

Current topics in CIGS solar cell R&D – Part 2: Buffer layers and metastabilities in CIGS

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ABSTRACT

This is the second part of a review article series about current topics in R&D concerning $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ – or CIGS – solar cells. In the first part, which appeared in the previous edition of *Photovoltaics International*, the focus was on CIGS absorber layer formation. This second part will discuss another essential part of CIGS solar cells – the buffer layer – in conjunction with metastabilities in these types of cell.

Introduction

Cadmium sulphide (CdS) deposited by chemical bath deposition (CBD) is commonly used as a buffer layer, but more and more emphasis is now being placed on alternative Cd-free materials and new dry techniques. However, metastabilities – which relate to changes in $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ (CIGS) solar cell performance due to light, thermal or voltage bias treatments – often occur with Cd-free buffer layers. In contrast to light-induced degradation (LID) in a-Si based solar cells [1], or thermal-induced degradation in CdTe-based cells [2] because of Cu diffusion, these metastabilities have mostly a beneficial effect on solar cell efficiency. There have been several empirical investigations [3] of these metastable effects in CIGS solar cells, showing the different changes in solar cell behaviour depending on the actual treatment of the device. All these observations can be explained by the $(V_{\text{Cu}} - V_{\text{Se}})$ divacancy complex [4], which leads to changes in the net doping in the CIGS absorber layer.

“Metastabilities often occur with Cd-free buffer layers.”

Buffer layer – the secret to creating good CIGS solar cells

In comparison with common crystalline silicon-based solar cells, CIGS solar cells have a so-called heterojunction, which creates the electric field necessary for charge separation. In the case of CIGS solar cells the heterojunction is accompanied by three features:

- The CIGS absorber layer, which is a p-type semiconductor and is the light-absorbing and current-generating part of the solar cell.
- A transparent conducting oxide (TCO) window layer, which serves as the front contact and – since the TCO layer consists of an undoped ZnO and highly doped degenerated ZnO – is part of the p-n junction.
- A buffer layer, commonly made of CdS, between the absorber and window layers. The buffer layer fulfils several different roles and will be discussed in this paper.

Drawing the band diagram of the hetero-structure offers further insights into its structure (Fig. 1). In the case of a CIGS

solar cell, at least three different materials with different band gaps and doping levels are involved. First, there is the window layer consisting of a bi-layer of Al-doped ZnO (AZO) and undoped ZnO (i-ZnO); both layers have a band gap of about 3.4eV and are transparent with respect to the visible and near-infrared light. The Fermi level lies just above the conduction band for the AZO layer and just below it for the i-ZnO layer. Next is the buffer layer: in the case of CdS, this layer is slightly n-doped and has a band gap of 2.4eV. This is followed by the p-type CIGS layer with a band gap of between 1.0eV and 1.3eV for most commercial devices.

As the energy of the Fermi level has to be the same in all layers this would lead to a stepwise increase either in the conduction band or in the valence at the interfaces between the layers. Band bending therefore occurs, which smooths out these barriers to achieve band alignment if possible. As can be seen in Fig. 1(b), between the chalcopyrite layer and the CdS layer, an electron barrier in the conduction occurs (a so-called ‘spike’). At this barrier, electrons are blocked and the device current collection is degraded. Numerical simulations show that, for CIGS solar cells, a small spike is beneficial, as it leads to an

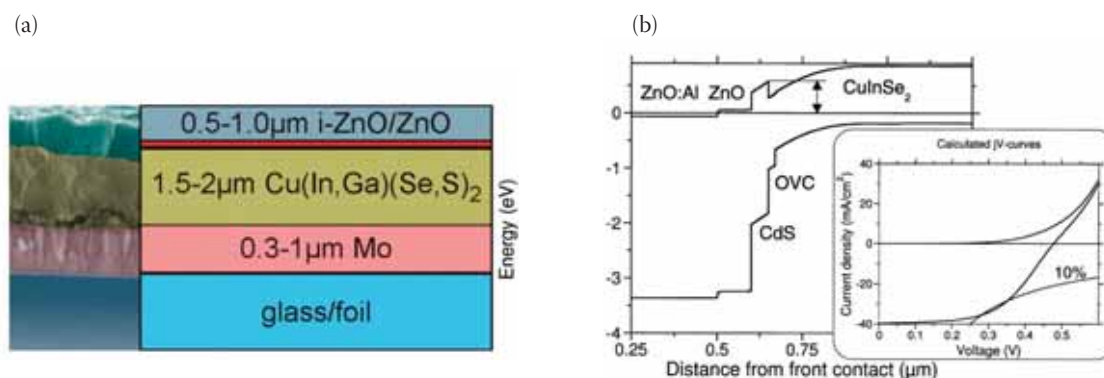


Figure 1. (a) Schematic of a CIGS solar cell (SEM cross-section on left). (b) Band diagram and simulated I-V curve (after Klenk [5]).

