe}_2$  layer [140] at the  $\text{Mo/CuInSe}_2$  interface may limit the reaction time and temperature. Reaction in  $\text{H}_2\text{Se}$  has the advantage that it can be done at atmospheric pressure and can be precisely controlled, but the gas is highly toxic and requires special precautions for its use. The precursor films can also be reacted in a Se vapor, which might be obtained by thermal evaporation, to form the  $\text{CuInSe}_2$  film [141]. A third reaction approach is rapid thermal processing (RTP) of either elemental layers, including Se [142, 143] or amorphous evaporated Cu-In-Se layers [144]. Recently, Chen et al. had tried one step sputtering using Cu-In-Ga alloy target followed by selenization [145].

**4.2.2. Nonvacuum-Based Approach.** Vacuum-evaporated, polycrystalline copper indium gallium diselenide (CIGS) thin films are used as the absorber layers in the highest efficiency thin film photovoltaic (PV) cells reported to date [5, 146]. However, the high cost and low material utilisation of the equipment used to produce these layers may be a barrier to their commercialization and will increase the cost of the electricity generated by CIGS based systems [147]. Nonvacuum techniques for CIGS deposition offer potential reductions in capital cost and many such techniques have been investigated [148]. These techniques generally split

CIGS formation into two stages, one in which the precursor is deposited and one in which the precursor is converted into CIGS.

Nonvacuum approaches to CIGS deposition can be divided into the following categories depending on the deposition method and the scale of mixing of the precursor materials:

- (1) electrochemical process,
- (2) particulate process,
- (3) solution based process.

A detailed review on nonvacuum process dealing with above process is recently published [149]. In view of this, the present section will only update the recent work done in this area, so as not to duplicate the recently published work. In the recent development, Kang et al. [150] have prepared CIGS absorber by selenizing electrodeposited precursor with rich Se and poor Se content. The Se-poor electrodeposited precursor had better crystallinity and increased Ga content. The best cell obtained has efficiency of 1.63% only. In another study, Lai et al. [151] investigated the electrodeposition of CIGS using cyclic voltammetry in a DMF-aqueous solution containing citrate as complexing agent. They performed the cyclic voltammetry study on a ternary Cu-In-Se system, a quaternary system Cu-In-Ga-Se and binary Cu-Se, In-Se, and Ga-Se systems.

Nanoparticle-based approach was carried out by Yoon et al. [152] for the formation of CIS solar cells. They concluded that the Se loss can be minimized by using high heating rate and core-shell structure with a binary compound. The highest efficiency reported was 1.11%. Park et al. [153] have synthesized CIGS absorber using a paste of a Cu, In, Ga, and Se with an aim to develop a simpler and lower cost method of fabricating the absorber layer. Kaigawa et al. [154] have also reported the absorber formation using spray and sintering the film using spot welding machine. Recently a nonvacuum process for preparing nanocrystalline CIGS materials involving an open-air solvothermal route has been demonstrated [155]. In continuation of their earlier work [156, 157], that is, hydrazine-based processor approach for the depositing CIGS and related chalcogenide-based absorber layer, Liu et al. have recently reported 12% efficient  $\text{CuIn(SeS)}_2$  solar cell [158]. Hou et al. [159] have also reported the formation of hydrazine-based  $\text{CuIn(SeS)}_2$  thin film solar cell.

## 5. Alternative CIS or CIGS Growth Process

The CIS or CIGS compound has been reported using other alternative techniques. In one of the studies, Ahmed et al. [160] have studied the thermal annealing of flash evaporated CIGS thin films. In another approach [161], efficiency as high as 15.4% was achieved using additional deposition of In, Ga, and Se at high temperatures. In spray pyrolysis, metal salts with a chalcogen reactant are sprayed on heated substrate to form CIS layer. However, a subsequent heat treatment in a reducing atmosphere is still required to improve crystallinity and purity [162–164]. Different other

approaches have also been successfully adopted for the fabrication of CIGS absorber layers. Flash evaporation has also been used to prepare CIGS film [165]. MOCVD has also been investigated [166] for the deposition of CGS layers as part of a tandem structure, but the growth rate and cell efficiency is rather low. CuInGaSe<sub>2</sub> thin films have been prepared by a low pressure metalorganic chemical vapor deposition technique using three precursors without additional Se [167]. A plasma-enhanced CVD has also been reported for fabricating stoichiometric CIS film [168]. CIS thin film has also been deposited by atmospheric pressure metal organic chemical vapor deposition (AP- MOCVD) [169, 170]. Brien et al. [171–173] have deposited CuInSe<sub>2</sub>, CuInS<sub>2</sub> and CuGaSe<sub>2</sub> thin film by low pressure MOCVD. Recently deposition of CuInSe<sub>2</sub> thin film on CuGaSe<sub>2</sub> thin film and vice versa has been achieved by a low pressure metal organic chemical vapor deposition technique with three precursors without additional Se [174]. No devices have been attempted by the authors.

Few different techniques have also been used to deposit and characterize CIGS thin film. The technique used are closed-spaced vapor transport [175–177] electrodeposition of CIS using ethylene glycol at 150°C [178] CIGSS films by sol-gel route [179] electron beam evaporated CIGS film [180–185] CuInSe<sub>2</sub> thin films prepared using sequential vacuum evaporation of In, Se, and Cu at moderately low substrate temperatures, avoiding any treatment using toxic H<sub>2</sub>Se gas [186], CIS using hot wall vacuum evaporation [187], MBE grown CIGS, CIS [188, 189] CIGS using ion-beam plasma evaporation in vacuum [190] and CIGS using a two-stage hybrid sputtering/evaporation method [191].

## 6. Influence of Sodium

The most important effect of the soda lime glass substrate on Cu(InGa)Se<sub>2</sub> film growth is that it supplies sodium to the growing chalcopyrite material. It has been clearly shown that this effect is distinct from the thermal expansion match of soda lime glass [192]. The sodium diffuses through the Mo back contact, which also means that it is important to control the properties of the Mo [193]. Na, incorporated into CIGS absorber layers are widely known to have significantly beneficial effects that lead to enhanced CIGS-related photovoltaic cell efficiencies.

The effect of Na include an improvement in p-type conductivity due to an increase in the effective hole carrier density and improved open circuit voltage ( $V_{OC}$ ) and fill factor for solar cells fabricated from Na doped CIGS [194, 195]. In addition to this, the effect of Na on the growth orientation of CIGS films results in an enhancement of (112) texture [194, 196, 197]. Among the various Na effects, variations in the electrical properties have been well discussed. The observed improvement in  $V_{OC}$  has been proposed to originate from an increase in the effective acceptor density [198]. Na in polycrystalline CIGS films is considered to act on the grain boundaries rather than in the bulk [199, 200]. Na substituting on a Cu site Na<sub>Cu</sub> results in the formation of a stable compound NaInSe<sub>2</sub>, which has a larger band

gap energy and in turn leads to a larger  $V_{OC}$  has also been proposed [201].

The correlation between the CIGS grain size and the presence of Na has been occasionally discussed. While some groups [192, 196, 202] have reported an increase of the grain size in CIGS films containing Na, others did not support these observations [203–206]. A decreasing grain size was observed for several Na incorporation methods in a direct comparison [200]. This may be due to the fact that the nature of the effects of Na on grain size depends on the CIGS growth method and the Na-doping process.

The CIS compound formation in rapid-thermal-processed layers was found to be delayed in the presence of Na, resulting in CIS growth at a higher mean temperature, which serves as an explanation for the observed increase in grain size [207]. In any case, the grain size of Na-doped CIGS films seems to have no critical role in solar cell performance [208, 209]. Higher doses of Na are shown to lead to smaller grain sizes, porous films and detrimental to the cell performance [204, 205]. The most obvious electronic effect of Na incorporation into CIGS films is a decrease in resistivity by up to two orders of magnitude [210–212]. In one of the recent studies [213] NaF was deposited prior to CIGS absorber and it reported that NaF precursors modify the CIGS growth kinetics: a reduction of the grain size and a slightly enhanced Ga-gradient through the absorber layer were observed.  $V_{OC}$  and FF (fill factor) increase when the Na content increases at  $T_{sub, max} = 500^\circ\text{C}$  during the absorber deposition.

In other studies, Erslev et al. [214] have studied the role of sodium in CIGS solar cells using junction capacitance methods. The increase in solar cell efficiency with sodium was attributed to passivation of a defect state near the CdS/CIGS junction. Recently, Ishizuka et al. [215] have studied the variations in the structural, optical, and electrical properties of polycrystalline Cu(In,Ga)Se<sub>2</sub> thin films with Na doping level. Na incorporation into CIGS absorber was controlled using alkali-silicate glass thin layers. They found that the Ga composition gradient in CIGS films became larger and the grain size decreased with increasing Na concentration.

## 7. CdS Buffer Layers

Semiconductor compounds with n-type conductivity and band gaps between 2.0 and 3.6 eV have been applied as buffer for CIGS solar cells. However, CdS remains the most widely investigated buffer layer, as it has continuously yielded high-efficiency cells. CdS for high-efficiency CIGS cells is generally grown by a chemical bath deposition (CBD), which is a low-cost, large-area process. However, incompatibility with in-line vacuum-based production methods is a matter of concern. Physical vapor deposition- (PVD-) grown CdS layers yield lower efficiency cells, as thin layers grown by PVD do not show uniform coverage of CIGS and are ineffective in chemically engineering the interface properties. For a comprehensive review on CBD-deposited CdS see Ortega-Borges and Lincot [216] and Hodes [217].

The recent trend in buffer layers is to substitute CdS with “Cd-free” wide-bandgap semiconductors and to replace the CBD technique with in-line-compatible processes. The first approach has been to omit CdS and form a direct junction between CIGS and ZnO, but the plasma (ions) during ZnO deposition by RF sputtering can damage the CIGS surface and enhance interface recombination. Possible solutions include ZnO deposited by metal organic chemical vapor deposition (MOCVD), atomic layer deposition (ALD) or a novel technique, called ion layer gas reaction (ILGAR) [218–220]. CIS and CIGS solar cells have yielded highest efficiencies with CdS buffer layers deposited by chemical bath deposition (CBD). Omitting the buffer layer always resulted in lower efficiencies [221]. Also, as-grown CIGS cells with CdS buffers deposited by physical vapor deposition (PVD) have always shown significantly lower efficiencies than cells with CBD-CdS buffers [222, 223].

The role of the CdS buffer layer is twofold: it affects both the electrical properties of the junction and protects the junction against chemical reactions and mechanical damage. From the electric point of view the CdS layer optimizes the band alignment of the device [224, 225] and builds a sufficiently wide depletion layer that minimizes tunneling and establishes a higher contact potential that allows higher open circuit voltage value [225]. The buffer layer also play a very important role as a “mechanical buffer” because it protects the junction electrically and mechanically against the damage that may otherwise be caused by the oxide deposition (especially by sputtering). Moreover, in large-area devices the electric quality of the CIGS film is not necessarily the same over the entire area, and recombination may be enhanced at grain boundaries or by local shunts. Together with the undoped ZnO layer, CdS enables self-limitation of electric losses by preventing defective parts of the CIGS film from dominating the open circuit voltage of the entire device [226].

The thickness as well as the deposition method of the CdS layer has a large impact on device performance. During the early days, the device structure consisted of a  $\text{CuInSe}_2/\text{CdS}$  junction with a thick (about 1–3  $\mu\text{m}$ ) CdS layer [227–229]. The CdS layer of these devices were most often prepared by evaporation at substrate temperatures between RT and about 200°C or in some cases by sputtering [229]. Also CdS film was often doped with either In [229] or Ga [106] and in some cases a CdS bilayer was used [230, 231] consisting of a thinner high-resistive layer, prepared either by evaporation [143] or chemical bath deposition [194, 230, 231] and a thicker low-resistivity layer, doped with 2% In [231] or Ga [194]. Alternatively, evaporated CdS has been used also in combination with the transparent conducting oxide layer [232–234]. Nowadays chemical bath deposition (CBD) is used almost exclusively [235, 236].

In contrast to evaporated films [237], CBD films contain high amounts of oxygen-related impurities that originate from the deposition solution; the amount of oxygen in the films can be as high as at 10–15 at % [237, 238]. Most of the oxygen is present as OH<sup>-</sup> and H<sub>2</sub>O [237, 238]. Thus, the composition of the CBD-CdS films is more accurately stated as Cd(S,O,OH) [237]. Additional impurities such as C and

N containing compounds result from the side reactions of thiourea [238]. The amount and identity of the impurities, and consequently the performance of the solar cell, depend strongly on the CdS deposition conditions [225, 239–241]. Negami et al. [242] for instance, reported an increase of conversion efficiency from 17.6 to 18.5% when the CBD-CdS process was improved.

In addition to the CdS film deposition, the chemical bath also modifies the absorber surface region [235, 243]. Thus, the interface between CIGS and CBD-CdS is not abrupt, but the layers are intermixing to some extent [238, 244]. Both Cu and Cd diffusion play a role, and the intermixing is further enhanced during the post deposition air-annealing [226]. According to Nakada and Kunioka [238], Cu was substituted by Cd at the surface region of CIGS. The diffusion depth of Cd atoms was about 10 nm, which may be related to the thickness of the Cu-deficient surface layer ( $\text{CuIn}_3\text{Se}_5$ ) of CIGS [238]. On the other hand, Heske et al. [244] observe diffusion of Se and In from CIGS into CdS and the diffusion of S from CdS into CIGS. The extent of interdiffusion depends on the structure of the absorber: (224/208) oriented CIGS films have been found to allow more Cd atoms to diffuse into the CIGS film [245].

One advantage of the CBD method as compared to evaporation is that a complete, conformal coverage of the CIGS surface can be obtained at very low thicknesses: already 10 nm has been reported to be sufficient [246]. The coverage depends on deposition conditions, particularly on the concentration ratio of the S and Cd precursors, being better with higher S/Cd precursor ratios [240].

