

## A STUDY OF CIGS AS A SOLAR CELL MATERIALS AND ITS OTHER APPLICATIONS

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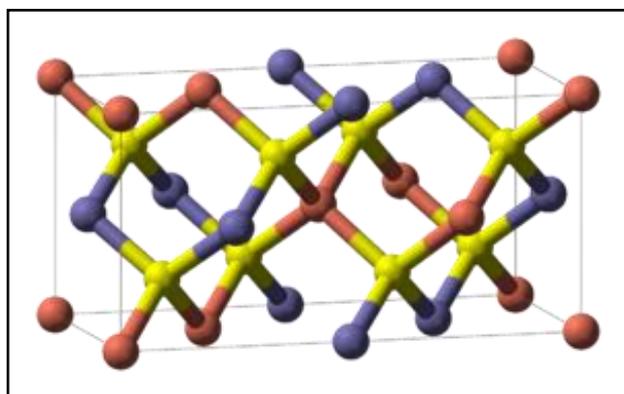
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## ABSTRACT

CIGS Solar Cell is a thin-film photovoltaic device that uses semiconductor layers of copper indium gallium selenide (CIGS) to absorb sunlight and convert it into electricity. It is manufactured by depositing a thin layer of copper, indium, gallium and selenium on glass or plastic backing, along with electrodes on the front and back to collect current. Because the material has a high absorption coefficient and strongly absorbs sunlight, a much thinner film is required than of other semiconductor materials. CIGS is one of three main stream thin-film photovoltaic (PV) technologies. CIGS outperforms polysilicon at the cell level; however its module efficiency is still lower, due to a less mature up-scaling. Thin-film market share is stagnated at around 15 percent, leaving the rest of the PV market to conventional solar cells made of crystalline silicon. In 2013, the market share of CIGS alone was about 2 percent and all thin-film technologies combined fell below 10 percent. Although CIGS solar cells are considered to be in the early stages of large-scale commercialization, they can be produced by using a process that has the potential to reduce the cost of producing photovoltaic devices. As the performance, uniformity, and reliability of CIGS products improve, the technology has the potential to expand its market share significantly and may eventually become a disruptive technology. Additionally, given the hazards of cadmium extraction and use, CIGS solar cells offer fewer health and environmental concerns than the cadmium telluride solar cells with which they compete. CIGS cells continue being developed, as they promise to reach silicon-like efficiencies, while maintaining their low costs as is typical for thin-film technology.

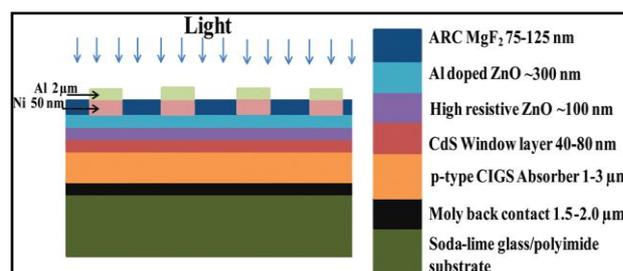
**KEYWORDS:** CIGS Solar Cell, Semiconductor, Photovoltaic Device

CIGS is a I-III-VI<sub>2</sub> compound semiconductor material composed of copper, indium, gallium, and selenium. The material is a solid solution of copper indium selenide (often abbreviated "CIS") and copper gallium selenide, with a chemical formula of CuIn<sub>x</sub>Ga(1-x)Se<sub>2</sub>, where the value of x can vary from 1 (pure copper indium selenide) to 0 (pure copper gallium selenide). It is a tetrahedrally bonded semiconductor, with the chalcopyrite crystal structure. The bandgap varies continuously with x from about 1.0 eV (for copper indium selenide) to about 1.7 eV (for copper gallium selenide) (Krasnov A., 2016).



CIGS has an exceptionally high absorption coefficient of more than 10<sup>5</sup>/cm for 1.5 eV and higher

energy photons. CIGS solar cells with efficiencies around 20% have been claimed by the National Renewable Energy Laboratory (NREL), the Swiss Federal Laboratories for Materials Science and Technology (Empa), and the German Zentrum für Sonnenenergie und Wasserstoff Forschung (ZSW) which is the record to date for any thin film solar cell in figure 1.



