Review

CIGS Thin Film Solar Cells by Electrodeposition

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Abstract : Thin film solar cells with chalcopyrite $CuInSe_2$/$Cu(In,Ga)Se_2$ absorber materials, commonly known as "CIS/CIGS solar cells" have recently attracted significant research interest as a potential alternative energy-harvesting system for the next generation. Among the different deposition techniques available for the CIGS absorber layer, electrodeposition is an effective and low cost alternative to vacuum based deposition methods. This article reviews progress in the area of CIGS solar cells with an emphasis on electrodeposited absorber layer. Existing challenges in fabrication of stoichiometric absorber layer are highlighted.

Keywords : Thin film solar cell, Chalcopyrite CIGS, Absorber layer, Electrodeposition

1. Introduction

1.1. Thin film solar cells

While fossil fuels end up with contaminating the global environment and changing the global climate, photovoltaics remains one of the clean energy options for a pollution-free globe and is going to be the major means for future energy-harvesting system. Solar cells utilize the mechanism of photovoltaic effect, and convert sunlight directly into electricity without any intermediate steps. Solar cells are easy to install and use, and their operational lifetimes are long, with minimal maintenance. To enhance the current conversion efficiency and to develop low cost cells, widespread research investigations are being conducted. The main component of a solar cell is the light absorber material, a semiconductor. The absorbed light excites dormant electrons in the semiconductor to higher energy levels. These electrons are captured in a typical *pn* junction before they regain their ground state energy level configuration. Typically some of the generated electrons are extracted from the device as current; while other electrons create a voltage giving rise to a power output from the cell. An ideal absorber material should be a direct band gap semiconductor having high absorption coefficient, long diffusion length and low recombination velocity and should be able to form a good electronic junction with suitably compatible materials.[1] Organic compounds are also explored as semiconductors, as alternatives to the inorganic counterparts; however their efficiency is found to be less. In an organic semiconductor, photon absorption leads to excitons formation rather than free charges.[2]

Depending upon the cell material and the processing technology, solar cells are of different type. Most commercial solar cells for use in terrestrial applications are "Si wafer solar cells" (single crystalline and polycrystalline), which constitute a significant fraction of the total solar cell market (more than 80%; maximum reported efficiency ~25%).[3] The second and the most promising class is "thin film solar cells". The market of thin film solar cell is expected to grow significantly in the coming years.[4] Thin film technology has made solar cells more feasible to be employed as solar shingles, roof tiles, building facades etc. However the efficiencies of these cells tend to be lower than the crystalline silicon solar cells. Many investigations are also going on other more recently invented solar cells which uses dye sensitized mesoporous nanocrystalline TiO_2 absorber layer (dye sensitized solar cells, maximum reported efficiency ~11-12%) as well as on organic photovoltaic cells (bulk heterojunction solar cells, maximum reported efficiency ~6-7%).[4] Arrangement of cells in tandem is an additional approach in exploring wider absorption window, by employing combination of different band gap absorbers.[5]

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Thin film solar cells have the key advantage of their dimensionality, having thickness a fraction of other types of solar cells and offer a wide variety of choices in terms of the device design and fabrication. A thin film solar cell uses a direct band gap semiconductor as the absorber material. Such direct band gap semiconductors have several advantages over the indirect band gap crystalline silicon. The indirect band gap necessitates thick layer of the absorber material to achieve sufficient light absorption which in turn may have disadvantageous outputs in terms of electron diffusion length and recombination kinetics. The thin film dimension is attractive in terms of materials cost factor and reduces impurities and crystalline imperfections of the layer and easier to mass produce. The fabrication process involves deposition of different layers (contact, absorber, buffer, reflector etc) and the overall efficiency of such cells depends on the final processed quality of the layers and their interfaces. The substrates used for fabrication can be an inexpensive rigid glass or a flexible metal/polymer. Flexible thin film solar cells have many advantages over rigid counterparts and have many application possibilities.