Some studies have been conducted on the fundamental properties of CdS films deposited by an ammonia-free CBD process [247] and very few studies have used an ammonia-free buffer layer for the fabrication of a CIGS solar cell [248]. In a recent work, Mann et al. [249] has also deposited CdS by CBD and used optical reflectance-based measurement of the growing film to determine in situ film thickness.

## 8. Alternative Buffer Layer

As an alternative to CdS, various materials show promising results. The different buffer layer used and the deposition method for the same is tabulated in Table 2.

The Zn-based compounds tend to form a blocking barrier due to the band alignment with CIGS [253]. Using layers of less than 50 nm thickness, the barrier can be crossed by tunneling of charge carriers, but this poses high requirements on the quality of the deposition process and the CIGS surface to obtain a uniform coverage. The band offset can be reduced as well, if impurities such as hydroxides that can be present in a CBD are incorporated in the CIGS/buffer layer interface [281].

## 9. Front Contact

There are two main requirements for the electric front contact of a CIGS solar cell device: sufficient transparency in order to let enough light through to the underlying parts of

TABLE 2: Alternative buffer layers and their deposition methods.

Buffer Layer	Deposition Method	References
ZnS	CBD	[250–253]
ZnS	MBE	[254]
ZnS(O,OH)	CBD	[25]
ZnSe	MOCVD	[255, 256]
ZnSe	ALCVD	[257]
ZnSe	ALD	[258]
ZnSe	CBD	[259]
ZnIn <sub>2</sub> Se <sub>4</sub>	PVD	[260]
ZnIn <sub>x</sub> Se <sub>y</sub>	Coevaporation	[261]
Zn <sub>x-y</sub> Mg <sub>x</sub> O	Co-sputtered	[262]
Zn <sub>x-y</sub> Mg <sub>x</sub> O	ALD	[263]
In <sub>2</sub> S <sub>3</sub>	ALD	[264, 265]
In <sub>2</sub> S <sub>3</sub>	ALCVD	[266]
In <sub>2</sub> S <sub>3</sub>	MOCVD	[267]
In <sub>2</sub> S <sub>3</sub>	PVD	[268, 269]
In <sub>2</sub> S <sub>3</sub>	US	[270]
In <sub>2</sub> S <sub>x</sub>	Coevaporation	[271]
In <sub>x</sub> S <sub>y</sub>	Sputtered	[272]
In <sub>x</sub> S <sub>y</sub>	Coevaporation	[273, 274]
In <sub>x</sub> (OH,S) <sub>y</sub>	CBD	[275]
Zn(Se,OH)	CBD	[276]
Zn(S,O,OH)	CBD	[256, 277]
Zn(S,O)	CBD	[278]
	ALD	[279]
ZnS/Zn(S,O)	CBD	[280]
ZnMgO	CBD	[263]
	ALD	[278]

CBD-Chemical Bath Deposition, MBE-Molecular Beam Epitaxy, MOCVD-metalorganic chemical vapour deposition, ALCVD-Atomic Layer CVD, ALD-Atomic Layer Deposition, PVD-Physical Vapour Deposition, US-Ultrasonic spray.

the device, and sufficient conductivity to be able to transport the photo-generated current to the external circuit without too much resistance losses. Transparent conducting metal oxides (TCO) are used almost exclusively as the top contacts. Narrow lined metal grids (Ni–Al) are usually deposited on top of the TCO in order to reduce the series resistance. The quality of the front contact is thus a function of the sheet resistance, absorption and reflection of the TCO as well as the spacing of the metal grids [282].

During the early days of CIS and CIGS substrate cell development, a bilayer of undoped and doped CdS served as a buffer and front contact, respectively [283, 284]. High conductivity in doped CdS was achieved either by controlling the density of donor type defects or by extrinsic doping with Al or In [283, 284]. Spectral absorption loss in the conducting CdS layer was reduced by increasing the bandgap, alloying with ZnS or later replacing it with TCOs with bandgaps of above 3 eV [283]. Transmission spectra of various TCOs are shown in Figure 6.

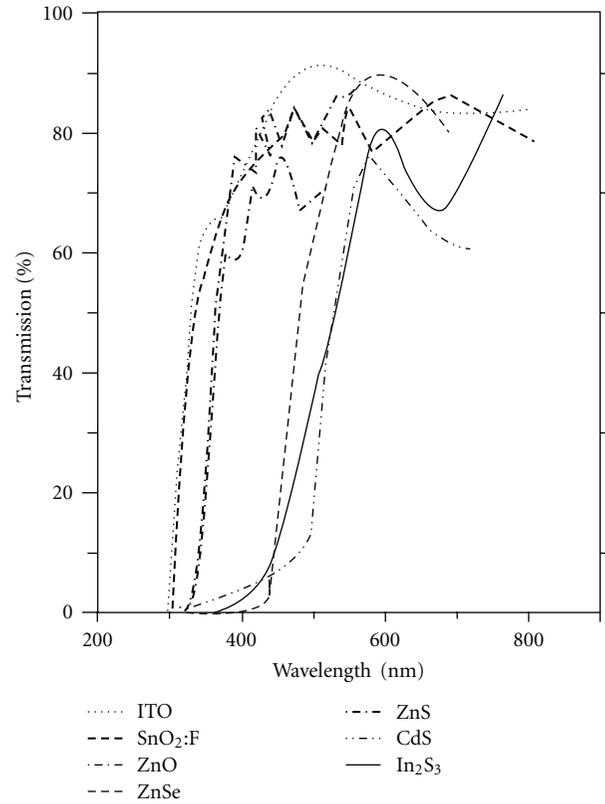


FIGURE 6: Optical transmission of different front contacts and buffer layers (from [38]).

Today, CIGS solar cells employ either tin doped In<sub>2</sub>O<sub>3</sub> (In<sub>2</sub>O<sub>3</sub>: Sn, ITO) [285–287] or, more frequently, RF-sputtered Al-doped ZnO. A combination of an intrinsic and a doped ZnO layer is commonly used, although this double layer yields consistently higher efficiencies, the beneficial effect of intrinsic ZnO is still under discussion [226]. It has been shown that device performance increases due to the increase in  $V_{OC}$  by 20–40 mV [226]. It has been discussed that resistive oxide layer provides, together with buffer, a series resistance that protects the device from local electrical losses that may originate from inhomogeneities of the absorber [226]. Doping of the conducting ZnO layer is achieved by group III elements, particularly with aluminum [194, 288–298]. However, investigations show boron to be a feasible alternative, as it yields a high mobility of charge carriers [290, 299–304] and a higher transmission in the long-wavelength spectral region, giving rise to higher currents [305]. For high-efficiency cells the TCO deposition temperature should be lower than 150°C in order to avoid the detrimental interdiffusion across CdS/CIGS interface.

There had been some recent studies of i-ZnO and doped ZnO. Yu et al. [306] have studied the Ni and Al codoped ZnO grown by dc magnetron cosputtering. A comparative study of i-ZnO and ZnO:Al using rf magnetron sputtering and electrodeposition done by Wellings et al. [307] to be used for CIGS solar cells. Pawar et al. [308] have studied the Boron doped ZnO using spray pyrolysis.

Few [309, 310] have reported the deposition of ZnO:Al on polyimide substrate. Recently, Calnan and Tiwari have discussed in detail regarding High Mobility Transparent Conductor Oxide (HMTCO) [311].

## 10. Conclusion

Remarkable progress has been made in the development of high efficiency CIGS solar cells. CIGS PV modules have the potential to reach cost-effective PV-generated electricity. Transition from lab to manufacturing has been much more difficult than anticipated.

Each component of the solar cell structure and its manufacturing requires further investigation to simplify the processing and to have more efficient solar cell with lower cost. Few of the key issues related to development of CIGS solar cells are: higher module efficiency, columnar CIGS structures deposited by alternative process for high efficiency cells and modules, thinner absorber layer ( $\leq 1 \mu\text{m}$ ), and CIGS absorber film stoichiometry and uniformity over large areas.

There is also a need to develop a robust and low temperature ( $\sim 400^\circ\text{C}$ ) deposition process for CIGS for the flexible substrate (polyimide) to facilitate roll to roll manufacturing and to extend the application for space market.

## Acknowledgments

The authors would like to thank Mr. Abdul Khader and Ms. Krishna Dalai, for their support during the work. This work has been supported by the Ministry of New & Renewable Energy (31/12/2009/PVSE), New Delhi, Department of Science & Technology (DST), New Delhi (SR/S2/CMP-30/2003), and AICTE, New Delhi (8023/BOR/RID/RPS-78/2007-08).

## References

- [1] M. Kaelin, D. Rudmann, and A. N. Tiwari, "Low cost processing of CIGS thin film solar cells," *Solar Energy*, vol. 77, no. 6, pp. 749–756, 2004.
- [2] F. Kessler and D. Rudmann, "Technological aspects of flexible CIGS solar cells and modules," *Solar Energy*, vol. 77, no. 6, pp. 685–695, 2004.
- [3] D. Graham-Rowe, "Solar cells get flexible," *Nature Photonics*, vol. 1, no. 8, pp. 433–435, 2007.
- [4] M. A. Green, K. Emery, D. L. King, S. Igari, and W. Warta, "Solar cell efficiency tables (Version 22)," *Progress in Photovoltaics: Research and Applications*, vol. 11, no. 5, pp. 347–352, 2003.
- [5] I. Repins, M. A. Contreras, B. Egaas et al., "19.9%-efficient ZnO/CdS/CuInGaSe<sub>2</sub> solar cell with 81.2% fill factor," *Progress in Photovoltaics: Research and Applications*, vol. 16, no. 3, pp. 235–239, 2008.
- [6] B. Dimmler and R. Wächter, "Manufacturing and application of CIS solar modules," *Thin Solid Films*, vol. 515, no. 15, pp. 5973–5978, 2007.
- [7] S. Wagner, J. L. Shay, P. Migliorato, and H. M. Kasper, "CuInSe<sub>2</sub>/CdS heterojunction photovoltaic detectors," *Applied Physics Letters*, vol. 25, no. 8, pp. 434–435, 1974.
- [8] R. R. Potter, C. Eberspacher, and L. B. Fabick, "Device analysis of CuInSe<sub>2</sub>/(Cd,Zn)S/ZnO solar cells," in *Proceedings of the Conference Record of the 18th IEEE Photovoltaic Specialists Conference*, pp. 1659–1664, 1985.
- [9] B. M. Başol, V. K. Kapur, C. R. Leidholm, A. Halani, and K. Gledhill, "Flexible and light weight copper indium diselenide solar cells on polyimide substrates," *Solar Energy Materials and Solar Cells*, vol. 43, no. 1, pp. 93–98, 1996.
- [10] A. N. Tiwari, M. Krejci, F.-J. Haug, and H. Zogg, "12.8% efficiency Cu(In,Ga)Se<sub>2</sub> solar cell on a flexible polymer sheet," *Progress in Photovoltaics: Research and Applications*, vol. 7, no. 5, pp. 393–397, 1999.
- [11] G. M. Hanket, U. P. Singh, E. Eser, W. N. Shafarman, and R. W. Birkmire, "Pilot-scale manufacture of Cu(InGa)Se<sub>2</sub> films on a flexible polymer substrate," in *Proceedings of the 29th IEEE Photovoltaic Specialists Conference*, pp. 567–569, May 2002.
- [12] R. Birkmire, E. Eser, S. Fields, and W. Shafarman, "Cu(InGa)Se<sub>2</sub> solar cells on a flexible polymer web," *Progress in Photovoltaics: Research and Applications*, vol. 13, no. 2, pp. 141–148, 2005.
- [13] S. Ishizuka, H. Hommoto, N. Kido, K. Hashimoto, A. Yamada, and S. Niki, "Efficiency enhancement of Cu(In,Ga)Se<sub>2</sub> solar cells fabricated on flexible polyimide substrates using alkali-silicate glass thin layers," *Applied Physics Express*, vol. 1, no. 9, Article ID 092303, pp. 1–3, 2008.
- [14] P. Gečys, G. Račiukaitis, M. Gedvilas, and A. Selskis, "Laser structuring of thin-film solar cells on polymers," *EPJ Applied Physics*, vol. 46, no. 1, Article ID 12508, 2009.
- [15] L. Zhang, Q. He, W.-L. Jiang, C.-J. Li, and Y. Sun, "Flexible Cu(In,Ga)Se<sub>2</sub> thin-film solar cells on polyimide substrate by low-temperature deposition process," *Chinese Physics Letters*, vol. 25, no. 2, pp. 734–736, 2008.
- [16] R. Caballero, C. A. Kaufmann, T. Eisenbarth et al., "The influence of Na on low temperature growth of CIGS thin film solar cells on polyimide substrates," *Thin Solid Films*, vol. 517, no. 7, pp. 2187–2190, 2009.
- [17] H. Zachmann, S. Heinker, A. Braun et al., "Characterisation of Cu(In,Ga)Se<sub>2</sub>-based thin film solar cells on polyimide," *Thin Solid Films*, vol. 517, no. 7, pp. 2209–2212, 2009.
- [18] T. Satoh, Y. Hashimoto, S. Shimakawa, S. Hayashi, and T. Negami, "Cigs solar cells on flexible stainless steel substrates," in *Proceedings of the Conference Record of the 28th IEEE Photovoltaic Specialists Conference*, p. 567, 2000.
- [19] K. Herz, F. Kessler, R. Wächter et al., "Dielectric barriers for flexible CIGS solar modules," *Thin Solid Films*, vol. 403–404, pp. 384–389, 2002.
- [20] D. Herrmann, F. Kessler, K. Herz et al., "High-performance barrier layers for flexible CIGS thin-film solar cells on metal foils," in *Proceedings of the Materials Research Society Symposium: Compound Semiconductor Photovoltaics*, vol. 763, pp. 287–292, San Francisco, Calif, USA, 2003.
- [21] D. R. Hollars, R. Dorn, P. D. Paulson, J. Titus, and R. Zubeck, "Large area Cu(In,Ga)Se<sub>2</sub> films and devices on flexible substrates made by sputtering," in *Proceedings of the Materials Research Society Spring Meeting*, pp. 477–482, April 2005, F14.34.1.
- [22] K. Otte, L. Makhova, A. Braun, and I. Konovalov, "Flexible Cu(In,Ga)Se<sub>2</sub> thin-film solar cells for space application," *Thin Solid Films*, vol. 511–512, pp. 613–622, 2006.
- [23] S. Ishizuka, A. Yamada, P. Fons, and S. Niki, "Flexible Cu(In,Ga)Se<sub>2</sub> solar cells fabricated using alkali-silicate glass thin layers as an alkali source material," *Journal of Renewable Sustainable Energy*, vol. 1, Article ID 013102, 8 pages, 2008.

