Current topics in CIGS solar cell R&D: Overcoming hurdles in mass production

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ABSTRACT

Since the demonstration of the first CuInSe₂ solar cell in 1974 by scientists at Bell Laboratories, a lot of effort has been put into the development of cost-effective processes for highly efficient Cu(In,Ga)(Se,S)₂ – or CIGS – solar cell devices. In 2012 these efforts led to the first gigawatt CIGS solar module production facility operated by Solar Frontier, a company that has a long history in R&D and originates from ARCO Solar, who developed the first commercial CIGS solar modules at the beginning of the 1990s. However, several start-up companies employing CIGS technology are presently struggling in the currently harsh market environment. Even though world-record laboratory solar cells now demonstrate 20.3% efficiency using a three-stage co-evaporation process, and full-size modules achieve 14.6% employing a similar method, efforts in research and development are more important than ever in order to increase cell efficiency, to bridge the gap between cell and module efficiencies, and to develop cost-effective and robust manufacturing processes. This paper gives an overview of current research topics under investigation by research institutes and industry, with a main focus on CIGS absorber formation. Along with other research results published by groups all over the world, this paper covers recent research results obtained at the Helmholtz-Zentrum Berlin für Materialien und Energie (HZB) and briefly mentions the work of the Photovoltaic Competence Center Berlin (PVcomB), a joint initiative of the Technical University of Berlin (TU Berlin) and HZB.

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Introduction and history

After a demonstration of the first $CuInSe_2$ solar cell in 1974 by scientists at Bell Laboratories [1], the first solar cells were made from single-crystal $CuInSe_2$ in 1975 by Shay and co-workers [2]. Since then there have been two main process routes for manufacturing CIGS thin-film solar cells:

- 1. Co-evaporation of elements the so-called 'Boeing process', developed by Boeing engineers [3].
- 2. Sequential processing of a Cu:Ga/ In precursor layer in an atmosphere containing selenium (Se) and/or sulphur (S), based on a process first published by Grindle et al. [4].

Solar cells from both processes having the typical design of a molybdenum (Mo) back contact / absorber layer / CdS buffer layer / zinc oxide (ZnO) window layer



Figure 1. Structure of a typical thin-film CIGS solar cell device developed by ARCO solar [5]: (left) SEM image of a cross-section of a CIGS-based solar cell; (right) schematic overview.

3.

were developed by ARCO Solar in 1987 [5], as shown in Fig. 1.

Milestones marking the evolution of thin-film CIGS solar cells are illustrated in Fig. 2 and are as follows:

 Control of the ratio of Cu to group III elements – best cells for Cu/III < 1 in the case of selenide-containing chalcopyrites to avoid the formation

of CuSe_x.

- 2. Preparation of a thin CdS buffer by chemical bath deposition, which leads to a conformal growth of a 50nm-thick CdS layer and eliminates shunting paths.
 - Cu-rich growth regime during CIGS absorber layer formation, which improves morphology and electronic properties.



Process	CIGS	Module	Hersteller
PVD	Co-evaporation	Monolithic glass/glass	Würth (D), Solibro (D)
		Flexible cells / flexible modules	Global (US,D), Ascent (US), Solarion (D)
	Reactive sputtering	Flexible cells / glass/glass modules	Miasole (US)
Sequential	Sputtering + RTP	Monolithic glass/glass	Avancis (D), Sulfurcell (D), Heliovolt (US), Stion (US)
	Sputtering + Annealing	Monolithic glass/glass	Solar Frontier (J), Honda Soltec (J), Bosch CISTech (D)
	Electrodepositing + RTP	Flexible cells / flexible modules	Solopower (US), Odersun (D)
	Inkjet printing + RTP	Flexible cells / glass/glass modules	Nanosolar (US), ISET (US)

4. Sodium supply during CIGS absorber layer formation, which further improves morphology and electronic

- properties.5. Incorporation of gallium (Ga) into the optimized band gap of the CIGS absorber layer.
- Incorporation of sulphur (S) into the CIGS absorber layer in the case of increased open-circuit voltage through sequential processing by increasing the band gap of the front part of the absorber layer.

As can be seen in the development chart (Fig. 2), in the past ten years no major improvement has been made in terms of solar cell efficiency. The record efficiency of 20.3% is mainly a result of fine-tuning the deposition parameters and not a fundamental improvement of the device or deposition process. From the theoretical point of view, a single-junction device should have a conversion efficiency of 25% or more. In the last decade R&D has concentrated on two topics:

- Understanding the device limitations by analyzing the material and device properties.
- Finding deposition processes and process control tools which are scalable and robust to achieve mass production.