The main low cost thin film absorber materials of current interest are amorphous Si, CdTe and $CuInSe_2$ (CIS) and its alloys with Ga and/or S. Amorphous Si:H solar cells have the merits such as non-toxicity, abundant resources, low temperature and low cost processing; however their efficiency is comparatively lower (~10%). Also, they suffer from light induced degradation leading to long term stability issues.[2] CdTe and (Cu(In/Ga)(Se/S)$_2$) are newer additions to the thin film family. The maximum reported efficiency of CdTe cells is ~17%.[6] However, the extremely toxic Cd and the environmental regulations make CdTe/CdS solar cells unattractive. The chalcopyrite (Cu(In/Ga)(Se/S)$_2$) is perhaps the most promising material in this category with a maximum reported laboratory scale cell efficiency of ~20%.[7] They have the highest light absorption coefficient (1×10^5/cm) which is advantageous over other thin film solar cells (Fig. 1). CIS-based cells have demonstrated excellent long term stability with high radiation resistance. One issue of concern is the availability of less common elements. Many efforts are currently going on in this field to enhance the efficiency to the theoretical maximum (~30%) as well as to develop cheaper deposition strategies for the chalcopyrite absorber layer.
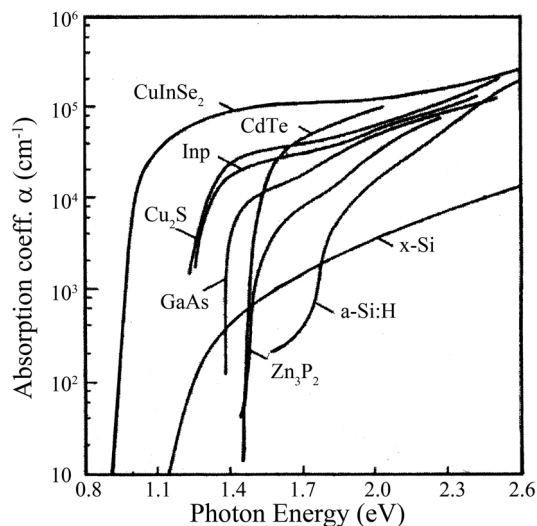

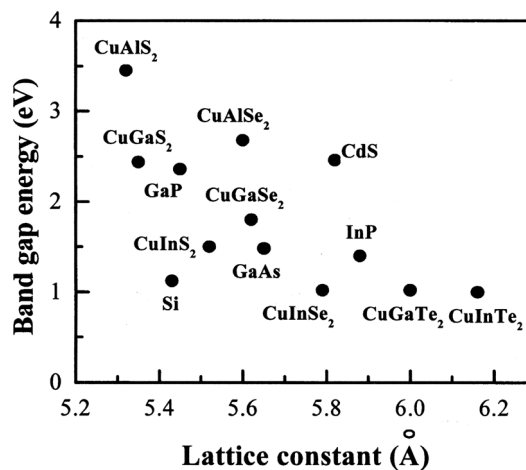**Fig. 1.** Absorption spectra of various semiconductors.[67]

Fig. 2. Plot of band gap energy versus lattice constant for tandem structure by composition control ($CuInSe_2$: 1.04 eV, $CuGaSe_2$: 1.68 eV, $CuInS_2$: 1.53 eV, $CuGaS_2$: 2.53 eV, $CuAlSe_2$: 2.72 eV).[68,69]

1.2. Cu(In/Ga)Se$_2$ (CIGS) solar cells

The band gap of CIS is relatively low (1.04 eV); slightly below the range of optimum conversion efficiency of solar cells (1.4-1.5 eV).[8] The band gap can be suitably adjusted to a desired value by alloying with Ga, Al and/or S. The ternary compound $CuInS_2$ has a direct bandgap of 1.53 eV. However relatively rapid diffusion of metals and impurity species occur in this phase even at low temperatures.[9] Fig. 2 shows band gap variation of different thin film materials as a function of lattice

constant. It is understood that Ga substitution for In ($Cu(In/Ga)Se_2$) is probably the best option for increasing the band gap (in between 1.04 eV of $CuInSe_2$ and 1.7 eV of $CuGaSe_2$) to a desired value and to achieve enhanced current conversion efficiency.[10-12] The CIS/CIGS compounds typically crystallize in a tetragonal chalcopyrite structure (Fig. 3), which can be considered as super-lattice structure of zinc blend structure.