- [24] R. Wuerz, A. Eicke, M. Frankenfeld et al., "CIGS thin-film solar cells on steel substrates," *Thin Solid Films*, vol. 517, no. 7, pp. 2415–2418, 2009.
- [25] T. Yagioka and T. Nakada, "Cd-free flexible Cu(In,Ga)Se<sub>2</sub> thin film solar cells with ZnS(O,OH) buffer layers on Ti foils," *Applied Physics Express*, vol. 2, no. 7, Article ID 072201, 3 pages, 2009.
- [26] D. Brémaud, D. Rudmann, M. Kaelin et al., "Flexible Cu(In,Ga)Se<sub>2</sub> on Al foils and the effects of Al during chemical bath deposition," *Thin Solid Films*, vol. 515, no. 15, pp. 5857–5861, 2007.
- [27] S. Ishizuka, A. Yamada, K. Matsubara, P. Fons, K. Sakurai, and S. Niki, "Development of high-efficiency flexible Cu(In,Ga)Se<sub>2</sub> solar cells: a study of alkali doping effects on CIS, CIGS, and CGS using alkali-silicate glass thin layers," *Current Applied Physics*, vol. 20, no. 2, supplement 1, pp. S154–S156, 2009.
- [28] C. Y. Shi, Y. Sun, Q. He, F. Y. Li, and J. C. Zhao, "Cu(In,Ga)Se<sub>2</sub> solar cells on stainless-steel substrates covered with ZnO diffusion barriers," *Solar Energy Materials and Solar Cells*, vol. 93, no. 5, pp. 654–656, 2009.
- [29] M. S. Kim, J. H. Yun, K. H. Yoon, and B. T. Ahn, "Fabrication of flexible CIGS solar cell on stainless steel substrate by co-evaporation process," *Diffusion and Defect Data B*, vol. 124–126, pp. 73–76, 2007.
- [30] D. Brémaud, D. Rudmann, G. Bilger, H. Zogg, and A. N. Tiwari, "Towards the development of flexible CIGS solar cells on polymer films with efficiency exceeding 15%," in *Proceedings of the 31st IEEE Photovoltaic Specialists Conference*, pp. 223–226, January 2005.
- [31] J. R. Tuttle, A. Szalaj, and J. Keane, "A 15.2 % AM0 / 1433 W/kg thin-film Cu(In,Ga)Se<sub>2</sub> solar cell for space applications," in *Proceedings of the 28th IEEE Photovoltaic Specialists Conference*, pp. 1042–1045, Anchorage, Alaska, 2000.
- [32] S. Ishizuka, "Flexible CIGS photovoltaic cell with energy conversion efficiency of 17.7%—enabling development of a sticker-type high-performance solar cell," *AIST Today*, vol. 8, no. 10, p. 20, 2008.
- [33] J. F. Guillemoles, "The puzzle of Cu(In,Ga)Se<sub>2</sub> (CIGS) solar cells stability," *Thin Solid Films*, vol. 403–404, pp. 405–409, 2002.
- [34] J. Poortmans and V. Archipov, *Thin Film Solar Cells*, John Wiley & Sons, New York, NY, USA, 2006.
- [35] A. Luque and S. Hegeds, Eds., *Handbook of Photovoltaic Science & Engineering*, John Wiley & Sons, New York, NY, USA, 2003.
- [36] T. Markvant and L. Castarier, Eds., *Practical handbook of Photovoltaics: Fundamentals and Applications*, Elsevier, Amsterdam, The Netherlands, 2003.
- [37] M. D. Archer and R. Hill, Eds., *Clean Electricity from Photovoltaics*, vol. 1, chapter 7 of *Series on Photoconversion of Solar Energy*, 2001.
- [38] A. Romeo, M. Terheggen, D. Abou-Ras et al., "Development of thin-film Cu(In,Ga)Se<sub>2</sub> and CdTe solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 12, no. 2–3, pp. 93–111, 2004.
- [39] M. Kemell, M. Ritala, and M. Leskelä, "Thin film deposition methods for CuInSe<sub>2</sub> solar cells," *Critical Reviews in Solid State and Materials Sciences*, vol. 30, no. 1, pp. 1–31, 2005.
- [40] J.-F. Guillemoles, L. Kronik, D. Cahen, U. Rau, A. Jasenek, and H.-W. Schock, "Stability issues of Cu(In,Ga)Se<sub>2</sub>-based solar cells," *Journal of Physical Chemistry B*, vol. 104, no. 20, pp. 4849–4862, 2000.
- [41] S. Duchemin, V. Chen, J. C. Yoyotte, J. Bougnot, and M. Savelli, "Backwall CdS(n)-CuInSe<sub>2</sub>(p) sprayed solar cells," in *Proceedings of the 8th European Photovoltaic Solar Energy Conference*, pp. 1038–1042, Florence, Italy, 1988.
- [42] T. Nakada, N. Okano, Y. Tanaka, H. Fukuda, and A. Kunioka, "Superstrate-type CuInSe<sub>2</sub> with chemically deposited CdS window layers," in *Proceedings of the IEEE 1st World Conference on Photovoltaic Energy Conversion*, pp. 95–98, Hawaii, USA, 1994.
- [43] T. Nakada and T. Mise, "High-efficiency superstrate type cigs thin film solar cells with graded bandgap absorber layers," in *Proceedings of the 17th European Photovoltaic Solar Energy Conference*, pp. 1027–1030, Munich, Germany, 2001.
- [44] F.-J. Haug, D. Rudmann, G. Bilger, H. Zogg, and A. N. Tiwari, "Comparison of structural and electrical properties of Cu(In,Ga)Se<sub>2</sub> for substrate and superstrate solar cells," *Thin Solid Films*, vol. 403–404, pp. 293–296, 2002.
- [45] F.-J. Haug, M. Krejci, H. Zogg, A. N. Tiwari, M. Kirsch, and S. Siebentritt, "Characterization of CuGa<sub>x</sub>Se<sub>y</sub>/ZnO for superstrate solar cells," *Thin Solid Films*, vol. 361, pp. 239–242, 2000.
- [46] M. Terheggen, H. Heinrich, G. Kostorz, F.-J. Haug, H. Zogg, and A. N. Tiwari, "Ga<sub>2</sub>O<sub>3</sub> segregation in Cu(In,Ga)Se<sub>2</sub>/ZnO superstrate solar cells and its impact on their photovoltaic properties," *Thin Solid Films*, vol. 403–404, pp. 212–215, 2002.
- [47] F.-J. Haug, D. Rudmann, H. Zogg, and A. N. Tiwari, "Light soaking effects in Cu(In,Ga)Se<sub>2</sub> superstrate solar cells," *Thin Solid Films*, vol. 431–432, pp. 431–435, 2003.
- [48] R. Klenk, R. Mauch, R. Schäffler, D. Schmid, and H. W. Schock, "Progress in CuGaSe<sub>2</sub> based thin film solar cells," in *Proceedings of the 22nd IEEE Photovoltaic Specialists Conference*, pp. 1071–1076, October 1991.
- [49] A. Kampmann, A. Abken, G. Leimkühler et al., "Cadmium-free CuInSe<sub>2</sub> superstrate solar cell fabricated by electrodeposition using a ITO/In<sub>2</sub>Se<sub>3</sub>/CuInSe<sub>2</sub>/Au structure," *Progress in Photovoltaics: Research and Applications*, vol. 7, no. 2, pp. 129–135, 1999.
- [50] T. Yoshida and R. W. Birkmire, "Fabrication of CuInSe<sub>2</sub> solar cells in a superstrate configuration," in *Proceedings of the 11th EC Photovoltaic Solar Energy Conference*, p. 811, 1992.
- [51] T. Negami, M. Nishitani, M. Ikeda, and T. Wada, "Preparation of CuInSe<sub>2</sub> films on large grain CdS films for superstrate-type solar cells," *Solar Energy Materials and Solar Cells*, vol. 35, no. C, pp. 215–222, 1994.
- [52] T. Nakada, Y. Hirabayashi, T. Tokado, D. Ohmori, and T. Mise, "Novel device structure for Cu(In,Ga)Se<sub>2</sub> thin film solar cells using transparent conducting oxide back and front contacts," *Solar Energy*, vol. 77, no. 6, pp. 739–747, 2004.
- [53] S. Nishiwaki, S. Siebentritt, P. Walk, and M. Ch. Lux-Steiner, "A stacked chalcopyrite thin-film tandem solar cell with 1.2 V open-circuit voltage," *Progress in Photovoltaics: Research and Applications*, vol. 11, no. 4, pp. 243–248, 2003.
- [54] S. A. Alagappan and S. Mitra, "Optimizing the design of CIGS-based solar cells: a computational approach," *Materials Science and Engineering B*, vol. 116, no. 3, pp. 293–296, 2005.
- [55] T. Nakada, S. Kijima, Y. Kuromiya et al., "Chalcopyrite thin-film tandem solar cells with 1.5 V open-circuit-voltage," in *Proceedings of the IEEE 4th World Conference on Photovoltaic Energy Conversion (WCPEC '06)*, vol. 1, pp. 400–403, May 2006.