This paper focuses on the hurdles which have to be overcome to achieve successful mass production and how these hurdles are tackled in current R&D activities. In particular, the R&D work performed at HZB and PVcomB will be discussed. PVcomB operates to 30×30cm² thin-film solar module R&D baselines to help bridge the gap between fundamental research and industry [6].

CIGS module production processes – what choices are available?

In contrast to a-Si solar module production, there is an abundance of different process routes available and under development by different companies for manufacturing CIGS-based solar cells. Only the back- and front-contact layers are the same for all approaches: Mo is used as the back contact, while a bi-layer made from intrinsic ZnO and doped ZnO serves as the front contact. The formation of the CIGS absorber layer is divided into two different process types:

- 1. Simultaneous co-evaporation of the elements in a high vacuum (PVD).
- 2. Sequential processing by performing first the deposition of a precursor layer, followed by a more or less fast annealing step to create the CIGS absorber layer.

In the case of sequential processing, there are several ways to deposit the metal precursor layer: magnetron sputtering, electrodeposition and ink printing of metal nanoparticles in a solution. Whether a selenium layer is added to the precursor depends on the annealing process: fast annealing processes deposit a selenium layer before the annealing, while slow annealing ones provide selenium via H_2 Se. Common to all sequential processing routes is an annealing in a H_2 S atmosphere after the selenization.

"Annealing at atmospheric pressure using elemental Se and S appears to avoid the highly toxic H₂Se."

Reactive sputtering of CIGS with H₂Se as the reactive gas is currently under investigation, as it might combine the advantages of the co-evaporation process in terms of stoichiometry control and magnetron sputtering. In particular the activation of Se in the plasma might lead to lower process temperatures. In addition, a process of annealing at atmospheric pressure using elemental Se and S appears to avoid the highly toxic H₂Se.

As well as the deposition process, one has the choice of using rigid or flexible substrates. Mostly standard float glass is used as a substrate since it has several advantages, such as low cost, flatness, shielding properties against environmental impacts, and a source of sodium (Na). Flexible substrates offer the possibility of new lightweight module designs and compact deposition tools, but Na has to be supplied by additional sources. In the case of metal substrates, barrier layers have to be applied in order to avoid metal diffusion into the CIGS absorber layer.

After the CIGS absorber formation, a buffer layer has to be deposited. Historically this layer has been CdS, and the chemical bath deposition (CBD) process works best, but other materials and deposition techniques are available and used for applying the buffer layer. In Japan especially, Cd-free buffer layers have to be used: CBD-Zn(O,OH,S) and CBD-InS are therefore established alternatives to the CdS buffer layer.

Last, but not least, one has to opt for either monolithic interconnection of cells within the deposition process, which is one of the advantages of thin-film solar modules, or making solar cells with contact grids.

Substrate and back contact – not so many options, but Na is necessary

As described earlier, soda-lime glass is the standard substrate for CIGS-based solar modules, its main purpose being to act as a Na source, as Na significantly improves the device performance. The control of the Na supply, however, is very limited and depends not only on the process temperature and duration, but also on the history of the glass. To achieve a better Na control, the application of a barrier layer and deposition of an additional Na source is therefore becoming standard in the industry.

Several different ways of supplying sodium are possible. In the case of co-evaporation, the deposition of a NaF layer onto the Mo back contact is common. In recent years, one manufacturer of targets for magnetron sputtering managed to dope the Mo target with Na, which can

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be used in combination with a standard Mo target in a sputtering system. But Cu-doped with Na and Na₂SeO₃ layers are also used. As a barrier layer, a SiO_xN_y layer is deposited onto the glass before the Mo back contact. During module production it is important to take special care not to damage the barrier layer, because a defective barrier will be an additional source of Na and might affect the CIGS absorber process.

Standard soda-lime glass, however, is limited in terms of the maximum temperature that can be applied during the growth process. Within the ComCIGS research project, HZB and Schott AG tested a new Na-containing hightemperature resistant glass as a substrate. Solar cells processed on the hightemperature resistant glass achieved 19.4% efficiency [7] - a gain of 1.6% absolute compared to solar cells processed onto standard float glass in the same process. It was mainly the electronic properties that improved, as observed by an increase in open-circuit voltage of about 90mV, but also the Ga distribution changed from a graded profile to a flat distribution.