Fig. 4 shows a schematic representation of a CIGS cell. Mo sputtered on a glass substrate is usually used as the back contact. The preferred window or transparent conducting oxide (TCO) film consists of ZnO deposited by sputtering or chemical vapor deposition methods. A thin CdS acts as buffer layer which protects the absorber layer against chemical reactions and mechanical damage, and further helps in widening the depletion layers at the interface allowing a higher open circuit voltage (V_{oc}). It also helps in optimizing the band alignment of the device. Typically this layer is deposited by a chemical bath deposition technique.[13,14] To avoid the toxic Cd, other materials have also been tried as buffer layer. However, the best results have been obtained with CdS and the material continues to be the preferred one. The device structure of the maximum efficiency cell consisted of: soda-lime *glass substrate*, sputtered *Mo back contact*, three stage co-evaporated *CIGS layer*, chemical bath-deposited *CdS*, sputtered resistive/conductive *ZnO bilayer*, e-beam-evaporated *Ni/Al grids*, *antireflective* MgF_2 coating, and photolithographic device isolation.[7]
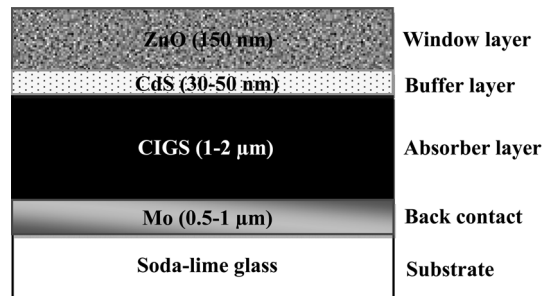

Fig. 4. Schematic layer sequence of a standard CIGS solar cell.

Many groups have categorically proved that CIGS solar cell efficiency exceeds 15%.[7,15-17] The highest module efficiency reported is ~13%.[18,19] In spite of having very high short circuit current density (J_{sc}), the main reason for the low cell efficiency in many of the reported laboratory works is the low fill factor (FF) values. The low FF was suggested to be due to external factors such as series and shunt resistance and not due to the junction limitations.[12] According to the reporters of the maximum efficiency cell, the enhancement in efficiency was mainly due to the small increment in FF which was attributed to the decreased recombination.[7] According to Rau *et al.* electron recombination varies with the film stoichiometry; recombination in bulk is the main loss mechanism in Cu poor absorbers, whereas recombination at CIGS/CdS interface dominates in devices with Cu-rich absorbers.[20] However, time-resolved photoluminescence studies
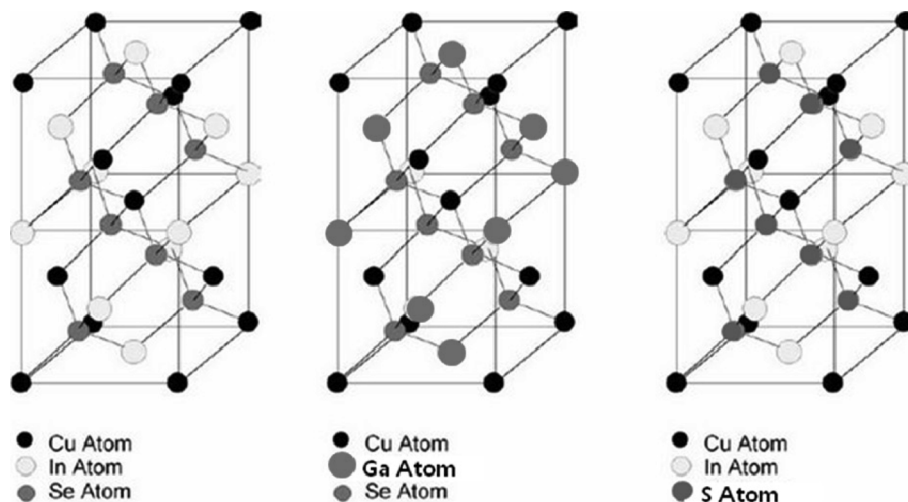