- [56] M. W. Wang, "Novel CdSe-based PV structure for high efficiency CdSe/CIGS tandem solar cells," in *Proceedings of the 34th IEEE Photovoltaic Specialists Conference (PVSC '09)*, pp. 489–493, Philadelphia, Pa, USA, June 2009.
- [57] J. H. Scofield, A. Duda, D. Albin, B. L. Ballard, and P. K. Predecki, "Sputtered molybdenum bilayer back contact for copper indium diselenide-based polycrystalline thin-film solar cells," *Thin Solid Films*, vol. 260, no. 1, pp. 26–31, 1995.
- [58] R. J. Matson, O. Jamjoum, A. D. Buonaquisti et al., "Metal contacts to CuInSe<sub>2</sub>," *Solar Cells*, vol. 11, no. 3, pp. 301–305, 1984.
- [59] E. Moons, T. Engelhard, and D. Cahen, "Ohmic contacts to p-CuInSe<sub>2</sub> crystals," *Journal of Electronic Materials*, vol. 22, no. 3, pp. 275–280, 1993.
- [60] M. Powalla and B. Dimmler, "Scaling up issues of CIGS solar cells," *Thin Solid Films*, vol. 361, pp. 540–546, 2000.
- [61] R. Menner, E. Gross, A. Eicke, et al., in *Proceedings of the 13th European Photovoltaic Solar Energy Conference*, p. 2067, Nice, France, 1995.
- [62] R. A. Hoffman, J. C. Lin, and J. P. Chambers, "The effect of ion bombardment on the microstructure and properties of molybdenum films," *Thin Solid Films*, vol. 206, no. 1-2, pp. 230–235, 1991.
- [63] K. Granath, A. Rockett, M. Bodegard, C. Nender, and L. Stolt, "Mechanical issues of Mo back contacts for Cu(In,Ga)Se<sub>2</sub> devices," in *Proceedings of the 13th European Photovoltaic Solar Energy Conference*, pp. 1983–1986, Nice, France, 1995.
- [64] G. Gordillo, M. Grizález, and L. C. Hernandez, "Structural and electrical properties of DC sputtered molybdenum films," *Solar Energy Materials and Solar Cells*, vol. 51, no. 3-4, pp. 327–337, 1998.
- [65] M. A. Martínez and C. Guillén, "Effect of r.f.-sputtered Mo substrate on the microstructure of electrodeposited CuInSe<sub>2</sub> thin films," *Surface and Coatings Technology*, vol. 110, no. 1-2, pp. 62–67, 1998.
- [66] K. H. Yoon, S. K. Kim, R. B. V. Chalapathy et al., "Characterization of a molybdenum electrode deposited by sputtering and its effect on Cu(In,Ga)Se<sub>2</sub> solar cells," *Journal of the Korean Physical Society*, vol. 45, no. 4, pp. 1114–1118, 2004.
- [67] K. Orgassa, H. W. Schock, and J. H. Werner, "Alternative back contact materials for thin film Cu(In,Ga)Se<sub>2</sub> solar cells," *Thin Solid Films*, vol. 431-432, pp. 387–391, 2003.
- [68] P. E. Russell, O. Jamjoum, R. K. Ahrenkiel, L. L. Kazmerski, R. A. Mickelsen, and W. S. Chen, "Properties of the Mo-CuInSe<sub>2</sub> interface," *Applied Physics Letters*, vol. 40, no. 11, pp. 995–997, 1982.
- [69] W. Jaegaermann, T. Löher, and C. Pettenkofer, "Surface properties of chalcopyrite semiconductors," *Crystal Research and Crystal Technology*, vol. 31, p. 273, 1996.
- [70] W. N. Shafarman and J. E. Phillips, "Direct current-voltage measurements of the Mo/CuInSe<sub>2</sub> contact on operating solar cells," in *Proceedings of the 25th IEEE Photovoltaic Specialists Conference*, pp. 917–919, Washington, DC, USA, May 1996.
- [71] S. Raud and M.-A. Nicolet, "Study of the CuInSe<sub>2</sub>/Mo thin film contact stability," *Thin Solid Films*, vol. 201, no. 2, pp. 361–371, 1991.
- [72] N. Kohara, S. Nishiwaki, Y. Hashimoto, T. Negami, and T. Wada, "Electrical properties of the Cu(In,Ga)Se<sub>2</sub>/MoSe<sub>2</sub>/Mo structure," *Solar Energy Materials and Solar Cells*, vol. 67, no. 1-4, pp. 209–215, 2001.
- [73] K. M. Jones, L. L. Kazmerski, and B. G. Yacobi, "Transmission electron microscopy and X-ray photoelectron spectroscopy investigations of the MoCuInSe<sub>2</sub> interface," *Thin Solid Films*, vol. 116, no. 1-3, pp. L59–L62, 1984.
- [74] D. Schmid, M. Ruckh, and H. W. Schock, "A comprehensive characterization of the interfaces in Mo/CIS/CdS/ZnO solar cell structures," *Solar Energy Materials and Solar Cells*, vol. 41-42, pp. 281–294, 1996.
- [75] T. Wada, N. Kohara, S. Nishiwaki, and T. Negami, "Characterization of the Cu(In,Ga)Se<sub>2</sub>/Mo interface in CIGS solar cells," *Thin Solid Films*, vol. 387, no. 1-2, pp. 118–122, 2001.
- [76] S. Nishiwaki, N. Kohara, T. Negami, M. Nishitani, and T. Wada, "Characterization of Cu(In,Ga)Se<sub>2</sub>/Mo interface in CIGS solar cells," in *Materials Research Society Symposium Proceedings*, vol. 485, p. 139, 1997.
- [77] S. Nishiwaki, N. Kohara, T. Negami, and T. Wada, "MoSe<sub>2</sub> layer formation at Cu(In,Ga)Se<sub>2</sub>/Mo interfaces in high efficiency Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> Solar Cells," *Japanese Journal of Applied Physics. Part 2*, vol. 37, no. 1, pp. L71–L73, 1998.
- [78] T. Wada, N. Kohara, T. Negami, and M. Nishitani, "Chemical and structural characterization of Cu(In, Ga)Se<sub>2</sub>/Mo interface in Cu(In, Ga)Se<sub>2</sub> solar cells," *Japanese Journal of Applied Physics*, vol. 35, no. 10, pp. L1253–L1256, 1996.
- [79] L. Assmann, J. C. Bernède, A. Drici, C. Amory, E. Halgand, and M. Morsli, "Study of the Mo thin films and Mo/CIGS interface properties," *Applied Surface Science*, vol. 246, no. 1–3, pp. 159–166, 2005.
- [80] Y. K. Shimizu, S. Shimada, M. Watanabe et al., "Effects of Mo back contact thickness on the properties of CIGS solar cells," *Physica Status Solidi A*, vol. 206, no. 5, pp. 1063–1066, 2009.
- [81] R. Würz, D. Fuertes Marwón, A. Meeder et al., "Formation of an interfacial MoSe<sub>2</sub> layer in CVD grown CuGaSe<sub>2</sub> based thin film solar cells," *Thin Solid Films*, vol. 431-432, pp. 398–402, 2003.
- [82] C. Ballif, H. R. Moutinho, F. S. Hasoon, R. G. Dhere, and M. M. Al-Jassim, "Cross-sectional atomic force microscopy imaging of polycrystalline thin films," *Ultramicroscopy*, vol. 85, no. 2, pp. 61–71, 2000.
- [83] L. Zhang, Q. He, W.-L. Jiang, F.-F. Liu, C.-J. Li, and Y. Sun, "Mo back contact for flexible polyimide substrate Cu(In, Ga)Se<sub>2</sub> thin-film solar cells," *Chinese Physics Letters*, vol. 25, no. 9, pp. 3452–3454, 2008.
- [84] C. Guillén and J. Herrero, "Low-resistivity Mo thin films prepared by evaporation onto 30 cm × 30 cm glass substrates," *Journal of Materials Processing Technology*, vol. 143-144, no. 1, pp. 144–147, 2003.
- [85] B. M. Basol, V. K. Kapur, C. R. Leidholm, A. Minnickand, and A. Halani, "Studies on substrates and contacts for CIS films and devices," in *Proceedings of the IEEE 1st World Conference on Photovoltaic Energy Conversion*, pp. 148–151, Hawaii, USA, 1994.
- [86] D. C. Fishor, I. L. Repins, J. Schafor, et al., "The effect of Mo morphology on the performance of Cu(In,Ga)Se<sub>2</sub> thin films," in *Proceedings of the 31st IEEE Photovoltaic Specialists Conference (PVSEC '05)*, p. 371, 2005.
- [87] V. Mohanakrishnaswamy, H. Sankaranarayanan, S. Pethe, C. S. Ferekides, and D. L. Morel, "The effect of Mo deposition conditions on defect formation and device performance for CIGS solar cells," in *Proceedings of the 31st IEEE Photovoltaic Specialists Conference (PVSEC '05)*, pp. 422–425, Tampa, Fla, USA, 2005.
- [88] J. H. Y., K. H. Kim, Y. T. Ahn, and K. H. Yoon, "Effect of Na-doped Mo/Mo bilayer on CIGS cells and its photovoltaic properties," in *Proceedings of the IEEE 4th World Conference on Photovoltaic Energy Conversion (WCPEC '06)*, pp. 509–511, May 2006.

- [89] T. Nakada, "Microstructural and diffusion properties of CIGS thin film solar cells fabricated using transparent conducting oxide back contacts," *Thin Solid Films*, vol. 480-481, pp. 419-425, 2005.
- [90] T. Haalboom, T. Godecke, F. Ernst, M. Ruhle, R. Herberholz, and H. W. Schock, "Phase relations and microstructure in bulk materials and thin films of the ternary system Cu-In-Se," in *Proceedings of the 11th International Conference on Ternary and Multinary Compounds*, pp. 249-252, Salford, UK, 1998.
- [91] J. C. Mikkelsen, "Ternary phase relations of the chalcopyrite compound  $\text{CuGaSe}_2$ ," *Journal of Electronic Materials*, vol. 10, no. 3, pp. 541-558, 1981.
- [92] H. Jitsukawa, H. Matsushita, and T. Takizawa, "Phase diagrams of the  $(\text{Cu}_2\text{Se}, \text{CuSe})\text{-CuGaSe}_2$  system and the crystal growth of  $\text{CuGaSe}_2$  by the solution method," *Journal of Crystal Growth*, vol. 186, no. 4, pp. 587-593, 1998.
- [93] U. Rau, M. Schmitt, J. Parisi, W. Riedl, and F. Karg, "Persistent photoconductivity in  $\text{Cu}(\text{In,Ga})\text{Se}_2$  heterojunctions and thin films prepared by sequential deposition," *Applied Physics Letters*, vol. 73, no. 2, pp. 223-225, 1998.
- [94] V. Nadenau, D. Hariskos, H.-W. Schock et al., "Microstructural study of the  $\text{CdS}/\text{CuGaSe}_2$  interfacial region in  $\text{CuGaSe}_2$  thin film solar cells," *Journal of Applied Physics*, vol. 85, no. 1, pp. 534-542, 1999.
- [95] D. Mattox, *Handbook of Physical Vapor Deposition (PVD) Processing*, Noyes, Park Ridge, NJ, USA, 1998.
- [96] W. N. Shafarman and J. Zhu, "Effect of substrate temperature and deposition profile on evaporated  $\text{Cu}(\text{In,Ga})\text{Se}_2$  films and devices," *Thin Solid Films*, vol. 361, pp. 473-477, 2000.
- [97] R. A. Mickelsen and W. S. Chen, "High photocurrent polycrystalline thin-film  $\text{CdS}/\text{CuInSe}_2$  solar cell," *Applied Physics Letters*, vol. 36, no. 5, pp. 371-373, 1980.
- [98] R. A. Mickelsen and W. S. Chen, "Development of a 9.4% efficient thin-film  $\text{CuInSe}/2/\text{CdS}$  solar cell," in *Proceedings of the 15th IEEE Photovoltaic Specialists Conference*, pp. 800-804, 1981.
- [99] R. Klenk, T. Walter, H.-W. Schock, and D. Cahen, "A model for the successful growth of polycrystalline films of  $\text{CuInSe}_2$  by multisource physical vacuum evaporation," *Advanced Materials*, vol. 5, no. 2, pp. 114-119, 1993.
- [100] J. R. Tuttle, M. Contreras, A. Tennant, D. Albin, and R. Noufi, "High efficiency thin-film  $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based photovoltaic devices: progress towards a universal approach to absorber fabrication," in *Proceedings of the 23rd IEEE Photovoltaic Specialists Conference*, pp. 415-421, New York, NY, USA, May 1993.
- [101] J. S. Park, Z. Dong, S. Kim, and J. H. Perepezko, " $\text{CuInSe}_2$  phase formation during  $\text{Cu}_2\text{Se}/\text{In}_2\text{Se}_3$  interdiffusion reaction," *Journal of Applied Physics*, vol. 87, no. 8, pp. 3683-3690, 2000.
- [102] J. Kessler, K. O. Velthaus, M. Ruekh, et al., in *Proceedings of the 6th Photovoltaic Science and Engineering Conference (PVSEC '92)*, pp. 1005-1010, New Delhi, India, 1992.
- [103] A. Gabor, J. Tuttle, D. Albin, et al., "High efficiency polycrystalline  $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based solar cells," in *Proceedings of the 12th NREL Photovoltaic Program Review*, pp. 59-66, Denver, Colo, USA, 1993.
- [104] S. Zweigart, T. Walter, C. Koble, S. M. Sun, U. Ruhle, and H. W. Schock, "Sequential deposition of  $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$ ," in *Proceedings of the IEEE 1st World Conference on Photovoltaic Energy Conversion*, vol. 1, pp. 60-67, Hawaii, USA, 1994.
- [105] A. M. Gabor, J. R. Tuttle, M. H. Bode et al., "Band-gap engineering in  $\text{Cu}(\text{In,Ga})\text{Se}_2$  thin films grown from  $(\text{In,Ga})_2\text{Se}_3$  precursors," *Solar Energy Materials and Solar Cells*, vol. 41-42, pp. 247-260, 1996.
- [106] L. Stolt, J. Hedström, J. Kessler, M. Ruckh, K.-O. Velthaus, and H.-W. Schock, " $\text{ZnO}/\text{CdS}/\text{CuInSe}_2$  thin-film solar cells with improved performance," *Applied Physics Letters*, vol. 62, no. 6, pp. 597-599, 1993.
- [107] G. M. Hanket, P. D. Paulson, U. P. Singh, et al., "Fabrication of graded  $\text{Cu}(\text{In,Ga})\text{Se}_2$  films by inline evaporation," in *Proceedings of the IEEE Photovoltaic Specialists Conference (PVSC '00)*, p. 499, 2000.
- [108] M. Marudachalam, H. Hichri, R. Klenk, R. W. Birkmire, W. N. Shafarman, and J. M. Schultz, "Preparation of homogeneous  $\text{Cu}(\text{In,Ga})\text{Se}_2$  films by selenization of metal precursors in  $\text{H}_2\text{Se}$  atmosphere," *Applied Physics Letters*, vol. 67, p. 3978, 1995.
- [109] A. M. Hermann, C. Gonzalez, P. A. Ramakrishnan et al., "Fundamental studies on large area  $\text{Cu}(\text{In,Ga})\text{Se}_2$  films for high efficiency solar cells," *Solar Energy Materials and Solar Cells*, vol. 70, no. 3, pp. 345-361, 2001.
- [110] J. Zank, M. Mehlin, and H. P. Fritz, "Electrochemical codeposition of indium and gallium for chalcopyrite solar cells," *Thin Solid Films*, vol. 286, no. 1-2, pp. 259-263, 1996.
- [111] K. T. Ramakrishna Reddy, P. K. Datta, and M. J. Carter, "Detection of crystalline phases in  $\text{CuInSe}_2$  films grown by selenization process," *Physica Status Solidi A*, vol. 182, no. 2, pp. 679-685, 2000.
- [112] F. O. Adurodija, J. Song, S. D. Kim et al., "Growth of  $\text{CuInSe}_2$  thin films by high vapour Se treatment of co-sputtered Cu-In alloy in a graphite container," *Thin Solid Films*, vol. 338, no. 1-2, pp. 13-19, 1999.
- [113] M. Marudachalam, R. W. Birkmire, H. Hichri, J. M. Schultz, A. Swartzlander, and M. M. Al-Jassim, "Phases, morphology, and diffusion in  $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$  thin films," *Journal of Applied Physics*, vol. 82, no. 6, pp. 2896-2905, 1997.
- [114] C. Guillén, M. A. Martínez, and J. Herrero, " $\text{CuInSe}_2$  thin films obtained by a novel electrodeposition and sputtering combined method," *Vacuum*, vol. 58, no. 4, pp. 594-601, 2000.
- [115] R. Caballero and C. Guillén, "Comparative studies between Cu-Ga-Se and Cu-In-Se thin film systems," *Thin Solid Films*, vol. 403-404, pp. 107-111, 2002.
- [116] Ö. F. Yüksel, B. M. Basol, H. Safak, and H. Karabiyik, "Optical characterisation of  $\text{CuInSe}_2$  thin films prepared by two-stage process," *Applied Physics A*, vol. 73, no. 3, pp. 387-389, 2001.
- [117] A. G. Chowles, J. H. Neethling, H. Van Niekerk, J. A. A. Engelbrecht, and V. J. Watters, "Deposition and characterization of  $\text{CuInSe}_2$ ," *Renewable Energy*, vol. 6, no. 5-6, pp. 613-618, 1995.
- [118] S. Bandyopadhyaya, S. Roy, S. Chaudhuri, and A. K. Pal, " $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$  films prepared by graphite box annealing of In/Cu stacked elemental layers," *Vacuum*, vol. 62, no. 1, pp. 61-73, 2001.
- [119] C. Guillén and J. Herrero, "Structure, morphology and photoelectrochemical activity of  $\text{CuInSe}_2$  thin films as determined by the characteristics of evaporated metallic precursors," *Solar Energy Materials and Solar Cells*, vol. 73, no. 2, pp. 141-149, 2002.
- [120] M. S. Sadigov, M. Özkan, E. Bacaksiz, M. Altunbaş, and A. I. Kopya, "Production of  $\text{CuInSe}_2$  thin films by a sequential processes of evaporations and selenization," *Journal of Materials Science*, vol. 34, no. 18, pp. 4579-4584, 1999.