**Figure 1: Schematic cross-section of CIGS based thin-film solar cells.**

A soda-lime glass substrate (SLG) is generally used. Through the Mo back contact, sodium diffuses from glass into the CIGS absorber and increases conductivity/carrier concentration in the absorber. Substrates such as plastic (polyimide) films and stainless-steel foils have been used to obtain flexible solar cells. When flexible substrates are used, for sodium doping, sodium containing precursor film such as sodium fluoride

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(NaF~10 nm) is deposited onto the Mo back contact. A hetero junction is formed between CdS and the CIGS layer. A high resistive intrinsic ZnO layer is deposited to prevent shunting paths due to diffusion of aluminum from the Al-doped ZnO layer into the absorber. An Al-doped ZnO layer is required for lateral conduction to transport photogenerated current into the Ni/Al grids. MgF<sub>2</sub> acts as an anti-reflective coating.

The CIGS bandgap can be tuned to match the solar spectrum by replacing indium with Ga. CIGS absorbs most parts of the solar spectrum within 1 μm, a thin layer of ~2.0–2.5 μm is sufficient for the device, and hence raw material usage can be reduced. Using various deposition techniques, the CIGS material can be deposited on rigid as well as flexible substrates. Apart from terrestrial applications, CIGS solar cells can be used for space applications due to their high radiation tolerance. Also, their suitability for monolithic integration (cell-to-cell interconnection) leads to low production cost due to there being fewer processing steps.

There are some limitations in commercialization. The compositional uniformity from run-to-run is a limitation, and in situ diagnostic tools are critical for process control. Standardization of equipment for both multisource co-evaporation and two-stage processing of CIGS for large scale manufacturing is another limitation. A large difference in efficiency exists between small area cells (>22.8%) and commercially available modules (16.1%). In mass production, there may be a problem of indium supply and the cost may rise suddenly. As a note, 31 tons of indium is required to produce a 1 GW PV module.

In light of the above, this review article focuses on the potential of CIGS based solar cells for energy applications. The beneficial effects of a graded bandgap and Na distribution in the CIGS absorber are reviewed. Concerns related to flexible solar cells, factors influencing cell efficiency and suggestions to improve efficiency are discussed. Current developments in R&D, issues in production, strategies to overcome the issues and future prospects of CIGS solar cells are briefly presented (Kazmerski *et al.*, 1976; Hahn *et al.*, 1953).

### Comparison with Conventional Crystalline Silicon and other Thin Films

Unlike conventional crystalline silicon cells based on a homojunction, the structure of CIGS cells is a more complex heterojunction system. A direct bandgap material, CIGS has very strong light absorption and a layer of only 1–2 micrometers (μm) is enough to absorb most of the sunlight. By comparison, a much greater thickness of about 160–190 μm is required for crystalline

silicon. The active CIGS-layer can be deposited in a polycrystalline form directly onto molybdenum (Mo) coated on a variety of several different substrates such as glass sheets, steel bands and plastic foils made of polyimide. This uses less energy than smelting large amounts of quartz sand in electric furnaces and growing large crystals, necessary for conventional silicon cells, and thus reduces its energy payback time significantly. Also unlike crystalline silicon, these substrates can be flexible.

In the highly competitive PV industry, pressure increased on CIGS manufacturers, leading to the bankruptcy of several companies, as prices for conventional silicon cells declined rapidly in recent years. However, CIGS solar cells have become as efficient as multi-crystalline silicon cells- the most common type of solar cells. CIGS and CdTe-PV remain the only two commercially successful thin-film technologies in a globally fast-growing PV market.

In photovoltaics "thinness" generally is in reference to so-called "first generation" high-efficiency silicon cells, which are manufactured from bulk wafers hundreds of micrometers thick. Thin films sacrifice some light gathering efficiency but use less material. In CIGS the efficiency tradeoff is less severe than in silicon. The record efficiencies for thin film CIGS cells are slightly lower than that of CIGS for lab-scale top performance cells. In 2008, CIGS efficiency was by far the highest compared with those achieved by other thin film technologies such as cadmium telluride photovoltaics (CdTe) or amorphous silicon (a-Si). CIS and CGS solar cells offer total area efficiencies of 15.0% and 9.5%, respectively. In 2015, the gap with the other thin film technologies has been closed, with record cell efficiencies in laboratories of 21.5% for CdTe (First Solar) and 21.7% for CIGS (ZSW) (Jeyakumar *et al.*, 1994; Wagner *et al.*, 1974).