Fig. 3. Crystal structure of chalcopyrite ($a = b = 5.78$ Å, $c = 11.62$ Å).

suggested that for a high quality CIGS film, the surface and grain-boundary recombinations are relatively too low; not greater than ~10^3 cm/s.[21] The electrical stability of the CIGS cell is described to be a dynamic one that is capable of sensing changes in its environment and responding to them.[22] In a recent work, Shirakata et al.[23] has showed that no remarkable change in the carrier-recombination dynamics occurred due to the deposition of CdS on CIGS, implying that the buffer layer does not affect the recombination kinetics significantly. Many debates are going on the photovoltaic active junction, p-CIGS/n-CdS interface. Chaure et al. suggested that a photovoltaic junction can be formed by a homo-junction buried within the CIGS layer itself due to the inhomogeneous distribution of elements within the material (Cu/Se- p type and In/Ga- n type).[24] The current understanding on the electron transport and recombination in the absorber layer and the CIGS/CdS interface seems inadequate, demanding more studies to characterize the fundamental properties.

CIGS solar cells employing a *flexible substrate* instead of the soda lime glass have attracted significant attention within the past few years.[25] The flexible substrate can be a metal (Ti, stainless steel, Mo, Cu etc) or polymer (polyimide) or a ceramic sheet (zirconia). Among these metallic foils offer the possibility to deposit the CIGS layer at temperatures similar or higher than those used for high-quality absorber on glass substrate. Efficiencies above 16% were reported on flexible metal substrates.[16,26] One major problem with the metal substrates is the undesirable diffusion of impurities into the absorber at higher processing temperatures. The efficiency achieved through polymer substrates is comparatively lower (less than 15%), mainly due to the limited thermal stability of polymers which demands novel low temperature pro-cessing.[26] Flexible CIGS solar cells usually require an additional Na-doping step into the absorber layers to enhance the cell efficiency.[27]

1.3. Difficulties in making CIGS layer - graded band gaping

The increasing number of alloy components makes the CIGS layer fabrication an extremely complex process. The film morphology and the resulting conversion efficiency depend on the relative ratio of the compo-nent elements in the fabricated layer. The Cu/(In+Ga) and Ga/(In+Ga) ratios are found to be critical in determining the cell efficiency.[28]

Theoretically, to achieve the optimal band gap (1.4-1.5 eV), addition of ~70% Ga is needed.[29] However, it has been shown that when the Ga content increases to this level, the cell efficiency get decreased. The highest efficiency was obtained when the Ga content was ~30% (band gap -1.2). This phenomenon was explained in terms of the film inhomogeneity, leading to band gap fluctuations.[30,31] Photoluminescence measurements indicated that a higher Ga content in the film leads to larger inhomogeneities.[31] Ludwig et al. conducted computer simulation studies on spatial distribution of In and Ga and showed that In-rich CIGS exhibits a higher homogeneity than Ga-rich CIGS.[28] Few groups reported that Ga preferentially enriches in the Mo back contact side.[7] In a very recent work Khelifi et al. suggested that Ga enrichment happened at both edges of the absorber, i.e. towards the buffer layer and the contact.[25] The spatial variation of the Ga content within the CIGS layer can be employed to optimize the CIGS absorber band-gap profile (band gap grading), and hence improve the cell efficiency.[32]

Due to the tunability of the band gap, chalcopyrite solar cells could be ideal candidates for application in tandem solar cells. Other thin film solar cells (amorphous Si, CdTe, or DSSC) can also be employed as the top cell in combination with CIGS based bottom cells. Currently many such attempts are going in this area.[33]

1.4. Different deposition strategies for CIGS layer

The available techniques for the deposition of the chalcopyrite absorber layer can be divided into two; vacuum based methods and solution based methods.[34] Techniques such as physical/chemical vapor deposition, magnetron sputtering, e-beam thermal evaporation etc are examples of vacuum based deposition methods whereas electrodeposition, chemical spray pyrolysis, printing, spin coating and paste coating come under the latter. The most widely employed vacuum based approach is co-evaporation in which all the four constituent elements were simultaneously delivered to the substrate and the film is formed in a single step. The co-evaporation generally requires a high degree of control and large area coatings with uniform properties are difficult to achieve. The deposition can be performed by sequential evaporation. In a typical sequential method, the metals are deposited first followed by a selenization

step (by exposure to Se vapor at high temperatures).[35] In spite of the fact that the cell efficiencies obtained from CIGS layer fabricated by the vacuum processes were higher, the cheap and convenient solution-based approaches magnetize significant research interest as a potential alternative. Among the different solution based methods, the most intensely investigated and striking strategy may be the electrodeposition.