- [121] T. L. Chu, S. S. Chu, S. C. Lin, and J. Yue, "Large grain copoer indium diselenide films," *Journal of the Electrochemical Society*, vol. 131, no. 9, pp. 2182–2185, 1984.
- [122] J. Bekker, V. Alberts, and M. J. Witcomb, "Influence of selenization techniques on the reaction kinetics of chalcopyrite thin films," *Thin Solid Films*, vol. 387, no. 1-2, pp. 40–43, 2001.
- [123] S. F. Chichibu, M. Sugiyama, M. Ohbasami et al., "Use of diethylselenide as a less-hazardous source for preparation of CuInSe<sub>2</sub> photo-absorbers by selenization of metal precursors," *Journal of Crystal Growth*, vol. 243, no. 3-4, pp. 404–409, 2002.
- [124] A. Garg, K. S. Balakrishnan, and A. C. Rastogi, "Structural properties and growth mechanism of copper and indium selenide films prepared by electrochemical selenization of metal layers," *Journal of the Electrochemical Society*, vol. 141, no. 6, pp. 1566–1572, 1994.
- [125] A. C. Rastogi, K. S. Balakrishnan, R. K. Sharma, and K. Jain, "Growth phases during electrochemical selenization of vacuum deposited CuIn metal layers for the formation of semiconducting CuInSe<sub>2</sub> films," *Thin Solid Films*, vol. 357, no. 2, pp. 179–188, 1999.
- [126] C. Guillén and J. Herrero, "New approaches to obtain CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> thin films by combining electrodeposited and evaporated precursors," *Thin Solid Films*, vol. 323, no. 1-2, pp. 93–98, 1998.
- [127] V. Alberts, M. Klenk, and E. Bucher, "Phase separation and compositional changes in two-stage processed chalcopyrite thin films," *Thin Solid Films*, vol. 387, no. 1-2, pp. 44–46, 2001.
- [128] F. B. Dejene, "The structural and material properties of CuInSe<sub>2</sub> and Cu(In,Ga)Se<sub>2</sub> prepared by selenization of stacks of metal and compound precursors by Se vapor for solar cell applications," *Solar Energy Materials and Solar Cells*, vol. 93, no. 5, pp. 577–582, 2009.
- [129] F. B. Dejene, "Material and device properties of Cu(In,Ga)Se<sub>2</sub> absorber films prepared by thermal reaction of InSe/Cu/GaSe alloys to elemental Se vapor," *Current Applied Physics*, vol. 10, no. 1, pp. 36–40, 2010.
- [130] N. M. Shah, C. J. Panchal, V. A. Kheraj, J. R. Ray, and M. S. Desai, "Growth, structural and optical properties of copper indium diselenide thin films deposited by thermal evaporation method," *Solar Energy*, vol. 83, no. 5, pp. 753–760, 2009.
- [131] N. M. Shah, J. R. Ray, K. J. Patel et al., "Structural, electrical, and optical properties of copper indium diselenide thin film prepared by thermal evaporation method," *Thin Solid Films*, vol. 517, no. 13, pp. 3639–3644, 2009.
- [132] S. P. Grindle, C. W. Smith, and S. D. Mittleman, "Preparation and properties of CuInS<sub>2</sub> thin films produced by exposing sputtered Cu-In films to an H<sub>2</sub>S atmosphere," *Applied Physics Letters*, vol. 35, no. 1, pp. 24–26, 1979.
- [133] R. Gay, et al., "Efficiency and process improvements in CuInSe<sub>2</sub>-based modules," in *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, pp. 935–938, 1994.
- [134] V. Alberts, J. Titus, and R. W. Birkmire, "Material and device properties of single-phase Cu(In,Ga)(Se,S)<sub>2</sub> alloys prepared by selenization/sulfurization of metallic alloys," *Thin Solid Films*, vol. 451–452, pp. 207–211, 2004.
- [135] K. Kushiya, M. Tachiyuki, T. Kase et al., "Fabrication of graded band-gap Cu(InGa)Se<sub>2</sub> thin-film mini-modules with a Zn(O,S,OH)<sub>x</sub> buffer layer," *Solar Energy Materials and Solar Cells*, vol. 49, no. 1–4, pp. 277–283, 1997.
- [136] Y. Tanaka, N. Akema, T. Morishita, D. Okumura, and K. Kushiya, "Improvement of V<sub>oc</sub> upward of 600 mV/cell with CIGS-based absorber prepared by Selenization/Sulfurization," in *Proceedings of the 17th European Photovoltaic Solar Energy Conference*, pp. 989–994, Munich, Germany, 2001.
- [137] Y. Goushi, H. Hakuma, K. Tabuchi, S. Kijima, and K. Kushiya, "Fabrication of pentanary Cu(InGa)(SeS)<sub>2</sub> absorbers by selenization and sulfurization," *Solar Energy Materials and Solar Cells*, vol. 93, no. 8, pp. 1318–1320, 2009.
- [138] V. Probst, W. Stetter, W. Riedl et al., "Rapid CIS-process for high efficiency PV-modules: development towards large area processing," *Thin Solid Films*, vol. 387, no. 1-2, pp. 262–267, 2001.
- [139] V. K. Kapur, B. M. Basol, and E. S. Tseng, "Low cost methods for the production of semiconductor films for CuInSe<sub>2</sub>/CdS solar cells," *Solar Cells*, vol. 21, no. 1–4, pp. 65–72, 1987.
- [140] H. Sato, et al., "Fabrication of high efficiency CuIn(Ga)Se<sub>2</sub> thin film solar cell by selenization with H<sub>2</sub>Se," in *Proceedings of the 23rd IEEE Photovoltaic Specialist Conference*, p. 521, 1993.
- [141] J. Kessler, H. Dittrich, F. Grunwald, and H. Schock, in *Proceedings of the 10th European Conference on Photovoltaic Solar Energy Conversion*, p. 879, 1991.
- [142] H. Oumous, in *Proceedings of the 9th European Conference on Photovoltaic Solar Energy Conversion*, p. 153, 1992.
- [143] F. Karg, et al., "Novel rapid-thermal-processing for CIS thin-film solar cells," in *Proceedings of the 23rd IEEE Photovoltaic Specialists Conference*, pp. 441–446, 1993.
- [144] G. D. Mooney, A. M. Hermann, J. R. Tuttle, D. S. Albin, and R. Noufi, "Formation of CuInSe<sub>2</sub> thin films by rapid thermal recrystallization," *Applied Physics Letters*, vol. 58, no. 23, pp. 2678–2680, 1991.
- [145] G. S. Chen, J. C. Yang, Y. C. Chan, L. C. Yang, and W. Huang, "Another route to fabricate single-phase chalcogenides by post-selenization of Cu-In-Ga precursors sputter deposited from a single ternary target," *Solar Energy Materials and Solar Cells*, vol. 93, no. 8, pp. 1351–1355, 2009.
- [146] M. A. Green, K. Emery, Y. Hishikawa, and W. Warta, "Solar cell efficiency tables (version 31)," *Progress in Photovoltaics: Research and Applications*, vol. 16, no. 1, pp. 61–67, 2008.
- [147] K. Zweibel, "Issues in thin film PV manufacturing cost reduction," *Solar Energy Materials and Solar Cells*, vol. 59, no. 1, pp. 1–18, 1999.
- [148] M. Kaelin, D. Rudmann, and A. N. Tiwari, "Low cost processing of CIGS thin film solar cells," *Solar Energy*, vol. 77, no. 6, pp. 749–756, 2004.
- [149] C. J. Hibberd, E. Chassaing, W. Liu, D. B. Mitzi, D. Lincot, and A. N. Tiwari, "Non-vacuum methods for formation of Cu(In,Ga)(Se,S)<sub>2</sub> thin film photovoltaic absorbers," *Progress in Photovoltaics: Research and Applications*.
- [150] F. Kang, J. Ao, G. Sun, Q. He, and Y. Sun, "Properties of CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub> thin films grown from electrodeposited precursors with different levels of selenium content," *Current Applied Physics*, vol. 10, no. 3, pp. 886–888, 2010.
- [151] Y. Lai, F. Liu, Z. Zhang et al., "Cyclic voltammetry study of electrodeposition of Cu(In,Ga)Se<sub>2</sub> thin films," *Electrochimica Acta*, vol. 54, no. 11, pp. 3004–3010, 2009.
- [152] S. Yoon, T. Yoon, K.-S. Lee, S. Yoon, J. M. Ha, and S. Choe, "Nanoparticle-based approach for the formation of CIS solar cells," *Solar Energy Materials and Solar Cells*, vol. 93, no. 6-7, pp. 783–788, 2009.