Buffer material	Band gap	Technology	Commercial application
CdS wet	2.4eV	CBD	Bosch, Würth, Solibro
CdS dry	2.4eV	Sputter	Miasole, Midsummer
Zn(O,S) dry	3.3–3.6eV Depends on S, with a minimum of 2.6eV at S/(S+O)=0.7	Sputter, ALD	–
Zn(O,OH,S) wet	3.7eV Mixture of ZnO, ZnS and Zn(OH) ₂	CBD	Solar Frontier
In ₂ S ₃ dry	2.0–2.8eV	Evaporation, ALD	Avancis (Evaporation)
In ₂ S ₃ wet	2.0–2.8eV	CBD, ILGAR, Spray Pyro	Honda (CBD)

Table 1. Band gaps, deposition technologies and commercial applications for different buffer materials.

interface inversion, or in other words n-type behaviour at the absorber–buffer interface.

On the other hand, if the conduction band drops at the interface (a so-called ‘cliff’), enhanced interface recombination will occur, which will cause a decrease in the open-circuit voltage of the device. If the conduction band arrangement cannot be modified, the band gap close to the interface should be widened by lowering the valence. This can be achieved by adding gallium or sulphur to the top region of the absorber layer or by creating a CIGS top layer that is very low in copper.

As already mentioned, CdS as the buffer layer works very well in CIGS solar cells, even if its band gap is not optimal because current in the blue part of the spectrum is lost. The use of CdS has a historical basis, as the original development of CIGS solar cells began with CuS/CdS devices; moreover, CdS works well in CdTe-based solar cells.

In most cases, CdS is deposited by chemical bath deposition using Cd acetate ($\text{Cd}(\text{OH})_2$) and thiourea ($\text{CH}_4\text{N}_2\text{S}$) as precursors in an ammoniac (NH_3) solution. The treatment of the CIGS absorber layer in the bath has its own advantage, as the absorber surface is cleaned again. As mentioned before, the band alignment between the CdS and the CIGS layers depends on the actual band structure at the absorber surface, and this alignment might lead to metastabilities, which will be discussed later. As the CdS deposition is the only wet-chemical process in a typical CIGS production line, a lot of research has been carried out on dry deposition methods, such as evaporation, sputtering and atomic layer deposition (ALD). Alternative Cd-free materials have also been investigated, to avoid the use of Cd and to increase the band gap of the buffer layer.

Nevertheless, CdS is the workhorse in almost all R&D CIGS-based production lines, because the deposition procedure is easy to perform and results in the best efficiencies. All record-breaking devices use CdS as the buffer layer – the reason why this is true, however, is still not known. The following possible explanations are under discussion:

- Optimal band alignment, even if there is a small spike
- Protection against sputter damage
- Cleaning of the absorber surface; removal of the secondary phase at the surface
- Best lattice matching between CIGS and ZnO
- Correct size of Cd atom to fit in a Cu-poor CIGS surface that is acting as an n-type dopant (shallow donor)

Cd-free buffer layer and alternative deposition methods

There are two reasons why the development of alternative buffer layers and deposition methods is important. First, a Cd-free buffer layer would create a more environmentally friendly product. This is required in Japan: two Japanese companies having CIGS module production facilities – Solar Frontier and Honda Soltec – both implement Cd-free buffer layers. Second, and more importantly, superior band gap materials would lead to greater current generation and better efficiencies.

In a review article, Naghavi et al. [6] summarized the efforts that have been made within the last few years regarding Cd-free buffer layers. Table 1 gives an

overview of the materials that were used as buffer layers, and the corresponding band gaps and deposition technologies. Only two Cd-free buffer layers were found to be comparable to CdS: Zn(O,S) and In₂S₃. In the case of Zn(O,S), the band gap depends on the S/(S+O) ratio, ranging from 3.3eV for pure ZnO to 3.6eV for pure ZnS, with a minimum of 2.6eV at a S/(S+O) ratio of 0.7. For the band gap with an In₂S₃ buffer material, however, several values between 2.0eV and 2.8eV were reported, but it is not clear whether In₂S₃ is a direct or an indirect semiconductor.

“A Cd-free buffer layer would create a more environmentally friendly product.”

Alternative techniques to CBD are under investigation because a wet-chemical deposition step interrupts an otherwise dry processing step during CIGS module production. In particular, direct evaporation and sputtering are promising methods for reducing the cost of deposition of the buffer layer. Two interesting alternatives are spray ILGAR – ion layer gas reaction – and ALD, since both of these methods allow a very conformal growth of the buffer layer.