Electrodeposition is a versatile technique in making nanomaterials and nanocoatings of metals, alloys and semiconductors. The main advantages of the method are low instrumental and materials cost, high deposition speed, efficient utilization of raw materials and feasibility in making large area films.[36,37] Usually, a simple three-electrode setup is employed for electrodeposition, consisting of the substrate on which film grows (working electrode), the inert counter electrode of often a Pt wire/plate and the reference electrode of SCE or Ag/AgCl etc. The use of flexible metal foils as the substrate is advantageous here as the metal foils itself can be employed as the working electrode, thus avoiding the Mo back contact deposition. When compared to the electrodeposition of a single element, deposition of multi-element compounds is usually complex as different elements have different redox potentials. The deposition gets intricate when one wishes to have a desired stoichiometry of the compound. Solubility of different salts in a common solvent is another usual problem that can be faced.

2. Electrodeposition of CIGS layer

While many reports are available on the electro-deposited CIS films, reported studies on electro-deposition of CIGS are limited. The reason behind this can be attributed to the difficulties in controlling the electrochemistry of the four species of wide-ranging potentials. The standard reduction potential values of Se^{4+}/Se, Cu^{2+}/Cu, In^{3+}/In and Ga^{3+}/Ga are +0.740, +0.342, −0.338 and −0.523 V vs SHE respectively. The significantly differing potentials often cause preferential deposition of single elements. Due to the more negative reduction potential of Ga, incorporating desired Ga levels into the deposited film is a difficult task. Avoiding co-deposition of oxides and other secondary phases and the instability of In^{3+} and Ga^{3+} ions in aqueous conditions at near neutral and alkaline pH are other issues.[38]

CIGS layer can be electrodeposited in one step or by a two stage approach. In a simultaneous (one step) deposition, the concentration and pH of the electrolyte ought to be adjusted such that the electrode potentials of all the individual elements may come closer to each other. The two-stage strategy can be employed via stacked layer structure deposition of pure elements or of combinations with binary or even ternary films followed by a selenization treatment.[39,40] In order to simplify thin film fabrication and reduce harmful emissions, one step deposition is often preferred. Hermann et al. reported that while films grown using multiple step electrodeposition have ultrasmooth surface, stoichiometric control of the films is difficult to achieve.[41] Usually the as-deposited CIGS films are Cu-rich, poorly crystalline and consist of Cu-Se second phases which necessitates a post-annealing treatment.[42,43] The high temperature post-annealing helps to make compact and crack free films with uniform grain size. Typically the post-annealing is performed in a Se-rich environment. The Se atmosphere prevent Se atom of the film from escaping and helps in maintaining the film stoichiometry.

2.1. Post vacuum deposition as a means to adjust the film stoichiometry

Many groups have employed a vacuum based physical vapor deposition (PVD of In, Ga, and Se at high substrate temperatures, ~500°C) approach to adjust the stoichiometry of the as-electrodeposited films. It was Bhattacharya et al. who employed a PVD on the as-electrodeposited CIGS layer to adjust the film quality and stoichiometry. The as-electrodeposited film was poor in Ga and rich in Cu and Se, having a composition of $Cu_{2.00}In_{0.71}Ga_{0.06}Se_{2.00}$. In addition, to adjust the final composition, the high operating temperature (~550°C) helped in crystallization. The film was selenized by exposing to Se vapor during cool down time. The final composition of the film was $Cu_{0.92}In_{0.76}Ga_{0.24}Se_{2.00}$. The absorber layer in a cell yielded an overall cell efficiency of 12.3%, with $J_{sc} = 30.60$ mA/cm^2, $V_{oc} = 0.54$ V and FF = 66.93%.[44] Addition of In and Ga by physical evaporation and also selenization at high temperature was found to be very important for obtaining the efficiency. In a subsequent work, the group reported a 14.1% efficient cell employing an electrodeposited and PVD adjusted film.[45] The cell parameters obtained were $J_{sc} = 29.03$ mA/cm^2, $V_{oc} = 0.656$ V and FF = 74.1%. They have reported a 15.4% efficient cell with the same