### Production

**(a) Film Production:** The most common vacuum-based process is to co-evaporate or co-sputter copper, gallium, and indium onto a substrate at room temperature, then anneal the resulting film with a selenide vapor. An alternative process is to co-evaporate copper, gallium, indium and selenium onto a heated substrate. A non-vacuum-based alternative process deposits nanoparticles of the precursor materials on the substrate and then sinters them in situ. Electroplating is another low cost alternative to apply the CIGS layer. The following sections outline the various techniques for precursor deposition processing, including sputtering of metallic layers at low temperatures, printing of inks containing

nanoparticles, electrodeposition, and a technique inspired by wafer-bonding.

### (i) Selenization

The Se supply and selenization environment is important in determining the properties and quality of the film. When Se is supplied in the gas phase (for example as H<sub>2</sub>Se or elemental Se) at high temperatures, the Se becomes incorporated into the film by absorption and subsequent diffusion. During this step, called Chalcogenization, complex interactions occur to form a chalcogenide. These interactions include formation of Cu-In-Ga intermetallic alloys, formation of intermediate metal-selenide binary compounds and phase separation of various stoichiometric CIGS compounds. Because of the variety and complexity of the reactions, the properties of the CIGS film are difficult to control (Scofield *et al.*, 1995).

The Se source affects the resulting film properties. H<sub>2</sub>Se offers the fastest Se incorporation into the absorber; 50 at % Se can be achieved in CIGS films at temperatures as low as 400 °C. By comparison, elemental Se only achieves full incorporation with reaction temperatures above 500 °C. Films formed at lower temperatures from elemental Se were Se deficient, but had multiple phases including metal selenides and various alloys. Use of H<sub>2</sub>Se provides the best compositional uniformity and the largest grain sizes. However, H<sub>2</sub>Se is highly toxic and is classified as an environmental hazard.

### (ii) Sputtering of Metallic Layers followed by Selenization

In this method a metal film of Cu, In and Ga is sputtered at or near room temperature and reacted in a Se atmosphere at high temperature. This process has higher throughput than coevaporation and compositional uniformity can be more easily achieved.

Sputtering a stacked multilayer of metal – for example a Cu/In/Ga/Cu/In/Ga... structure – produces a smoother surface and better crystallinity in the absorber compared to a simple bilayer (Cu-Ga alloy/In) or trilayer (Cu/In/Ga) sputtering. These attributes result in higher efficiency devices, but forming the multilayer is a more complicated deposition process and did not merit the extra equipment or the added process complexity. Additionally, the reaction rates of Cu/Ga and Cu/In layers with Se are different. If the reaction temperature is not high enough, or not held long enough, CIS and CGS form as separate phases.

Companies currently that used similar processes include Showa Shell, Avancis, Miasolé, Honda Soltec, and Energy Photovoltaics (EPV). Showa Shell sputtered a

Cu-Ga alloy layer and an In layer, followed by selenization in H<sub>2</sub>Se and sulfurization in H<sub>2</sub>S. The sulfurization step appears to passivate the surface in a way similar to CdS in most other cells. Thus, the buffer layer used is Cd-free, eliminating any environmental impact of Cd. Showa Shell reported a maximum module efficiency of 13.6% with an average of 11.3% for 3600 cm<sup>2</sup> substrates. Shell Solar uses the same technique as Showa Shell to create the absorber; however, their CdS layer comes from chemical vapor deposition. Modules sold by Shell Solar claim 9.4% module efficiency.

Miasolé had procured venture capital funds for its process and scale up. A record 17.4% aperture efficiency module was confirmed by Fraunhofer in 2019. EPV uses a hybrid between coevaporation and sputtering in which In and Ga are evaporated in a Se atmosphere. This is followed by Cu sputtering and selenization. Finally, In and Ga are again evaporated in the presence of Se. Based on Hall measurements, these films have a low carrier concentration and relatively high mobility. EPV films have a low defect concentration (Kazmerski and Sanborn, 1977; Yadav *et al.*, 2015).