Spray ILGAR was developed at the Helmholtz-Zentrum Berlin [7] and

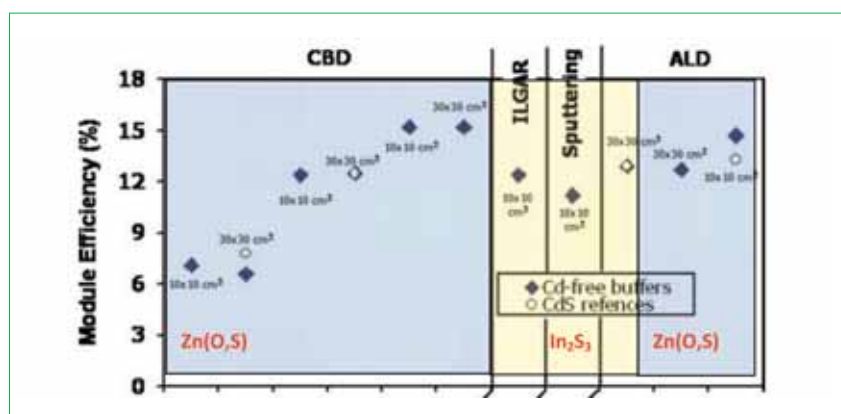


Figure 2. Best chalcopyrite solar cells and mini-modules with Cd-free buffer layers prepared using different technologies (after Naghavi et al. [6]).

involves the generation of an InCl_3 /alcohol aerosol, which is transported in a N_2 stream to the hot substrate (200–250°C); by using a chemical vapour deposition process, an $\text{In}(\text{Cl}, \text{O}, \text{OH})$ precursor layer is formed and subsequently converted into In_2S_3 in a H_2S atmosphere. The chlorine in the process seems to have an active role and has to be adapted to every absorber layer.

ALD of $\text{Zn}(\text{O}, \text{S})$ allows conformal growth of the buffer layer, avoiding pinholes. The scalability of the ALD process is currently being investigated at PVcomB, using a batch reactor system for up to seven $30 \times 30 \text{ cm}^2$ substrates.

Both of these alternative technologies have the disadvantage that they cannot be integrated into other deposition tools in a CIGS production line. However, efficiencies similar to those of solar cells undergoing CBD CdS have been demonstrated (Fig. 2).

From a production perspective, techniques such as sputtering or evaporation of the buffer layer material are much more interesting. Avancis announced that they have developed a buffer layer process using evaporated In_2S_3 . This process could be integrated into the CIGS-formation equipment using the heat of the evaporation process or thermal annealing process, whereas sputtering could be combined with the window layer deposition.

Most alternative buffer layer technologies require higher deposition temperatures or more post-annealing steps. In the case of CBD $\text{Zn}(\text{O}, \text{S})$, up to 30 minutes' annealing at 200°C and light soaking are required to produce high-efficiency solar cells [8]. In_2S_3 buffer layers are generally deposited at a temperature of around 200°C. Whether this high temperature is necessary to form a 'better' buffer layer or to cause some interdiffusion between the absorber and buffer layers is not fully understood. In the case of In_2S_3 ,

however, interdiffusion has been observed [9]. Nevertheless, solar cell devices employing alternative buffer layers are more sensitive to metastable behaviour, which will be discussed next.

“Solar cell devices employing alternative buffer layers are more sensitive to metastable behaviour.”

Metastabilities in CIGS solar cells

Transient or metastable effects in CIGS-based solar cells have been reported since the beginning of their development. After preparation, the CIGS-based solar cell in a relaxed state has a very low net acceptor doping density of less than 10^{15} cm^{-3} , leading to a reduced open-circuit voltage (V_{oc}) and fill factor (FF), a kink in the I - V curve, a reduced short-circuit current density (J_{sc}), or a crossover of dark and light in the I - V curve around V_{oc} . Table 2 summarizes the observed changes in a CIGS-based device which was stressed under different conditions.

A device will generally see increased performance after illumination and forward bias, which is the case in normal solar cell operation. This increase is caused by a change in the net acceptor concentration. However, special care has to be taken during development because of the following:

1. The CIGS solar cell after processing might not be in a relaxed state or at the maximum net acceptor density.
2. Storage in a dark environment will lead to changes, especially since some of the effects have time constants of several days.

3. Measuring a device will change it. Extra care has to be taken especially if the device is put under reverse bias. A hysteresis effect may be observed if the I - V curve measurements are taken from reverse to forward bias and back. Before taking measurements for I - V curves, the following rules should therefore be considered:

- a. Define a pretreatment of the CIGS-based solar cells, including light soaking and/or thermal annealing.
 - b. Always measure in the same direction, preferably from forward to reverse bias.
 - c. Do not stress the cell too long under reverse bias, and do not apply too high a reverse-bias voltage.
4. Alternative buffer layers are more sensitive to metastable changes.
 5. Dark I - V curves should always be inspected, as not all optimal devices will exhibit voltage-dependent current collection (extreme cases show crossover).