- [153] J. W. Park, Y. W. Choi, E. Lee, O. S. Joo, S. Yoon, and B. K. Min, "Synthesis of CIGS absorber layers via a paste coating," *Journal of Crystal Growth*, vol. 311, no. 9, pp. 2621–2625, 2009.
- [154] R. Kaigawa, T. Uesugi, T. Yoshida, S. Merdes, and R. Klenk, "Instantaneous preparation of CuInSe<sub>2</sub> films from elemental In, Cu, Se particles precursor films in a non-vacuum process," *Thin Solid Films*, vol. 517, no. 7, pp. 2184–2186, 2009.
- [155] J. Olejníček, C. A. Kamler, A. Mirasano et al., "A non-vacuum process for preparing nanocrystalline CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> materials involving an open-air solvothermal reaction," *Solar Energy Materials and Solar Cells*, vol. 94, no. 1, pp. 8–11, 2010.
- [156] D. B. Mitzi, M. Yuan, W. Liu et al., "A high-efficiency solution-deposited thin-film photovoltaic device," *Advanced Materials*, vol. 20, no. 19, pp. 3657–3662, 2008.
- [157] D. B. Mitzi, M. Yuan, W. Liu et al., "Hydrazine-based deposition route for device-quality CIGS films," *Thin Solid Films*, vol. 517, no. 7, pp. 2158–2162, 2009.
- [158] W. Liu, D. B. Mitzi, M. Yuan, A. J. Kellock, S. J. Chey, and O. Gunawan, "12% efficiency CuIn(S<sub>2</sub>)<sub>2</sub> photovoltaic device prepared using a hydrazine solution process," *Chemistry of Materials*, vol. 22, no. 3, pp. 1010–1014, 2010.
- [159] W. W. Hou, B. Bob, S.-h. Li, and Y. Yang, "Low-temperature processing of a solution-deposited CuInSSe thin-film solar cell," *Thin Solid Films*, vol. 517, no. 24, pp. 6853–6856, 2009.
- [160] E. Ahmed, A. Zegadi, A. E. Hill, R. D. Pilkington, R. D. Tomlinson, and W. Ahmed, "Thermal annealing of flash evaporated Cu(In, Ga)Se<sub>2</sub> thin films," *Journal of Materials Processing Technology*, vol. 300, no. 3-4, pp. 260–265, 1998.
- [161] R. N. Bhattacharya, J. F. Hiltner, W. Batchelor, M. A. Contreras, R. N. Noufi, and J. R. Sites, "15.4% CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>-based photovoltaic cells from solution-based precursor films," *Thin Solid Films*, vol. 361, pp. 396–399, 2000.
- [162] M. Krunk, O. Kijatkina, H. Rebane, I. Oja, V. Mikli, and A. Mere, "Composition of CuInS<sub>2</sub> thin films prepared by spray pyrolysis," *Thin Solid Films*, vol. 403-404, pp. 71–75, 2002.
- [163] A. Katerski, A. Mere, V. Kazlauskienė et al., "Surface analysis of spray deposited copper indium disulfide films," *Thin Solid Films*, vol. 516, no. 20, pp. 7110–7115, 2008.
- [164] K. T. R. Reddy and R. W. Miles, "Surface characterization of sprayed CuGa<sub>x</sub>In<sub>1-x</sub>Se<sub>2</sub> layers," *Journal of Materials Science: Materials in Electronics*, vol. 14, no. 9, pp. 529–532, 2003.
- [165] N. Romeo, V. Canevari, G. Sberveglieri, O. Vigil, and L. Zanotti, "CuGa<sub>x</sub>In<sub>1-x</sub>Se<sub>2</sub> thin films for solar cells prepared by flash-evaporation," *Solar Energy Materials*, vol. 3, no. 3, pp. 367–370, 1980.
- [166] A. Bauknecht, S. Siebentritt, A. Gerhard et al., "Defects in CuGaSe<sub>2</sub> thin films grown by MOCVD," *Thin Solid Films*, vol. 361, pp. 426–431, 2000.
- [167] I. H. Choi and D. H. Lee, "Preparation of CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> films by metalorganic chemical vapor deposition using three precursors," *Thin Solid Films*, vol. 515, no. 11, pp. 4778–4782, 2007.
- [168] P. A. Jones, A. D. Jackson, P. D. Lickiss, R. D. Pilkington, and R. D. Tomlinson, "The plasma enhanced chemical vapour deposition of CuInSe<sub>2</sub>," *Thin Solid Films*, vol. 238, no. 1, pp. 4–7, 1994.
- [169] S. Duchemin, M. C. Artaud, F. Ouchen, and J. Bougnot, "Growth of CuInSe<sub>2</sub> by metallorganic chemical vapour deposition (MOCVD): new copper precursor," *Journal of Materials Science: Materials in Electronics*, vol. 7, no. 3, pp. 201–205, 1996.
- [170] M. C. Artaud, F. Ouchen, L. Martin, and S. Duchemin, "CuInSe<sub>2</sub> thin films grown by MOCVD: characterization, first devices," *Thin Solid Films*, vol. 324, no. 1-2, pp. 115–123, 1998.
- [171] J. M. Aleese, P. O. Brien, and D. J. Otway, *Chemical Vapor Deposition*, vol. 4, p. 94, 1998.
- [172] J.-H. Park, M. Afzaal, M. Kemmler et al., "The deposition of thin films of CuME<sub>2</sub> by CVD techniques (M = In, Ga and E = S, Se)," *Journal of Materials Chemistry*, vol. 13, no. 8, pp. 1942–1949, 2003.
- [173] M. Afzaal, D. J. Crouch, P. O. Brien, et al., "The synthesis, X-ray structures and Cvd studies of some group 11 complexes of imino-bis(diisopropylphosphine Selenides) and their use in the deposition of I/iii/vi photovoltaic materials," *Journal of Materials Chemistry*, vol. 14, pp. 233–237, 2004.
- [174] I.-H. Choi and P. Y. Yu, "Preparation of CuInSe<sub>2</sub>/CuGaSe<sub>2</sub> two layers absorber film by metal-organic chemical vapor deposition," *Current Applied Physics*, vol. 9, no. 1, pp. 151–154, 2009.
- [175] A. Bouloufa, K. Djessas, and D. Todorovic, "Structural and optical properties of Cu(In,Ga)Se<sub>2</sub> grown by close-spaced vapor transport technique," *Materials Science in Semiconductor Processing*, vol. 12, no. 1-2, pp. 82–87, 2009.
- [176] G. W. El Haj Moussa, Ariswan, A. Khoury, F. Guastavino, and C. Llinarés, "Fabrication and study of photovoltaic material CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> bulk and thin films obtained by the technique of close-spaced vapor transport," *Solid State Communications*, vol. 122, no. 3-4, pp. 195–199, 2002.
- [177] G. Massé, K. Djessas, C. Monty, and F. Sibieude, "Morphology of Cu(In,Ga)Se<sub>2</sub> thin films grown by close-spaced vapor transport from sources with different grain sizes," *Thin Solid Films*, vol. 414, no. 2, pp. 192–198, 2002.
- [178] J. S. Wellings, A. P. Samantilleke, S. N. Heavens, P. Warren, and I. M. Dharmadasa, "Electrodeposition of CuInSe<sub>2</sub> from ethylene glycol at 150 °C," *Solar Energy Materials and Solar Cells*, vol. 93, no. 9, pp. 1518–1523, 2009.
- [179] L. Oliveira, T. Todorov, E. Chassaing, D. Lincot, J. Carda, and P. Escribano, "CIGSS films prepared by sol-gel route," *Thin Solid Films*, vol. 517, no. 7, pp. 2272–2276, 2009.
- [180] B. M. Basol, V. K. Kapur, A. Halani, et al., "Cu(In,Ga)Se<sub>2</sub> thin films and solar cells prepared by selenization of metallic precursors," *The Journal of Vacuum Science and Technology A*, vol. 14, pp. 2251–2256, 1996.
- [181] R. Caballero, C. Guillén, M. T. Gutiérrez, and C. A. Kaufmann, "CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>-based thin-film solar cells by the selenization of sequentially evaporated metallic layers," *Progress in Photovoltaics: Research and Applications*, vol. 14, no. 2, pp. 145–153, 2006.
- [182] R. Caballero and C. Guillen, in *Proceedings of the International Conference on Advances in Materials and Processing Technologies*, p. 583, Madrid, Spain, 2001.
- [183] R. Caballero and C. Guillén, "CuInSe<sub>2</sub> Formation by selenization of sequentially evaporated metallic layers," *Solar Energy Materials and Solar Cells*, vol. 86, no. 1, pp. 1–10, 2005.
- [184] H. Sato, T. Hama, E. Niemi, Y. Ichikawa, and H. Sakai, *Japanese Journal of Applied Physics*, vol. 32, p. 50, 1993.
- [185] M. Venkatachalam, M. D. Kannan, N. Muthukumarasamy et al., "Investigations on electron beam evaporated Cu(In<sub>0.85</sub>Ga<sub>0.15</sub>)Se<sub>2</sub> thin film solar cells," *Solar Energy*, vol. 83, no. 9, pp. 1652–1655, 2009.
- [186] K. G. Deepa, R. Jayakrishnan, K. P. Vijayakumar, C. Sudha Kartha, and V. Ganesan, "Sub-micrometer thick CuInSe<sub>2</sub> films for solar cells using sequential elemental evaporation," *Solar Energy*, vol. 83, no. 7, pp. 964–968, 2009.

- [187] S. Agilan, D. Mangalaraj, S. A. K. Narayandass, S. Velumani, and A. Ignatiev, "Structural and optical characterization of CuInSe<sub>2</sub> films deposited by hot wall vacuum evaporation method," *Vacuum*, vol. 81, no. 7, pp. 813–818, 2007.
- [188] M. M. Islam, T. Sakurai, S. Ishizuka et al., "Effect of Se/(Ga+In) ratio on MBE grown Cu(In,Ga)Se<sub>2</sub> thin film solar cell," *Journal of Crystal Growth*, vol. 311, no. 7, pp. 2212–2214, 2009.
- [189] S. Niki, P. J. Fons, A. Yamada, et al., "High quality CuInSe<sub>2</sub> epitaxial films—molecular beam epitaxial growth and intrinsic properties," *Institute of Physics Conference Series*, vol. 152E, p. 221, 1994.
- [190] E. P. Zaretskaya, V. F. Gremenok, V. B. Zalesski, K. Bente, S. Schorr, and S. Zukotynski, "Properties of Cu(In,Ga)(S,Se)<sub>2</sub> thin films prepared by selenization/sulfurization of metallic alloys," *Thin Solid Films*, vol. 515, no. 15, pp. 5848–5851, 2007.
- [191] A. F. da Cunha, F. Kurdesau, D. Rudmann, and P. M. P. Salomé, "Performance comparison of hybrid sputtering/evaporation CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> solar cells with different transparent conducting oxide window layers," *Journal of Non-Crystalline Solids*, vol. 352, no. 9–20, pp. 1976–1980, 2006.
- [192] M. Bodegard, L. Stolt, and J. Hedstrom, "The influence of sodium on the grain structure of CuInSe<sub>2</sub> films for photovoltaic applications," in *Proceedings of the 12th European Conference on Photovoltaic Solar Energy Conversion*, pp. 1743–1746, 1994.
- [193] M. Bodegård, K. Granath, L. Stolt, and A. Rockett, "Behaviour of Na implanted into Mo thin films during annealing," *Solar Energy Materials and Solar Cells*, vol. 58, no. 2, pp. 199–208, 1999.
- [194] J. Hedstrom, H. Ohlsen, M. Bodegard et al., "ZnO/CdS/Cu(In,Ga)Se<sub>2</sub> thin film solar cells with improved performance," in *Proceedings of the 23rd IEEE Photovoltaic Specialists Conference*, pp. 364–371, New York, NY, USA, May 1993.
- [195] M. Ruckh, D. Schmid, M. Kaiser, R. Schaffler, T. Walter, and H. W. Schock, "Influence of substrates on the electrical properties of Cu(In,Ga)Se<sub>2</sub> thin films," in *Proceedings of the Conference Record of the IEEE 1st World Conference on Photovoltaic Energy Conversion*, pp. 156–159, Hawaii, USA, 1994.
- [196] M. Bodegård, K. Granath, and L. Stolt, "Growth of Cu(In,Ga)Se<sub>2</sub> thin films by coevaporation using alkaline precursors," *Thin Solid Films*, vol. 361, pp. 9–16, 2000.
- [197] D. Rudmann, G. Bilger, M. Kaelin, F.-J. Haug, H. Zogg, and A. N. Tiwari, "Effects of NaF coevaporation on structural properties of Cu(In,Ga)Se<sub>2</sub> thin films," *Thin Solid Films*, vol. 431–432, pp. 37–40, 2003.
- [198] T. Nakada, D. Iga, H. Ohbo, and A. Kunioka, "Effects of sodium on Cu(In, Ga)Se<sub>2</sub>-based thin films and solar cells," *Japanese Journal of Applied Physics. Part 1*, vol. 36, no. 2, pp. 732–737, 1997.
- [199] D. W. Niles, M. Al-Jassim, and K. Ramanathan, "Direct observation of Na and O impurities at grain surfaces of CuInSe<sub>2</sub> thin films," *Journal of Vacuum Science and Technology A*, vol. 17, no. 1, pp. 291–296, 1999.
- [200] D. Rudmann, A. F. Da Cunha, M. Kaelin et al., "Efficiency enhancement of Cu(In,Ga)Se<sub>2</sub> solar cells due to post-deposition Na incorporation," *Applied Physics Letters*, vol. 84, no. 7, pp. 1129–1131, 2004.
- [201] S.-H. Wei, S. B. Zhang, and A. Zunger, "Effects of Na on the electrical and structural properties of CuInSe<sub>2</sub>," *Journal of Applied Physics*, vol. 85, no. 10, pp. 7214–7218, 1999.
- [202] V. Probst, J. Rimmasch, W. Riedl, et al., "The impact of controlled sodium incorporation on rapid thermal processed Cu(In,Ga)Se<sub>2</sub>-thin films and devices," in *Proceedings of the Conference Record of the IEEE 1st World Conference on Photovoltaic Energy Conversion*, p. 144, New York, NY, USA, 1994.
- [203] A. Rockett, J. S. Britt, T. Gillespie et al., "Na in selenized Cu(In,Ga)Se<sub>2</sub> on Na-containing and Na-free glasses: distribution, grain structure, and device performances," *Thin Solid Films*, vol. 372, no. 1, pp. 212–217, 2000.
- [204] J. E. Granata and J. R. Sites, "Impact of sodium in the bulk and in grain boundaries of CuInSe<sub>2</sub>," in *Proceedings of the 2nd World Conference on Photovoltaic Solar Energy Conversion*, vol. 1, pp. 604–607, Vienna, Austria, July 1998.
- [205] R. J. Matson, J. E. Granata, S. E. Asher, and M. R. Young, "Effects of substrate and Na concentration on device properties, junction formation, and film microstructure in CuInSe<sub>2</sub> PV devices," in *Proceedings of the 15th NCPV Photovoltaic Program Review*, vol. 462, pp. 542–552, Denver, Colo, USA, March 1999.
- [206] T. Nakada, H. Ohbo, M. Fukuda, and A. Kunioka, "Improved compositional flexibility of Cu(In,Ga)Se<sub>2</sub>-based thin film solar cells by sodium control technique," *Solar Energy Materials and Solar Cells*, vol. 49, no. 1–4, pp. 261–267, 1997.
- [207] D. Wolf, G. Muller, W. Stetter, and F. Karg, "In-situ investigation of Cu-In-Se reactions: impact of Na on CIS formation," in *Proceedings of the 2nd World Conference on Photovoltaic Solar Energy Conversion*, pp. 2426–2430, Vienna, Austria, 1998.
- [208] W. N. Shafarman and J. Zhu, "Effect of substrate temperature and deposition profile on evaporated Cu(In,Ga)Se<sub>2</sub> films and devices," *Thin Solid Films*, vol. 361, pp. 473–477, 2000.
- [209] S. Ishizuka, H. Shibata, A. Yamada et al., "Growth of polycrystalline Cu (In,Ga) Se<sub>2</sub> thin films using a radio frequency-cracked Se-radical beam source and application for photovoltaic devices," *Applied Physics Letters*, vol. 91, no. 4, Article ID 041902, 2007.
- [210] J. Holz, F. Karg, and H. V. Philipsborn, "The effect of substrate impurities on the electronic conductivity in CIS thin films," in *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, pp. 1592–1595, Amsterdam, The Netherlands, 1994.
- [211] R. Kirmura, T. Mouri, T. Nakada, et al., "Photoluminescence properties of sodium incorporated in CuInSe<sub>2</sub> thin films," *Japanese Journal of Applied Physics*, vol. 38, pp. L289–L291, 1999.
- [212] M. Lammer, U. Klemm, and M. Powalla, "Sodium coevaporation for low temperature Cu(In,Ga)Se<sub>2</sub> deposition," *Thin Solid Films*, vol. 387, no. 1–2, pp. 33–36, 2001.
- [213] R. Caballero, C. A. Kaufmann, T. Eisenbarth et al., "The influence of Na on low temperature growth of CIGS thin film solar cells on polyimide substrates," *Thin Solid Films*, vol. 517, no. 7, pp. 2187–2190, 2009.
- [214] P. T. Erslev, J. W. Lee, W. N. Shafarman, and J. D. Cohen, "The influence of Na on metastable defect kinetics in CIGS materials," *Thin Solid Films*, vol. 517, no. 7, pp. 2277–2281, 2009.
- [215] S. Ishizuka, A. Yamada, M. M. Islam et al., "Na-induced variations in the structural, optical, and electrical properties of Cu (In,Ga) Se<sub>2</sub> thin films," *Journal of Applied Physics*, vol. 106, no. 3, Article ID 034908, 2009.