### (iii) Chalcogenization of Particulate Precursor Layers

In this method, metal or metal-oxide nanoparticles are used as the precursors for CIGS growth. These nanoparticles are generally suspended in a water based solution and then applied to large areas by various methods, such as printing. The film is then dehydrated and, if the precursors are metal-oxides, reduced in a H<sub>2</sub>/N<sub>2</sub> atmosphere. Following dehydration, the remaining porous film is sintered and selenized at temperatures greater than 400 °C. Nanosolar and International Solar Electric Technology (ISET) unsuccessfully attempted to scale up this process. ISET uses oxide particles, while Nanosolar did not discuss its ink. The advantages of this process include uniformity over large areas, non-vacuum or low-vacuum equipment and adaptability to roll-to-roll manufacturing. When compared to laminar metal precursor layers, sintered nanoparticles selenize more rapidly. The increased rate is a result of the greater surface area associated with porosity. Porosity produces rougher absorber surfaces. Use of particulate precursors allows for printing on a large variety of substrates with materials utilization of 90% or more. Little research and development supported this technique (Singh *et al.*, 2014; Zhang *et al.*, 1998).

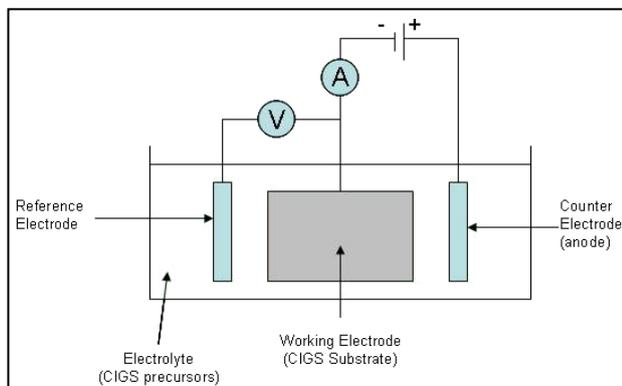
Nanosolar reported a cell (not module) efficiency of 14%, however this was not verified by any national laboratory testing, nor did they allow onsite inspections. In independent testing, ISET's absorber had the 2<sup>nd</sup> lowest efficiency at 8.6%. However, all the

modules that beat ISET's module were coevaporated, a process which has manufacturing disadvantages and higher costs. ISET's sample suffered most from low VOC and low fill factor, indicative of a rough surface and/or a high number of defects aiding recombination. Related to these issues, the film had poor transport properties including a low Hall mobility and short carrier lifetime.

#### (iv) Electrodeposition Followed By Selenization

Precursors can be deposited by electrodeposition. Two methodologies exist: deposition of elemental layered structures and simultaneous deposition of all elements (including Se). Both methods require thermal treatment in a Se atmosphere to make device quality films. Because electrodeposition requires conductive electrodes, metal foils are a logical substrate. Electrodeposition of elemental layers is similar to the sputtering of elemental layers.

Simultaneous deposition employs a working electrode (cathode), a counter electrode (anode), and a reference electrode as in Figure 3. A metal foil substrate is used as the working electrode in industrial processes. An inert material provides the counter electrode and the reference electrode measures and controls the potential. The reference electrode allows the process to be performed potentiostatically, allowing control of the substrate's potential.



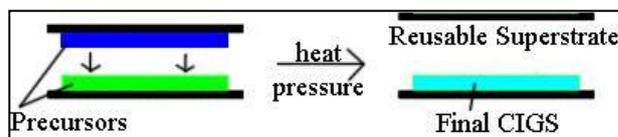
**Figure 3: CIGS electrodeposition apparatus**

Simultaneous electrodeposition must overcome the fact that the elements' standard reduction potentials are not equal, causing preferential deposition of a single element. This problem is commonly alleviated by adding countering ions into solution for each ion to be deposited ( $\text{Cu}^{2+}$ ,  $\text{Se}^{4+}$ ,  $\text{In}^{3+}$ , and  $\text{Ga}^{3+}$ ), thus changing that ion's reduction potential. Further, the Cu-Se system has a complicated behavior and the film's composition depends on the  $\text{Se}^{4+}/\text{Cu}^{2+}$  ion flux ratio which can vary over the film surface. This requires the precursor concentrations and deposition potential to be optimized. Even with optimization, reproducibility is low over large areas due

to composition variations and potential drops along the substrate (Devaney *et al.*, 1985).