sequence in the year 2000.[46] The composition of the as-deposited film was $CuIn_{0.32}Ga_{0.01}Se_{0.93}$ which was adjusted by adding about 3000 Å Ga and 7200 Å In by the PVD step. The final compositions of the CIGS absorber film was $CuIn_{0.72}Ga_{0.47}Se_{2.05}$. In a successive work, the authors achieved a near stoichiometric film employing a buffered bath. The as-deposited precursors were found to be almost stoichiometric or slightly Cu-rich and thereby reduced the post-deposition to only a minimal amount of In.[47] Current-voltage characteristic of the device prepared from the electrodeposited precursor film was $J_{sc} = 35.41\ mA/cm^2$, $V_{oc} = 0.413\ V$, FF = 64% and efficiency = 9.4%. The authors attributed the low efficiency to the micro-cracks observed in the film and not to the reduced PVD step.

Efficient CIGS solar cells prepared directly from electrodeposited near stoichiometric precursor films without the post PVD process were reported by several research groups. Lincot et al.[43] reported an efficiency of 11.3% ($J_{sc} = 23.2\ mA/cm^2$, $V_{oc} = 0.77\ V$, FF = 63.4%) for an electrodeposited CIGS absorber with a band gap of 1.47 eV. Guimard et al.[48] recorded a cell efficiency of 10.2% without the PVD step. The cell parameters were $J_{sc} = 23.2\ mA/cm^2$, $V_{oc} = 0.74\ V$ and FF = 59.6%. Electrodeposition of an elemental layer stack followed by the selenization treatment led to 7-10% efficient devices [49]. Ganchev et al.[50] deposited the absorber film from a thiocynate assisted bath, followed by selenization in a quartz tube furnace at 560°C under the Se pressure of 10 mbar. However, the efficiency of the best cell (Mo/CIGS/CdS/i-ZnO/Al : ZnO) was of only 4.35%, with $J_{sc} = 31.7\ mA/cm^2$, $V_{oc} = 300\ mV$ and FF = 45.6%. Dale et al. reported a cell efficiency of 4.5%.[51]

These reported works showed that the cell efficiency increased considerably as a result of the post vacuum deposition. This increase was attributed to the near film stoichiometry and the resulting band gap. However stoichiometric films prepared without the post vacuum deposition always showed lower efficiency. It can be noticed that the cells constructed with the post vacuum deposited CIGS layer always showed higher FF values. This may be another reason for the obtained higher efficiency. The post-deposition may also be beneficial in avoiding micro cracks and defects in the film. However, it should be noted that the post PVD step is not acceptable in terms of cost factor.

2.2. Role of deposition parameters

Electrodeposition of high-quality CIGS film requires strict control of chemical composition of the plating bath, pH and deposition potential. In conventional plating, different agents such as complexing agents, conductivity salts, stabilizing agents, wetting agent etc are added to the bath besides the precursor salts, to enhance the deposition.[36] Process conditions like bath temperature, agitation etc can significantly affect the film composition and quality. Many attempts were made to optimize the electrolyte bath by the addition of complexing agents and buffering agents to make good quality CIGS films. The co-deposition bath used by Bhattacharya et al.[44] was 0.016 M $Cu(NO_3)_2 \cdot 6H_2O$, 0.08 M $InCl_3$, 0.024 M H_2SeO_3, and 0.08 M $Ga(NO_3)_3$ (pH = 1.6). The electrolyte was stagnant. The bath used by the group to achieve 14.1% and 15.4% efficiency was 0.009 M $CuCl_2$, 0.027 M $InCl_3$, 0.040 M $GaCl_3$, 0.009 M H_2SeO_3, and 0.28 M LiCl. Addition of the supporting electrolyte (LiCl) was found to help to incorporate more Ga in the precursor and improved the film morphology.[45,52] Usually acidic pH (1.5-2.5) is employed in CIGS electrodeposition as In and Ga salts are unstable in neutral and alkaline media.