In the case of foil substrates, Na always has to be supplied during the absorber formation. During the last few years, extensive research has been undertaken on the deposition of CIGS onto polyamide (PI) foils. Here, an additional challenge presents itself: PI foils can only withstand temperatures below 420°C without damage. Caballero et al. [8] carried out a study on the influence of the NaF precursor thickness on the device performance at a deposition temperature of 420°C. One result of this study was that Na reduces the In-Ga interdiffusion and decreases the absorber grain size. To achieve optimal device performance the amount of Na has to be carefully chosen depending on the process temperature and the Cu content of the film. Even higher efficiencies on PI foil of 18.7% were achieved by Chirilă et al. [9] at the Swiss-based research institute EMPA. They found that NaF deposition prior to the evaporation process leads to a stronger Ga gradient and therefore lower open-circuit voltages than when NaF is deposited in the last stage of the deposition process; the importance of the Ga profile will be discussed in the next section. Unfortunately, for highly efficient lowtemperature processes, the process time increases significantly to more than 60 minutes.

CIGS absorber formation – the key to success, but no golden rule

As mentioned in the introduction, there are two different ways of forming the CIGS absorber layer: 1) co-evaporation of the elements and 2) annealing of a metal precursor in a chalcogen atmosphere. The co-evaporation process, which has led to the highest solar cell efficiencies so far of 20.3% [10], will be discussed first. In Fig. 3 the profile of a state-of-the-art three-stage co-evaporation process is illustrated, as first published by Gabor et al. [11].

The three stages are defined by the fluxes of the elements and the substrate temperatures (all process steps are performed in the presence of selenium vapour and in a high-vacuum chamber):

- 1. InSe and GaSe layers are sequentially deposited.
- 2. InSe/GaSe multi-stack is transformed into chalcopyrite by supplying Cu.
- 3. Shortly after the transition from Cu-poor (Cu/III < 1) CIGS absorber layer to Cu-rich (Cu/III > 1), the Cu source is closed and the In and Ga sources are activated again, to achieve a Cu-poor stoichiometry.

The transition from the Cu-poor to Cu-rich phase is necessary in order to achieve the so-called recrystallization. The grains look larger, as revealed by the scanning electron microscopy (SEM) images of a CIGS cross section presented in Fig. 4, and the electrical properties improve after this step.

To avoid CuSe_x formation it is crucial to switch back to a Cu-poor absorber

Thin Film

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light-scattering' has been developed at HZB that allows the detection of the transition very precisely [13]. The excess Cu during the second stage increases the interdiffusion of In and Ga [14] at temperatures about 470°C, as Rissom et al. found out by time-resolved energydispersive X-ray diffraction (EDXRD) experiments at the EDDI beamline located at the Berlin synchrotron radiation source BESSY. A growth model proposed by Caballero suggests that at the beginning of the second stage a vacancy compound is formed and that Na occupies the In_{Cu} or Ga_{Cu} antisite. Small grains are formed at the beginning of stage two, and Na is mainly found at the grain boundaries. As soon as the chalcopyrite phase dominates, Na concentration is highest on the film surface, allowing the growth of the grains in the Cu-In-Ga-Se layer. Large grains and a columnar structure are achieved at Cu/ III = 0.70-0.95. However, the mobility of Ga atoms is reduced with increasing Cu content, leading to a single Ga gradient with an increased accumulation at the Mo back-contact layer. Progressing to a Cu-rich composition pushes Na to the surface and the back-contact interface. The deposition of In-Ga-Se during the third stage leads to an increase in Ga concentration at the film surface, creating the so-called V-shape Ga gradient as shown in Fig. 5, which is beneficial for device performance. The final CIGS composition should have a CU/

layer. An in situ technique called 'laser-

"In the case of sequential processing, the control of Ga is much trickier."

III = 0.8 - 0.9.

In the case of sequential processing, the control of Ga is much trickier. Because Ga is liquid at temperatures close to room temperature, the Ga has to be supplied via a Cu:Ga target when magnetron sputtering is used for precursor deposition. Today, Cu:Ga targets with up to 30% Ga are available, so that in general the same Ga concentration as for highly efficient co-evaporated CIGS solar cells can be achieved. Unfortunately, it is not possible to tune the Ga distribution within the film as easily as in the case of co-evaporation. Moreover, the Cu content of the film is closely related to the Ga content.