The resulting films have small grains, are Cu-rich, and generally contain  $\text{Cu}_{2-x}\text{Se}_x$  phases along with impurities from the solution. Annealing is required to improve crystallinity. For efficiencies higher than 7%, a stoichiometry correction is required. The correction was originally done via high temperature physical vapor deposition, which is not practical in industry. Solopower is currently producing cells with >13.7% conversion efficiency as per NREL.

#### (v) Precursor Combination by Wafer-Bonding Inspired Technique



**Figure 4: Schematic of wafer-bonding inspired technique**

In this process, two different precursor films are deposited separately on a substrate and a superstrate. The films are pressed together and heated to release the film from the reusable superstrate, leaving a CIGS absorber on the substrate. Heliovolt patented this procedure and named it the FASST process. In principle, the precursors can be deposited at low temperature using low-cost deposition techniques, lowering module cost. However, the first generations of products use higher temperature PVD methods and do not achieve full cost cutting potential. Flexible substrates could eventually be used in this process (Figure 4).

Typical film characteristics are not known outside of the company, as no research has been conducted by independently funded laboratories. However, Heliovolt claimed a top cell efficiency of 12.2%.

#### (b) Coevaporation

Coevaporation, or codeposition, is the most prevalent CIGS fabrication technique. Boeing's coevaporation process deposits bilayers of CIGS with different stoichiometries onto a heated substrate and allows them to intermix.

NREL developed another process that involves three deposition steps and produced the current CIGS efficiency record holder at 20.3%. The first step in NREL's method is codeposition of In, Ga, and Se. This is followed by Cu and Se deposited at a higher temperature to allow for diffusion and intermixing of the elements. In

the final stage In, Ga, and Se are again deposited to make the overall composition Cu deficient.

Wurth Solar began producing CIGS cells using an inline coevaporation system in 2005 with module efficiencies between 11% and 12%. They opened another production facility and continued to improve efficiency and yield. Other companies scaling up coevaporation processes include Global Solar and Ascent Solar. Global Solar used an inline three stage deposition process. In all of the steps Se is supplied in excess in the vapor phase. In and Ga are first evaporated followed by Cu and then by In and Ga to make the film Cu deficient. These films performed quite favorably in relation to other manufacturers and to absorbers grown at NREL and the Institute for Energy Conversion (IEC). However, modules of Global Solar's films did not perform as well. The property in which the module most obviously underperformed was a low VOC, which is characteristic of high defect density and high recombination velocities. Global Solar's absorber layer outperformed the NREL absorber in carrier lifetime and hall mobility. However, as completed cells the NREL sample performed better. This is evidence of a poor CIGS/CdS interface, possibly due to the lack of an ODC surface layer on the Global Solar film.

Disadvantages include uniformity issues over large areas and the related difficulty of coevaporating elements in an inline system. Also, high growth temperatures raise the thermal budget and costs. Additionally, coevaporation is plagued by low material utilization (deposition on chamber walls instead of the substrate, especially for selenium) and expensive vacuum equipment. A way to enhance Se utilisation is via a thermal or plasma-enhanced selenium-cracking process, which can be coupled with an ion beam source for ion beam assisted deposition.

### Chemical Vapor Deposition

Chemical vapor deposition (CVD) has been implemented in multiple ways for the deposition of CIGS. Processes include atmosphere pressure metal organic CVD (AP-MOCVD), plasma-enhanced CVD (PECVD), low-pressure MOCVD (LP-MOCVD), and aerosol assisted MOCVD (AA-MOCVD). Research is attempting to switch from dual-source precursors to single-source precursors. Multiple source precursors must be homogeneously mixed and the flow rates of the precursors have to be kept at the proper stoichiometry. Single-source precursor methods do not suffer from these drawbacks and should enable better control of film composition.