With the selection of appropriate complexing agents such as thiocynate, Cu, In and Ga ions could be solubilized at high pH regime and their reduction potentials could be brought down, closer to that of Se reduction potential.[36,50] Citrate ions present a complexing effect on Cu^{2+} and H_2SeO_3 but have no apparent effect on In^{3+} and Ga^{3+}.[53] It was found that tartrate and citrate were suitable complexing agents to solubilize In and Ga ions at high pH, respectively.[54] To enhance the stability of the bath and to avoid metal oxides or hydroxides precipitation, many groups employed a buffer solution-based bath. The use of the pH buffer solution permits the absorption of the free OH^- and H^+ ions that exist in the deposition bath. The buffer (pH 3) solution employed was a mixture of sulphamic acid and potassium biphthalate and the as-deposited precursors were found to be stoichiometric or slightly Cu-rich.[47] However there is no obvious proof on the precise role of such additives and in fact the usage of such organic additives may complicate the deposition to result in impure products.

The film composition changes significantly even for small changes in the deposition potential. At lower potentials (~ −0.1 V vs SCE), the film formed found

constitutes of Cu-Se (50 : 50 at.%) phases. To more negative potentials, the Se profile initially increased for the film deposited at −0.2 V, before decreased to stabilize at 50 at.% at potentials below −0.35 V. Cu levels showed a significant decrease at −0.2 V and a further decrease for the film grown at −0.4 V, dropping to ~25 at.%. The latter decrease corresponds with a significant increase in In uptake to ~18 at.%. Around 6 at.% Ga is consistently detected in films deposited at cathodic potentials above −0.2 V.[38] Most of the reported works suggest that the potential range of −0.5 to −0.8 V *vs* SCE is the best to achieve nearly stoichiometric composition.[55]

By suitably adjusting the bath parameters, it may be possible to make films with different grain morphology. In conventional plating, the deposited films can have different structure based on their grain morphology such as a) columnar, b) fibrous c) fine grained/very fine grained and d) banded.[36] The usual film morphology of electrodeposited CIGS is columnar.[56] Such columnar structures are characteristic of deposits from simple ion acidic solutions containing no addition agents, operated at elevated temperature or low current density. Deposits of this type usually exhibit lower strength and hardness than other structures but high ductility.[36] Studies indicate that CIGS films having columnar structure with large grains (~1 μm) are attractive as they can enhance the conductivity. However grain boundaries in CIGS are found to be less active and hence even fine grain sized films may also yield high conversion efficiency.

The percentage composition of the precursor chemicals also affects the film morphology. Fernandez and Bhattacharya[57] suggested that at low CuCl₂ concentration, formation of micro cracks in the film were observed. On the other hand, when the concentration of CuCl₂ was increased, the morphology of the film was smooth and free of micro cracks. Many groups have reported similar results showing that film morphology is more compact and homogeneous when the amount of Cu^{2+} is increased in the chemical bath. A similar effect occurs when there is an increment of InCl₃ concentration in the electrolytic bath.[57] Many other parameters determine the film quality and the resulting conversion efficiency. For example a thorough substrate cleaning before deposition is important to get good adhesion. The film thickness is a direct function of the electrodeposition time. Usually a deposition time of 1 h is suitable

to make CIGS films with thickness of ~2 μm.

2.3. Challenges in making stoichiometric film

As discussed above, the major difficulty in electrodeposition of stoichiometric CIGS film lies in the incorporation of optimum Ga in the film. Optimization of both the Ga content and Ga distribution in the film is essential to enhance the cell efficiency. AES depth profile analysis of the electrodeposited layer by Bhattacharya *et al.* revealed a non-uniform distribution of Ga concentration in the film, which was suggested not to be helpful for the electron collection mechanism.[58] Some studies reported that absorber layer having more Ga on the back facilitates electron collection.[50,58] Few groups suggested that parameters such as electrolyte agitation can influence the Ga deposition.[50,59] According to Ganchev *et al.* the Ga content found to decrease with increasing rate of electrolyte agitation.[50] Kang *et al.* showed that absorber layers processed from Se-poor precursors give better crystalline quality and increased Ga incorporation, compared to the layers grown using Se rich precursors [60].