Often devices from the early beginnings of ramping-up CIGS solar cell production lines, in either research or industry, show more pronounced light-soaking effects than devices from established laboratories. Additionally, CIGS cells with Cd-free buffer layers are more sensitive to experiencing changes. The theoretical background of the underlying effect and its consequences will be discussed in the next section.

Theoretical explanation of metastabilities in CIGS and how to avoid them

All observed changes can be explained by a change in the net acceptor concentration.

Solar cell bias	Observed change	Derived change	Comment	Relaxed condition
Red light, r.t.	$V_{oc}+$, $C+$, $\sigma+$, N_d+	Persistent photoconductivity Increase in net acceptor density	Same as forward bias	Dark, annealing at 340–360K
Blue light, V_{oc} r.t.	$FF+$	Change in buffer layer	Reduction of barrier between buffer layer and CIGS	Dark, annealing at 340–360K
White light, V_{oc}	$V_{oc}+$, $FF+$, $C+$, $\sigma+$	Persistent photoconductivity Increase in net acceptor density Change in buffer layer (Cd-free)	No barrier in buffer layer	Dark, annealing at 340–360K
Forward bias, dark, r.t.	$V_{oc}+$, $C+$, $\sigma+$, N_d+	Increase in net acceptor density Creation of hole trap $E_d = 0.26 \text{ eV}$	Same as red light bias	Dark, annealing at 340–360K
Reverse bias, dark, r.t., -1V, 1h	$C+$, $FF-$	Increase in net acceptor density	Can be accumulated; drastically reduces efficiency	Dark, annealing at 340–360K

Table 2. Observed metastable change in a CIGS solar cell for different bias conditions at room temperature (r.t.).
(C = capacitance, σ = conductivity, E_d = deep-defect energy, N_d = doping density.)

Lany and Zunger [4] therefore proposed a ($V_{\text{Se}} - V_{\text{Cu}}$) divacancy complex (VV), whose charging state depends on the locations of the Fermi level having the characteristics of a relaxed donor model. The main results can be summarized as follows:

1. Donor configuration VV^+ and deep defect VV^0 : the In–In bond and defect level are close to the conduction band minimum (CBM).
2. Acceptor configuration VV^- : the In–In bond is broken, the distance is large between the In atoms, and the defect level moves close to the valence band maximum (VBM).
3. The reaction involves the rearrangement of bonds and the change of a shallow donor to a shallow acceptor:

$$VV^+ + 2e \rightarrow VV^- \quad (\text{A1})$$
 or,

$$VV^+ \rightarrow VV^- + 2h \quad (\text{A2})$$
4. The reverse reaction involves the capture of two holes, together with a lattice relaxation:

$$VV^- + 2h \rightarrow VV^+ \quad (\text{D1})$$
5. The energy barrier in CIGS is approximately 0.1eV for reaction A1 and approximately 0.7eV for reaction A2, while the reverse reaction has a barrier of around 0.3eV.
6. The distribution of the two states of the VV complex depends on the Fermi level. In a solar cell device, the acceptor configuration VV^- prevails.
7. The VV complex introduces a shallow acceptor state and an anti-bonding level of 0.85eV above the VBM, which might trap two electrons at that level if the Fermi level is close enough to the conduction band.

Reaction A1 explains the light-soaking and forward-bias effects (capture of electrons), whereas reaction A2 explains the reverse-bias effect (hole emission) – both of which are metastable states. Reaction D1 describes the relaxation into the stable state over a high barrier, which can be enhanced by temperature [3].

In terms of device properties, it can be concluded that white-light illumination provides extra holes close to the interface, creating a beneficial p^+ layer by increasing the number of VV complexes in the donor

state. Unfortunately, these complexes have detrimental effects in both charging states, so processes which lead to a reduced number of such VV complexes should therefore be used. This can be achieved by growing CIGS layers in a multi-stage approach that includes a copper-rich stage to reduce the number of Cu vacancy defects.

“White-light illumination provides extra holes close to the interface, creating a beneficial p^+ layer by increasing the number of VV complexes in the donor state.”

Conclusion

Resulting in similar efficiencies and lower production costs, Cd-free buffer layers created by dry deposition methods – such as evaporation, sputtering and atomic layer deposition – are viable alternatives to CdS buffer layers. Moreover, they may even lead to higher CIGS module efficiencies, since less light is lost in the buffer layer. Metastabilities are intrinsic to CIGS-based solar cells and caused by a defect complex of Se and Cu vacancies. Light soaking of CIGS-based devices will improve efficiency, while reverse bias or dark annealing at 80°C will return the devices to a stable, low-performing state. Nevertheless, high-efficiency solar cell devices show less improvement during light soaking, as the number of vacancies is reduced by choosing the ‘right’ preparation recipe consisting of a Cu-rich phase during CIGS formation.

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