As of 2014 CVD was not used for commercial CIGS synthesis. CVD produced films have low efficiency and a low VOC, partially a result of a high defect concentration. Additionally, film surfaces are generally quite rough which serves to further decrease the VOC. However, the requisite Cu deficiency has been achieved using AA-MOCVD along with a (112) crystal orientation.

CVD deposition temperatures are lower than those used for other processes such as co-evaporation and selenization of metallic precursors. Therefore, CVD has a lower thermal budget and lower costs. Potential manufacturing problems include difficulties converting CVD to an inline process as well as the expense of handling volatile precursors.

### Electrospray Deposition

CIS films can be produced by electrospray deposition. The technique involves the electric field assisted spraying of ink containing CIS nano-particles onto the substrate directly and then sintering in an inert environment. The main advantage of this technique is that the process takes place at room temperature and it is possible to attach this process with some continuous or mass production system like roll-to-roll production mechanism.

### Rear Surface Passivation

Concepts of the rear surface passivation for CIGS solar cells show the potential to improve the efficiency. The rear passivation concept has been taken from passivation technology of Silicon solar cells,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  have been used as the passivation materials. Nano-sized point contacts on  $\text{Al}_2\text{O}_3$  layer and line contacts on  $\text{SiO}_2$  layer provide the electrical connection of CIGS absorber to the rear electrode Molybdenum. The point contacts on the  $\text{Al}_2\text{O}_3$  layer are created by e-beam lithography and the line contacts on the  $\text{SiO}_2$  layer are created using photolithography. It is also seen that the implementation of the passivation layers does not change the morphology of the CIGS layers.

### Factors Influencing the Efficiency of CIGS Solar Cells

There are several factors affecting efficiency including stoichiometry, grain size, surface morphology, defects in the absorber and its interfaces with Mo and CdS. Roughness less than 50 nm in the CIGS film results in smaller surface area at the CIGS/CdS interface and hence both recombination at the interface and saturation current are reduced. Nevertheless, one disadvantage of a smoother film is the increased reflection from the film.

### Current Status, Challenges and Future Prospects

For the CIGS bandgap of 1.14 eV, the theoretical efficiency limit is 33.5%. In the near future cell efficiency as high as 25% can be reached. An improvement from the current value (22.8%) can be achieved by using the following approaches:

- (i) Improving CIGS absorber properties such as maximizing absorption by using innovative doping methods for high  $J_{sc}$ ,
- (ii) Reducing defect density by employing surface passivation on both sides of the CIGS layer to reduce recombination losses at the interfaces leading to high Voc,
- (iii) Using a Cd-free large bandgap window layer for high  $J_{sc}$ ,
- (iv) Utilizing a reflector (mirror) layer at the rear side of the cell to redirect unused light back to the absorber for electron–hole pair generation etc.

Most of the stability studies have been performed on unencapsulated CIGS cells. It is reported that Mo rear contact causes instability due to its oxidation and degradation. Also, interfacial reaction at the rear contact is crucial. To improve the long term stability of CIGS solar cells, an alternative back contact is required. To prevent oxygen and moisture entering the module, a robust encapsulation technology is required.

For a production capacity of 1000 MW  $y^{-1}$  (15% module efficiency), the CIGS module production cost is estimated to be \$0.34 per W. Cumulative CIGS module production has reached over 1.6 GW in 2015 and its current market share among all technologies is around 2%. Due to process complexity, CIGS panel production is lagging behind that of CdTe modules.

Using the vacuum technique, an efficiency of 22.6% has been reported. The about 0.3% gain in efficiency from the previous record of 22.3% was due to post deposition treatment over the CIGS surface using alkaline metal compounds and other improved processes. By tuning the Cu  $(In_{1-x}, Ga_x)(S_{1-x}, Se_x)_2$  material properties for a single junction, and combining with other materials such as perovskites for multi-junctions, the cell efficiency can be improved further. There are several challenges/issues in CIGS solar cell production:

- CIGS is a quaternary compound; film uniformity (thickness and composition) across the large area substrates is an issue. Uniformity is the main requirement for electronic and optical properties of high efficiency solar cells. Reproducibility and uniformity over a large area directly influence yield in production. For large area substrates, sputter

deposition is suitable.