- [216] R. Ortega-Borges and D. Lincot, "Mechanism of chemical bath deposition of cadmium sulfide thin films in the ammonia-thiourea system," *Journal of the Electrochemical Society*, vol. 140, no. 12, pp. 3464–3473, 1993.
- [217] G. Hodes, *Chemical Solution Deposition of Semiconductor Films*, Marcel Dekker, New York, NY, USA, 2002.
- [218] L. Olsen, P. Eschbach, and S. Kundu, "Role of buffer layers in CIS based solar cells," in *Proceedings of the 29th IEEE Photovoltaic Specialists Conference*, p. 652, New York, NY, USA, 2002.
- [219] S. Chaisitsak, A. Yamada, and M. Konagai, "Comprehensive study of light-soaking effect in ZnO/Cu(InGa)Se<sub>2</sub> Solar Cells with Zn-Based Buffer Layers," in *Proceedings of the Materials Research Society Spring Meeting*, San Francisco, Calif, USA, 2001, v.668:H9.10.1.5.
- [220] M. Bär, Ch.-H. Fischer, and H.-J. Muffier, in *Proceedings of the 29th IEEE Photovoltaic Specialists Conference*, p. 636, New Orleans, La, USA, 2002.
- [221] J. Kessler, M. Ruckh, D. Hariskos, U. Ruhle, R. Menner, and H. W. Schock, "Interface engineering between CuInSe<sub>2</sub> and ZnO," in *Proceedings of the 23rd IEEE Photovoltaic Specialists Conference*, pp. 447–452, Louisville, Ky, USA, May 1993.
- [222] A. Romeo, R. Gysel, and S. Buzzi, "Properties of CIGS solar cells developed with evaporated II–VI buffer layers," in *Proceedings of the Technical Digest of the 14th International Photovoltaic Science and Engineering Conference*, p. 705, Bangkok, Thailand, 2004.
- [223] M. Rusu, T. Glatzel, C. A. Kaufmann et al., "High-efficient ZnO/PVD-CdS/Cu(In,Ga)Se<sub>2</sub> thin film solar cells: formation of the buffer-absorber interface and transport properties," in *Proceedings of the Materials Research Society Symposium: Thin-Film Compound Semiconductor Photovoltaics*, vol. 865, pp. F14.25.1–F14.25.7, San Francisco, Calif, USA, April 2005.
- [224] D. Schmid, M. Ruckh, and H. W. Schock, "A comprehensive characterization of the interfaces in Mo/CIS/CdS/ZnO solar cell structures," *Solar Energy Materials and Solar Cells*, vol. 41–42, pp. 281–294, 1996.
- [225] M. A. Contreras, M. J. Romero, B. To et al., "Optimization of CBD CdS process in high-efficiency Cu(In,Ga)Se<sub>2</sub>-based solar cells," *Thin Solid Films*, vol. 403–404, pp. 204–211, 2002.
- [226] U. Rau and M. Schmidt, "Electronic properties of ZnO/CdS/Cu(In,Ga)Se<sub>2</sub> solar cells—aspects of heterojunction formation," *Thin Solid Films*, vol. 387, no. 1–2, pp. 141–146, 2001.
- [227] P. Garg, A. Garg, A. C. Rastogi, and J. C. Garg, "Growth and characterization of electrodeposited CuInSe<sub>2</sub> thin films from seleno-sulphate solution," *Journal of Physics D*, vol. 24, no. 11, pp. 2026–2031, 1991.
- [228] S. N. Sahu, R. D. L. Kristensen, and D. Haneman, "Electrodeposition of CuInSe<sub>2</sub> thin films from aqueous solution," *Solar Energy Materials*, vol. 18, no. 6, pp. 385–397, 1989.
- [229] C. X. Qiu and I. Shih, "Investigation of electrodeposited CuInSe<sub>2</sub> films," *Canadian journal of physics*, vol. 65, no. 8, pp. 1011–1014, 1987.
- [230] V. K. Kapur, B. M. Basol, and E. S. Tseng, "Low cost methods for the production of semiconductor films for CuInSe<sub>2</sub>/CdS solar cells," *Solar Cells*, vol. 21, no. 1–4, pp. 65–72, 1987.
- [231] S. N. Qiu, L. Li, C. X. Qiu, I. Shih, and C. H. Champness, "Study of CuInSe<sub>2</sub> thin films prepared by electrodeposition," *Solar Energy Materials and Solar Cells*, vol. 37, no. 3–4, pp. 389–393, 1995.
- [232] A. Rockett and R. W. Birkmire, "CuInSe<sub>2</sub> for photovoltaic applications," *Journal of Applied Physics*, vol. 70, no. 7, pp. R81–R97, 1991.
- [233] D. Schmid, M. Ruckh, F. Grunwald, and H. W. Schock, "Chalcopyrite/defect chalcopyrite heterojunctions on the basis of CuInSe<sub>2</sub>," *Journal of Applied Physics*, vol. 73, no. 6, pp. 2902–2909, 1993.
- [234] Y. Sudo, S. Endo, and T. Irie, "Preparation and characterization of electrodeposited CuInSe<sub>2</sub> thin films," *Japanese Journal of Applied Physics. Part 1*, vol. 32, no. 4, pp. 1562–1567, 1993.
- [235] R. W. Birkmire and E. Eser, "Polycrystalline thin film solar cells: present status and future potential," *Annual Review of Materials Science*, vol. 27, no. 1, pp. 625–653, 1997.
- [236] H.-W. Schock and R. Noufi, "CIGS-based solar cells for the next millennium," *Progress in Photovoltaics: Research and Applications*, vol. 8, no. 1, pp. 151–160, 2000.
- [237] A. Kylner, A. Rockett, and L. Stolt, "Oxygen in solution grown CdS films for thin film solar cells," *Diffusion and Defect Data B*, vol. 51–52, pp. 533–540, 1996.
- [238] T. Nakada and A. Kunioka, "Direct evidence of Cd diffusion into Cu(In,Ga)Se<sub>2</sub> thin films during chemical-bath deposition process of CdS films," *Applied Physics Letters*, vol. 74, no. 17, pp. 2444–2446, 1999.
- [239] Y. Hashimoto, N. Kohara, T. Negami, N. Nishitani, and T. Wada, "Chemical bath deposition of CdS buffer layer for CIGS solar cells," *Solar Energy Materials and Solar Cells*, vol. 50, no. 1–4, pp. 71–77, 1998.
- [240] C. Guillén, M. A. Martínez, C. Maffiotte, and J. Herrero, "Chemistry of CdS/CuInSe<sub>2</sub> structures as controlled by the CdS deposition bath," *Journal of the Electrochemical Society*, vol. 148, no. 11, pp. G602–G606, 2001.
- [241] A. Kylner, "Effect of impurities in the CdS buffer layer on the performance of the Cu(In, Ga)Se<sub>2</sub> thin film solar cell," *Journal of Applied Physics*, vol. 85, no. 9, pp. 6858–6865, 1999.
- [242] T. Negami, Y. Hashimoto, and S. Nishiwaki, "Cu(In,Ga)Se<sub>2</sub> thin-film solar cells with an efficiency of 18%," *Solar Energy Materials and Solar Cells*, vol. 67, no. 1–4, pp. 331–335, 2001.
- [243] L. Kronik, U. Rau, J.-F. Guillemoles, D. Braunger, H.-W. Schock, and D. Cahen, "Interface redox engineering of Cu(In,Ga)Se<sub>2</sub>-based solar cells: oxygen, sodium, and chemical bath effects," *Thin Solid Films*, vol. 361, pp. 353–359, 2000.
- [244] C. Heske, D. Eich, R. Fink et al., "Observation of intermixing at the buried CdS/Cu(In, Ga)Se<sub>2</sub> thin film solar cell heterojunction," *Applied Physics Letters*, vol. 74, no. 10, pp. 1451–1453, 1999.
- [245] S. Chaisitsak, A. Yamada, and M. Konagai, "Preferred orientation control of Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> (x ≈ 0.28) thin films and its influence on solar cell characteristics," *Japanese Journal of Applied Physics. Part 1*, vol. 41, no. 2, pp. 507–513, 2002.
- [246] T. M. Friedlmeier, D. Braunger, D. Hariskos, M. Kaiser, H. N. Wanka, and H. W. Schock, "Nucleation and growth of the CdS buffer layer on Cu(In,Ga)Se<sub>2</sub> thin films," in *Proceedings of the 25th IEEE Photovoltaic Specialists Conference*, pp. 845–848, May 1996.
- [247] M. G. Sandoval-Paz, M. Sotelo-Lerma, A. Mendoza-Galvan, and R. Ramírez-Bon, "Optical properties and layer microstructure of CdS films obtained from an ammonia-free chemical bath deposition process," *Thin Solid Films*, vol. 515, no. 7–8, pp. 3356–3362, 2007.
- [248] H. Komaki, A. Yamada, K. Sakurai et al., "CIGS solar cell with CdS buffer layer deposited by ammonia-free process," *Physica Status Solidi A*, vol. 206, no. 5, pp. 1072–1075, 2009.
- [249] J. R. Mann, N. Vora, and I. L. Repins, "In Situ thickness measurements of chemical bath-deposited CdS," *Solar Energy Materials and Solar Cells*, vol. 94, no. 2, pp. 333–337, 2010.

- [250] N. Naghavi, C. Hubert, O. Kerrec, et al., in *Proceedings of the 22nd European Photovoltaic Solar Energy Conference*, p. 2304, 2007.
- [251] M. Powalla, G. Voorwinden, D. Hariskos, P. Jackson, and R. Kniese, "Highly efficient CIS solar cells and modules made by the co-evaporation process," *Thin Solid Films*, vol. 517, no. 7, pp. 2111–2114, 2009.
- [252] T. Nakada and M. Mizutani, "18% efficiency Cd-free Cu(In, Ga)Se<sub>2</sub> thin-film solar cells fabricated using chemical bath deposition (CBD)-ZnS buffer layers," *Japanese Journal of Applied Physics. Part 2*, vol. 41, no. 2 B, pp. L165–L167, 2002.
- [253] A. J. Nelson, C. R. Schwerdtfeger, S.-H. Wei et al., "Theoretical and experimental studies of the ZnSe/CuInSe<sub>2</sub> heterojunction band offset," *Applied Physics Letters*, vol. 62, no. 20, pp. 2557–2559, 1993.
- [254] M. M. Islam, S. Ishizuka, A. Yamada et al., "CIGS solar cell with MBE-grown ZnS buffer layer," *Solar Energy Materials and Solar Cells*, vol. 93, no. 6-7, pp. 970–972, 2009.
- [255] S. Siebentritt, T. Kampschulte, A. Bauknecht et al., "Cd-free buffer layers for CIGS solar cells prepared by a dry process," *Solar Energy Materials and Solar Cells*, vol. 70, no. 4, pp. 447–457, 2002.
- [256] F. Engelhardt, M. Schmidt, Th. Meyer, O. Seifert, and J. Parisi, in *Proceedings of the 2nd World Conference on PV Solar Energy Conversion*, 1998.
- [257] Y. Ohtake, K. Kushiya, A. Yamada, and M. Konagai, "Development of ZnO/ZnSe/CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> thin-film solar cells with band gap of 1.3 to 1.5 eV," in *Proceedings of the 1st World Conference on Photovoltaic Solar Energy Conversion*, p. 218, 1994.
- [258] Y. Ohtake, K. Kushiya, M. Ichikawa, A. Yamada, and M. Konagai, "Polycrystalline Cu(InGa)Se<sub>2</sub> thin-film solar cells with ZnSe buffer layers," *Japanese Journal of Applied Physics. Part 1*, vol. 34, no. 11, pp. 5949–5955, 1995.
- [259] A. Ennaoui, S. Siebentritt, M. Ch. Lux-Steiner, W. Riedl, and F. Karg, "High-efficiency Cd-free CIGSS thin-film solar cells with solution grown zinc compound buffer layers," *Solar Energy Materials and Solar Cells*, vol. 67, no. 1–4, pp. 31–40, 2001.
- [260] Y. Ohtake, S. Chaisitsak, A. Yamada, and M. Konagai, "Characterization of ZnIn<sub>x</sub>Se<sub>y</sub> thin films as a buffer layer for high efficiency Cu(InGa)Se<sub>2</sub> thin-film solar cells," *Japanese Journal of Applied Physics. Part 1*, vol. 37, no. 6, pp. 3220–3225, 1998.
- [261] Y. Ohtake, T. Okamoto, A. Yamada, M. Konagai, and K. Saito, "Improved performance of Cu(InGa)Se<sub>2</sub> thin-film solar cells using evaporated Cd-free buffer layers," *Solar Energy Materials and Solar Cells*, vol. 49, no. 1–4, pp. 269–275, 1997.
- [262] T. Negami, T. Aoyagi, T. Satoh, et al., "Cd free CIGS solar cells fabricated by dry processes," in *Proceedings of the 29th IEEE Photovoltaic Specialists Conference*, p. 656, 2002.
- [263] D. Hariskos, B. Fuchs, R. Menner et al., "The Zn(S,O,OH)/ZnMgO buffer in thin-film Cu(In,Ga)(Se,S)<sub>2</sub>-based solar cells part II: magnetron sputtering of the ZnMgO buffer layer for in-line co-evaporated Cu(In,Ga)Se<sub>2</sub> solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 17, no. 7, pp. 479–488, 2009.
- [264] E. B. Yousfi, B. Weinberger, F. Donsanti, P. Cowache, and D. Lincot, "Atomic layer deposition of zinc oxide and indium sulfide layers for Cu(In,Ga)Se<sub>2</sub> thin-film solar cells," *Thin Solid Films*, vol. 387, no. 1-2, pp. 29–32, 2001.
- [265] S. Spiering, D. Hariskos, M. Powalla, N. Naghavi, and D. Lincot, "CD-free Cu(In,Ga)Se<sub>2</sub> thin-film solar modules with In<sub>2</sub>S<sub>3</sub> buffer layer by ALCVD," *Thin Solid Films*, vol. 431-432, pp. 359–363, 2003.
- [266] J.-F. Guillemoles, B. Canava, E. B. Yousfi et al., "Indium-based interface chemical engineering by electrochemistry and atomic layer deposition for copper indium diselenide solar cells," *Japanese Journal of Applied Physics. Part 1*, vol. 40, no. 10, pp. 6065–6068, 2001.
- [267] S. Spiering, L. Bürkert, D. Hariskos et al., "MOCVD indium sulphide for application as a buffer layer in CIGS solar cells," *Thin Solid Films*, vol. 517, no. 7, pp. 2328–2331, 2009.
- [268] F. Couzinié-Devy, N. Barreau, and J. Kessler, "Influence of absorber copper concentration on the Cu(In,Ga)Se<sub>2</sub>/(PVD)In<sub>2</sub>S<sub>3</sub> and Cu(In,Ga)Se<sub>2</sub>/(CBD)CdS based solar cells performance," *Thin Solid Films*, vol. 517, no. 7, pp. 2407–2410, 2009.
- [269] A. Darga, D. Mencaraglia, Z. Djebbour et al., "Comparative study of Cu(In,Ga)Se<sub>2</sub>/(PVD)In<sub>2</sub>S<sub>3</sub> and Cu(In,Ga)Se<sub>2</sub>/(CBD)CdS heterojunction based solar cells by admittance spectroscopy, current-voltage and spectral response measurements," *Thin Solid Films*, vol. 517, no. 7, pp. 2423–2426, 2009.
- [270] S. Buecheler, D. Corica, D. Guettler et al., "Ultrasonically sprayed indium sulfide buffer layers for Cu(In,Ga)(S,Se)<sub>2</sub> thin-film solar cells," *Thin Solid Films*, vol. 517, no. 7, pp. 2312–2315, 2009.
- [271] A. Eicke, S. Spiering, A. Dresel, and M. Powalla, "Chemical characterisation of evaporated In<sub>2</sub>S<sub>x</sub> buffer layers in Cu(In,Ga)Se<sub>2</sub> thin-film solar cells with SNMS and SIMS," *Surface and Interface Analysis*, vol. 40, no. 3-4, pp. 830–833, 2008.
- [272] D. Abou-Ras, G. Kostorz, D. Hariskos et al., "Structural and chemical analyses of sputtered In<sub>x</sub>S<sub>y</sub> buffer layers in Cu(In,Ga)Se<sub>2</sub> thin-film solar cells," *Thin Solid Films*, vol. 517, no. 8, pp. 2792–2798, 2009.
- [273] Y. Ohtake, M. Ichikawa, T. Okamoto, A. Yamada, M. Konagai, and K. Saito, "Cu(InGa)Se<sub>2</sub> thin-film solar cells with continuously evaporated Cd-free buffer layers," in *Proceedings of the 25th IEEE Photovoltaic Specialists Conference*, pp. 793–796, May 1996.
- [274] N. Barreau, A. Mokrani, F. Couzinié-Devy, and J. Kessler, "Bandgap properties of the indium sulfide thin-films grown by co-evaporation," *Thin Solid Films*, vol. 517, no. 7, pp. 2316–2319, 2009.
- [275] D. Hariskos, R. Herberholz, M. Ruckh, et al., in *Proceedings of the 3th European Photovoltaic Solar Energy Conference*, p. 1995, France, 1995.
- [276] A. Ennaoui, U. Blieske, and M. CH. Lux-Steiner, "13.7%-efficient Zn(Se,OH)<sub>x</sub>/Cu(In,Ga)(S,Se)<sub>2</sub> thin-film solar cell," *Progress in Photovoltaics: Research and Applications*, vol. 6, no. 6, pp. 447–451, 1998.
- [277] C. Hubert, N. Naghavi, O. Roussel et al., "The Zn(S,O,OH)/ZnMgO buffer in thin film Cu(In,Ga)(S,Se)<sub>2</sub>-based solar cells part I: fast chemical bath deposition of Zn(S,O,OH) buffer layers for industrial application on co-evaporated Cu(In,Ga)Se<sub>2</sub> and electrodeposited CuIn(S,Se)<sub>2</sub> solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 17, no. 7, pp. 470–478, 2009.
- [278] R. Sáez-Araoz, A. Ennaoui, T. Kropp, E. Veryaeva, T. P. Niesen, and M. CH. Lux-Steiner, "Use of different Zn precursors for the deposition of Zn(S,O) buffer layers by chemical bath for chalcopyrite based Cd-free thin-film solar