Other options are the use of CuInGa (CIG) targets plus a Cu target to adjust for the Cu/III ratio. CIG targets currently offer lower Ga concentration than CuGa targets. During the annealing process – regardless of whether it is a short or long process and whether Se is supplied via an elemental layer onto the metal precursor layer or via H_2Se – the Cu becomes mobile and forms CuSe_x, both of which are essential



Figure 5. Band structure of a CIGS solar cell (a) with V-shape Ga gradient and (b) without. (From Chirilă et al. [9].)

for grain growth of the CIGS layer. This process leaves behind Ga at the Mo backcontact layer and often no Ga is found at the surface of the CIGS layer. Only longterm annealing at high temperatures will lead to an interdiffusion of the Ga- and In-rich phases. Most companies using sequential processing therefore add a sulphurization step after the selenization. Sulphur increases the band gap of the CIGS semiconductor material and therefore has a similar effect to increasing the Ga concentration. It is important here to have a CIGS layer with low Se content to allow sulphur diffusion in the top layer of the CIGS film. The actual reaction pathway



Thin Film depends on the process conditions and will be discussed later.

Along with sputtering the metal precursors, electrodeposition and ink printing of metal or metal-selenium precursors, mainly using roll-to-roll processing, is currently being investigated and developed by a few companies. The goal is to achieve a non-vacuum process approach for manufacturing CIGS solar modules, but up to now no successful nonvacuum ZnO process which is compatible with the requirements of CIGS material has been found.

To study the reaction pathway during the formation of chalcopyrite layers, intensive research has been carried out at HZB at the EDDI beamline of the synchrotron facility BESSY, which offers the possibility of recording time-resolved EDXRD and X-ray fluorescence (XRF) data with a fivesecond resolution (Fig. 6). Weber et al. [15] investigated the formation of Cu(In,Ga) Se₂ layers from a metal precursor with Cu/ III = 0.8 and Cu and Ga sputtered from a Cu_{0.85}Ga_{0.15} which were heated up to 600°C in an evacuated graphite box. Selenium was introduced by means of selenium particles, which melt during the heating-up phase and establish a selenium atmosphere within the graphite box.

From these results the following reaction pathways are derived. The reaction starts at room temperature from crystalline In and at least one Cu_x(In,Ga)_y phase (either Cu₁₆(In,Ga)₉ or Cu₉(In,Ga)₄). An In-melt is formed around 150°C, and the Cu_x(In,Ga)_y phase becomes more Ga-rich, resulting in a reduced d-spacing of the lattice. Between 200°C and 400°C, InSe and In₄Se₃ are formed. No traces of Cu_{2-x}Se are detected, which is in contrast to the results of Kötschau et al. [16] using a similar technique but with a different precursor (Cu/III = 0.89, $Cu_{0.75}Ga_{0.25}$ target and elemental Se on top of the metal precursor) and an atmospheric pressure process. This finding is also in contrast to the proposed necessity of Cu_{2-x}Se for forming large grains. At temperatures above 400°C, the $Cu_x(In,Ga)_y$ decompose into Cu(In,Ga)Se₂ within approximately ten seconds. Break-off experiments showed that the resulting chalcopyrite layer consists of two separate layers: a Ga-rich layer close to the Mo back contact and an In-rich layer at the surface. Solar cells made from this material therefore yielded a relatively low $V_{oc} = 536$ mV but an efficiency of 14.2%, which is quite good for sequentially processed CIGS solar cells without any sulphur.

PVcomB will be looking further into the optimization of the sequential processing of CIGS solar cells using an in-line RTP furnace which operates under a nitrogen atmosphere and has controllable Se and S sources based on the evaporation of elemental Se and S.

Conclusion: how research will help to overcome the hurdles in mass production of CIGS solar modules

To help in achieving a successful mass production, research institutes will aim to deliver in situ process control tools such as laser-light-scattering – the clarification of process pathways by in situ measurements at advanced analytical facilities for optimizing 1) process windows and 2) deposition systems.

In addition, a better understanding of metastabilities (light-soaking effects) of CIGS cells (not covered in this article) will be necessary. Last, but not least, new deposition methods for highly efficient solar cells and low-cost production will need to be conceived. This is being addressed by joint research initiatives such as PVcomB, who are testing new lower-cost deposition methods (for example atmospheric pressure RTP ovens, elemental selenium and sulphur sources, and alternative buffer layer materials and deposition techniques) and laser patterning during monolithic integration.

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