- Cell efficiency in large area manufacturing is low. A nondestructive technique is required to evaluate the thickness and composition of the CIGS film.
- The main challenge for commercialization is scaling up lab-scale techniques to industrial production while maintaining high efficiency. A large gap exists between lab-scale efficiency (22.8%) and commercial module efficiency (16.1%). Module performance is usually limited due to inhomogeneity in the CIGS film. To reduce the efficiency gap, a homogeneous CIGS film is required over a large area. In-line process controls improve module manufacturing.
- If both non-vacuum and vacuum processes (for example, CdS by CBD, CIGS by the vacuum technique) are involved for CIGS solar cell fabrication, substrate handling between different tools is an issue. Also, difference in throughput between the processes is another issue. This can be avoided by using a vacuum process for all film depositions, viz. the sputtering technique.
- Since cadmium is toxic, disposal of the cadmium containing product causes adverse effect on the environment, and produces toxic effects on humans. Decommissioning is a major issue in developing countries. Cadmium-free CIGS panels are required.
- Indium is mainly obtained as a by-product from zinc and its availability is restricted from zinc production. Indium demand may increase with large production of CIGS modules and price escalation can occur due to a supply–demand gap. To solve this issue, a thinner CIGS layer of  $\leq 1$   $\mu\text{m}$  should be used in the device without compromising  $J_{sc}$ .
- The processing time for CIGS and TCO layers should be reduced. This can be done by using a thinner CIGS layer and a high speed growth technique for TCO.
- CIGS modules with EVA/glass have shown degradation since module performance is sensitive to water vapor; the main reason is an increase in ZnO resistance and Mo corrosion. To avoid moisture ingress, a suitable edge seal with better properties such as adhesion, durability, low moisture vapor transmission rate and thermal stability etc. is required.
- There are cleaning issues after laser scribing for monolithic integration for series interconnection. This issue can be solved by using a short pulse width laser.
- A graded CIGS bandgap profile improves the electrical and optical properties. A high throughput process can lower the production cost.
- For high efficiency lab-scale cells, a static

deposition process (substrates in a fixed position) is used. On the other hand, in manufacturing, a dynamic deposition process (substrates are in motion in the in-line process) is used for the production of large area solar cells. The growth kinetics are different between static and dynamic processes. Consequently, small area high efficiency is not reproducible over a large area. The deposition process should be identical in both cases. Due to the scarcity and price volatility of indium and Ga used in CIGS, CZTS with a kesterite structure is a candidate for replacing CIGS, and has attracted attention as an absorber for solar cells. CZTS is a quaternary absorber material consisting of copper, zinc, tin, and sulfur, which are non-toxic and abundant in the earth. CZTS is similar to the CIGS absorber, but the scarce elements indium and Ga present in CIGS are replaced by Zn and Sn, respectively, in CZTS. However, the highest cell efficiency reported is only 12.6% due to high  $V_{oc}$  losses associated with recombination due to defects in the bulk and at the interfaces. In other words,  $V_{oc}$  losses are associated with CZTS material quality. No further improvement in efficiency has been reported in the past few years. The low efficiency limits the implementation of CZTS based solar cells.

Looking further into the future of CIGS solar cells, studies on optimization of materials and interface properties are required to improve efficiency. For large area and large scale production, standardization of equipment for multi-source evaporation and a two-stage selenization process are required. At present, about a 3 mm thick CIGS layer is used in high efficiency solar cells which requires a deposition time of about 60 min. For industrial production, about a 10 min deposition time is required for high throughput without deteriorating device performance. Also, for the two-stage selenization technique, a faster selenization process is required. To reduce the production cost, CIGS layer thickness should be reduced to about 1  $\mu$ m without any degradation in device properties, particularly  $J_{sc}$  losses from the long wavelength region. A higher bandgap (than CdS) and cadmium-free window layer are required for high  $J_{sc}$ . To obtain an ideal bandgap (1.4 eV) for the CIGS layer, Ga incorporation in CIGS should be increased without compromising device performance. Meta-stability in CIGS cells fabricated by the two-stage selenization technique should be eliminated.