Vapor pressure of Se is low and Se volatizes from the film during the high temperature post-annealing step. In earlier reports, the films were selenized by exposing to Se vapor during the cool down time after the high temperature PVD step.[44] To maintain the film stoichiometry, the high temperature annealing (at 450-600°C) of electrodeposited films is usually performed in a Se atmosphere (such as H₂Se gas), in a tubular furnace in flowing Ar atmosphere.[61]

As an alternative to the H₂Se gas, excessive Se powder can be used during the sintering.[62] Some groups have employed a two-zone furnace with the temperature of the substrate at ~500°C and that of the Se source at ~250°C.[50] Rapid thermal processer can be employed in the selenization process. More convenient and novel selenization/crystallization treatment is required to be developed for the realization of cost-effective CIGS solar cells.

2.4. Novel deposition strategies

As an alternative to conventional dc electrodeposition, pulse electrodeposition techniques were employed recently.[63] The pulsed electrodeposition process allows independent variation of three parameters: potential/current, period, and duty cycle and can produce a smooth, more compact and more homogeneous film.

In dc plating, constant current is used, and the rate of arrival of metal ions depends on their diffusion coefficient whereas in pulse plating and pulse reverse plating, modulated current waveforms are used to get a better leveling of the deposit, and to minimize the porosity, contamination, etc. Grain size can be suitably adjusted with the duty cycle and the bath.

Novel multi-step depositions were reported. Bhattacharya reported fabrication of CIGS absorber layers using a two-step electrodeposition process: Cu-rich CIGS is electrodeposited first, followed by In-Se thin film.[64] The deposited Cu layer facilitates the electrodeposition of subsequent In, Ga, and Se layers. In another interesting approach, a sequential alloy deposition was employed for co-deposition of In-Se and Ga-Se films with high repeatability and controllable In/Se and Ga/Se molar ratios by a two-stage process.[54]

In aqueous deposition baths, In and Ga deposition efficiencies are limited by H^+ reduction, which causes composition inhomogeneity and pinholes in the film whereby limiting the cell efficiencies. As an alternative to the acidic aqueous bath for CIGS deposition, ionic liquid (e.g. choline chloride/urea eutectic mixture) based systems were introduced recently.[65] Such an electrolyte has advantages such as wide electrochemical window, high thermal stability, very low vapor pressures, low toxicity, and good solubility of organic and inorganic materials. Their wide potential windows and high thermal stability should give higher deposition efficiencies for electronegative species and allow higher deposition temperatures to promote in-situ crystallization, possibly avoiding the need for the post-deposition heat treatments.[65] However any such attempts discussed here has so far not resulted in a higher efficiency cell. Semiconductor one dimensional structures are attractive as light can be absorbed along the rod length and charge carriers diffuse radially for a shorter distance toward the junction. Inguanta et al. reported some preliminary work concerning the deposition of CIGS nanowires using AAO templates.[66]

3. Concluding remarks

Electrodeposition is a very cost-effective and simple method for fabrication of large area films. However, the conversion efficiencies reported for the cells fabricated by this method are by far low. With suitable modifi-

cations, it is expected that this simple and cheaper manufacturing process turns out to be the best alternative to vacuum deposition methods in fabrication of flexible CIGS solar cells in near future. Development of novel plating methods without employing the post vacuum deposition is required. Precise control of grain geometry and distribution by optimizing the post crystallization temperatures and the rate of heating and cooling may have advantageous results. Pulse deposition is a hopeful strategy. Effective doping of the CIGS by either one step deposition or by multilayer deposition may be beneficial in reducing the processing temperature to achieve crystallization. One dimensional nanostructures such as nanorods and nanowires of CIGS materials can be synthesized by employing template assisted electrodeposition, which may be beneficial to achieve higher current conversion efficiencies.

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