- cells," *Physica Status Solidi A*, vol. 205, no. 10, pp. 2330–2334, 2008.
- [279] A. Hultqvist, C. Platzer-Björkman, J. Pettersson, T. Törndahl, and M. Edoff, "CuGaSe<sub>2</sub> solar cells using atomic layer deposited Zn(O,S) and (Zn,Mg)O buffer layers," *Thin Solid Films*, vol. 517, no. 7, pp. 2305–2308, 2009.
- [280] R. Sáez-Araoz, D. Abou-Ras, T. P. Niesen et al., "In situ monitoring the growth of thin-film ZnS/Zn(S,O) bilayer on Cu-chalcopyrite for high performance thin film solar cells," *Thin Solid Films*, vol. 517, no. 7, pp. 2300–2304, 2009.
- [281] T. Nakada, M. Hongo, and E. Hayashi, "Band offset of high efficiency CBD-ZnS/CIGS thin film solar cells," *Thin Solid Films*, vol. 431–432, pp. 242–248, 2003.
- [282] W. E. Devaney, W. S. Chen, J. M. Stewart, and R. A. Mickelsen, "Structure and properties of high efficiency ZnO/CdZnS/CuInGaSe<sub>2</sub> solar cells," *IEEE Transactions on Electron Devices*, vol. 37, no. 2, pp. 428–433, 1990.
- [283] Rothwarf, "A p-i-n heterojunction model for the thin-film CuInSe<sub>2</sub>/CdS solar cell," *IEEE Transactions on Electron Devices*, vol. 29, no. 10, pp. 1513–1515, 1982.
- [284] N. Romeo, A. Bosio, and V. Canevari, "R.F. sputtered CuInSe<sub>2</sub> thin films for photovoltaic applications," in *Proceedings of the 8th European Photovoltaic Solar Energy Conference*, vol. 2, pp. 1092–1096, Florence, Italy, 1988.
- [285] S. H. Kwon, S. C. Park, B. T. Ahn, K. H. Yoon, and J. Song, "Effect of CuIn<sub>3</sub>Se<sub>5</sub> layer thickness on CuInSe<sub>2</sub> thin films and devices," *Solar Energy*, vol. 64, no. 1–3, pp. 55–60, 1998.
- [286] T. Negami, Y. Hashimoto, and S. Nishiwaki, "Cu(In,Ga)Se<sub>2</sub> thin-film solar cells with an efficiency of 18%," *Solar Energy Materials and Solar Cells*, vol. 67, no. 1–4, pp. 331–335, 2001.
- [287] T. Negami, T. Satoh, Y. Hashimoto et al., "Production technology for CIGS thin film solar cells," *Thin Solid Films*, vol. 403–404, pp. 197–203, 2002.
- [288] T. Minami, H. Sato, H. Nanto, and S. Takata, "Group III impurity doped zinc oxide thin films prepared by RF magnetron sputtering," *Japanese Journal of Applied Physics. Part 2*, vol. 24, no. 10, pp. L781–L784, 1985.
- [289] M. A. Contreras, B. Egaas, K. Ramanathan et al., "Progress toward 20% efficiency in Cu(In,Ga)Se<sub>2</sub> polycrystalline thin-film solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 7, no. 4, pp. 311–316, 1999.
- [290] Y. Hagiwara, T. Nakada, and A. Kunioka, "Improved J<sub>sc</sub> in CIGS thin film solar cells using a transparent conducting ZnO:B window layer," *Solar Energy Materials and Solar Cells*, vol. 67, no. 1–4, pp. 267–271, 2001.
- [291] M. A. Contreras, J. Tuttle, A. Gabor, et al., "High efficiency Cu(In,Ga)Se<sub>2</sub> based solar cells: processing of novel absorber structures," in *Proceedings 1st World conference on Photovoltaic Solar Energy Conversion*, pp. 68–75, IEEE, Hawaii, USA, 1994.
- [292] K. Granath, M. Bodegård, and L. Stolt, "Effect of NaF on Cu(In,Ga)Se<sub>2</sub> thin film solar cells," *Solar Energy Materials and Solar Cells*, vol. 60, no. 3, pp. 279–293, 2000.
- [293] M. Klenk, O. Schenker, V. Alberts, and E. Bucher, "Preparation of device quality chalcopyrite thin films by thermal evaporation of compound materials," *Semiconductor Science and Technology*, vol. 17, no. 5, pp. 435–439, 2002.
- [294] M. Powalla and B. Dimmler, "Scaling up issues of CIGS solar cells," *Thin Solid Films*, vol. 361, pp. 540–546, 2000.
- [295] F. H. Karg, "Development and manufacturing of CIS thin film solar modules," *Solar Energy Materials and Solar Cells*, vol. 66, no. 1–4, pp. 645–653, 2001.
- [296] C. Eberspacher, C. Fredric, K. Pauls, and J. Serra, "Thin-film CIS alloy PV materials fabricated using non-vacuum, particles-based techniques," *Thin Solid Films*, vol. 387, no. 1–2, pp. 18–22, 2001.
- [297] S. Siebentritt, T. Kampschulte, A. Bauknecht et al., "Cd-free buffer layers for CIGS solar cells prepared by a dry process," *Solar Energy Materials and Solar Cells*, vol. 70, no. 4, pp. 447–457, 2002.
- [298] Z. A. Wang, J. B. Chu, H. B. Zhu, Z. Sun, Y. W. Chen, and S. M. Huang, "Growth of ZnO:Al films by RF sputtering at room temperature for solar cell applications," *Solid-State Electronics*, vol. 53, no. 11, pp. 1149–1153, 2009.
- [299] T. Nakada, N. Murakami, and A. Kunioka, "Transparent conducting Al-, AlB12-, and B-doped ZnO films for solar cells by dc magnetron sputtering," in *Proceedings of the 12th European Photovoltaic Solar Energy Conference*, pp. 1507–1610, Amsterdam, The Netherlands, 1994.
- [300] S. Chaisitsak, A. Yamada, and M. Konagai, "Preferred orientation control of Cu(In<sub>1-x</sub>Ga<sub>x</sub>)Se<sub>2</sub> (x ≈ 0.28) thin films and its influence on solar cell characteristics," *Japanese Journal of Applied Physics*, vol. 41, pp. 507–513, 2002.
- [301] V. Probst, W. Stetter, W. Riedl et al., "Rapid CIS-process for high efficiency PV-modules: development towards large area processing," *Thin Solid Films*, vol. 387, no. 1–2, pp. 262–267, 2001.
- [302] B. M. Basol, V. K. Kapur, G. Norsworthy, A. Halani, C. R. Leidholm, and R. Roe, "Efficient CuInSe<sub>2</sub> solar cells fabricated by a novel ink coating approach," *Electrochemical and Solid-State Letters*, vol. 1, no. 6, pp. 252–254, 1998.
- [303] T. Sugiyama, S. Chaisitsak, A. Yamada et al., "Formation of pn homojunction in Cu(InGa)Se<sub>2</sub> thin film solar cells by Zn doping," *Japanese Journal of Applied Physics. Part 1*, vol. 39, no. 8, pp. 4816–4819, 2000.
- [304] N. F. Cooray, K. Kushiya, A. Fujimaki et al., "Large area ZnO films optimized for graded band-gap Cu(InGa)Se<sub>2</sub>-based thin-film mini-modules," *Solar Energy Materials and Solar Cells*, vol. 49, no. 1–4, pp. 291–297, 1997.
- [305] Y. Hagiwara, T. Nakada, and A. Kunioka, "Improved J<sub>sc</sub> in CIGS thin film solar cells using a transparent conducting ZnO:B window layer," *Solar Energy Materials and Solar Cells*, vol. 67, no. 1–4, pp. 267–271, 2001.
- [306] M. Yu, H. Qiu, X. Chen, H. Liu, and M. Wang, "Structural and physical properties of Ni and Al co-doped ZnO films grown on glass by direct current magnetron co-sputtering," *Physica B*, vol. 404, no. 12–13, pp. 1829–1834, 2009.
- [307] J. S. Wellings, A. P. Samantilleke, P. Warren, S. N. Heavens, and I. M. Dharmadasa, "Comparison of electrodeposited and sputtered intrinsic and aluminium-doped zinc oxide thin films," *Semiconductor Science and Technology*, vol. 23, no. 12, Article ID 125003, 2008.
- [308] B. N. Pawar, G. Cai, D. Ham et al., "Preparation of transparent and conducting boron-doped ZnO electrode for its application in dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 93, no. 4, pp. 524–527, 2009.
- [309] X.-T. Hao, J. Ma, D.-H. Zhang et al., "Comparison of the properties for ZnO:Al films deposited on polyimide and glass substrates," *Materials Science and Engineering B*, vol. 90, no. 1–2, pp. 50–54, 2002.
- [310] S. Fernández, A. Martínez-Steele, J. J. Gandía, and F. B. Naranjo, "Radio frequency sputter deposition of high-quality conductive and transparent ZnO:Al films on polymer substrates for thin film solar cells applications," *Thin Solid Films*, vol. 517, no. 10, pp. 3152–3156, 2009.
- [311] S. Calnan and A. N. Tiwari, "High mobility transparent conducting oxides for thin film solar cells," *Thin Solid Films*, vol. 518, no. 7, pp. 1839–1849, 2010.