## CONCLUSION

We have reviewed material properties, recent developments of CIGS solar cells, and various growth techniques used for fabrication. To obtain high efficiency for CIGS based solar cells, the Ga/(Ga + In) ratio and Cu/(Ga + In) ratio should be around 0.26 and 0.88–0.92

respectively. If the Ga/(Ga + In) ratio exceeds 0.3, the number of defects in the film increases. For CIGS/Se based solar cells, to obtain a high fill factor, the S/(S + Se) ratio should be less than 0.61. High efficiency CIGS based solar cells are made from Cu-poor absorbers due to reduced recombination at the CIGS/CdS interface. For high efficiency, the  $E_g$  of the absorber can be increased from 1.04 eV to 1.14 eV by incorporating Ga. However, if  $E_g > 1.14$  eV mid gap defects/recombination in the device increases and discontinuity in the conduction band increases from a small spike to a cliff. A graded bandgap profile in the absorber improves cell performance. Front grading (close to CdS) improves  $V_{oc}$  and back grading (close to the back contact) improves the collection efficiency and  $J_{sc}$ . Also, sodium diffusion from glass to the absorber improves lab-scale efficiency. In industrial production, the three-stage co-evaporation process is used. A large difference exists between lab-scale efficiency (22.8%) and commercial module efficiency (16.1%). Lab-scale high efficiency is not reproducible over a large area since a static deposition process (substrate in a fixed position) is used for lab-scale devices, whereas in industrial production, a dynamic deposition process is used; the difference in efficiency is due to the difference in growth kinetics. About a 3  $\mu$ m CIGS layer is used in the cell; it requires ~ 60 min for growth. For high throughput, a 1  $\mu$ m thick CIGS film and about a 10 min deposition time is required without deteriorating device performance. Electronic inhomogeneity is a key issue for efficiency limitation.

## REFERENCES

- Devaney W.E., Michelsen R.A. and Chen W. S., 1985. 18<sup>th</sup> IEEE Photovoltaic Specialists Conference, IEEE Publishing, NY, p. 173.
- Hahn H., Frank G., Klingler W., Meyer A.D. and Störger G., 1953. Untersuchungen über ternäre Chalkogenide. V. Über einige ternäre Chalkogenide mit Chalkopyritstruktur. *Journal of inorganic and General Chemistry*. **271**(3–4): 153–170.  
<https://doi.org/10.1002/zaac.19532710307>
- Jeyakumar R., Ramamurthy S., Jayachandran M. and Chockalingam M.J., 1994. Electrochemical preparation and characterization of copper indium diselenide thin films. *Materials research bulletin*, **29**(2): 195–202.
- Kazmerski L.L., White F.R. and Morgan G.K., 1976. Thin-film CuInSe<sub>2</sub>/CdS heterojunction solar cells. *Applied Physics Letters*, **29**(4): 268–270.

- Kazmerski L.L. and Sanborn G.A., 1977. CuInS<sub>2</sub> thin-film homojunction solar cells. *Journal of Applied Physics*, **48**(7): 3178-3180.
- Krasnov A., 2016. High-reflectivity back contact for photovoltaic devices such as copper—indium-diselenide solar cells. U.S. Patent No. 9,419,151. Washington, DC: U.S. Patent and Trademark Office.
- Singh G., Verma A. and Jeyakumar R., 2014. Fabrication of c-Si solar cells using boric acid as a spin-on dopant for back surface field. *RSC Advances*, **4**(9): 4225-4229.
- Scofield J.H., Duda A., Albin D., Ballard B.L. and Predecki P.K., 1995. Sputtered molybdenum bilayer back contact for copper indium diselenide-based polycrystalline thin-film solar cells. *Thin solid films*, **260**(1): 26-31.
- Wagner S., Shay J.L., Migliorato P. and Kasper H.M., 1974. CuInSe<sub>2</sub>/CdS heterojunction photovoltaic detectors. *Applied Physics Letters*, **25**(8): 434-435.
- Yadav A., Singh G., Nekovei R. and Jeyakumar R., 2015. c-Si solar cells formed from spin-on phosphoric acid and boric acid. *Renewable Energy*, **80**: 80-84.
- Zhang S.B., Wei S.H., Zunger A. and Katayama-Yoshida H., 1998. Defect physics of the CuInSe<sub>2</sub> chalcopyrite semiconductor. *Physical Review B*, **57**(16): 9642-9656.