Stability, reliability, upscaling and possible technological applications of kesterite solar cells

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Abstract

We review the stability and reliability results of kesterite (Cu₂ZnSn(S,Se)₄, CZTSSe)-based solar cells and we complete the reviewed data with additional as yet unpublished data on these matters. We also review published and new data on upscaling and the possible technological applications for this material. Kesterite material is composed of mainly earth-abundant elements and is therefore very attractive for large-scale applications. Stability data are so far quite scarce and the main results are the accelerated aging tests carried out for CZTSSe monograin technology, as well as yet unpublished data on long indoor and outdoor irradiance tests carried out on thin-film CZTSSe technology deposited by a wet processing method. On upscaling and technological applications we point out the works on three main large-scale photovoltaic technologies (monograin, in-line vacuum thin film, and wet-deposited thin film), as well as some work on water-splitting applications.

1. Introduction

The kesterite solar cell absorber Cu₂ZnSn(S,Se)₄ (CZTSSe) is a relatively earth-abundant material [1]. In particular, the sulfur-based kesterite solar cell absorber Cu₂ZnSnS₄ (CZTS) has the potential to be able to supply a very large amount of energy at modest prices, because the raw materials are widely available. Its selenium-based counterpart Cu₂ZnSnSe₄ (CZTSe) is a bit less abundant due to the presence of selenium in the lattice. In addition to the abundance of the raw elements, kesterite solar cells can be fabricated in roll-to-roll (R2R)-produced modules from powders or as very thin film layers, allowing for use of the solar cells in applications where low weight and flexibility are an advantage. However, there are remaining issues to be addressed like lower efficiency as compared to its peers Cu(In,Ga)(S,Se)₂ and CdTe[2], as well as the reliability aspects of the solar cells, which have to be able to show lifetimes in excess of 20 years. Whereas the efficiency gap is addressed in another contribution of this journal issue, we review in this contribution the different studies of the reliability and stability of kesterite-based solar cells and modules and we discuss the different technological applications that are under investigation and that will possibly open up commercial opportunities for kesterite material.

2. Stability and reliability of kesterite solar cells

Despite many years of research on kesterite solar cells, until today only a few publications have reported stability data on this type of cells because most papers so far have concentrated on improving the conversion efficiency of the devices. Several stability tests can be carried out on photovoltaic cells and modules. First are
indoor continuous irradiance tests, as well as outdoor (in-field) irradiance tests, done under real environmental conditions. Accelerated tests can be damp heat tests in the dark, damp/irradiance tests, heating tests in the dark, heating cycles, etc. On the other hand, international standards for the measurement of photovoltaic modules are published by the International Electrotechnical Commission. While there is no standard for kesterite technology available, a standard can be found for CIGS (the closest material to kesterite) in IEC 61215–1-4 [3], which directs to the testing standard IEC 61215–2 [4]. In these documents, various testing standards are described, including tests for the stability of modules, such as thermal cycling and humidity-freeze tests. In the damp heat test a temperature of 85 ± 2 °C, a relative humidity of 85 ± 5% and a test duration of 1000 to 1048 h should lead to less than 5% loss in conversion efficiency [3]. For any new technology, both non-standard and standard tests have to be considered, the latter being more appropriate when the product is close to the market or a new standard has to be defined.

2.1. Review of stability of thin-film kesterite solar cells

Peng et al reported thermal cycling and damp heat tests on CZTS cells [5], and analyzed performance evolution and scanning electron microscopy (SEM) of the device cross-section. The losses were attributed to the degradation of the top transparent conductive oxide (TCO) being either indium tin oxide (ITO) or Al-doped ZnO (AZO), a mechanism also pointed out for other thin film technologies using them. For two tested sets out of the three, they also claim moisture ingress as the cause of the degradation damaging the CZTS absorber and the junction of the cells.

Theelen et al reported some temperature effects and damp heat and illumination exposures mainly on Cu(In,Ga)Se₂ cells, but with a few results on CZTSe cells as well [6], analyzing performance and series resistance evolution. An unexpected increase of the open circuit voltage (V_{oc}) and efficiency was observed after 150 h of damp, heat and illumination exposures, but the starting efficiencies are not mentioned and only a normalized increase is reported.

A model for the decomposition of CZTS thin films was proposed by Yin et al [7]. They use analysis from x-ray diffraction, SEM-energy-dispersive x-ray and transmission electron microscopy. Here, a Cu–Zn separation was observed when applying directional heat with a heat plate. These investigations were carried out at temperatures between 350°C and 600 °C. Due to the relatively high temperatures far higher than the temperatures required in the above-mentioned standards or the temperatures reached in outdoor conditions, the published results of Yin et al are hard to utilize and to compare with aging mechanisms occurring at lower temperatures.

Darvishzadeh et al [8, 9] developed a degradation model and tried to fit literature data to the aging behavior of the short-circuit current (J_{sc}) or the open circuit voltage (V_{oc}) of perovskite and other thin-film technologies including kesterites. For the simulation of J_{sc} they took the data of an unusual n-type CZTSe cell, whereas for V_{oc} they took the data of Peng et al [5]. According to their modeling, the explanation for the degradation would be due to ion diffusion (defects) which would change the depletion layer; a different explanation, hence, to that of Peng et al, but in line with the results obtained by Neubauer et al for the unstable crystalsol powders reported below [10–12].

In summary, these scarce literature data do not give a clear picture of the stability of thin-film kesterite devices, though a few possible loss mechanisms were proposed in cases of durability issues.

In what follows we show as yet unpublished studies of stability, both indoor and outdoor (in-field) tests, on solution-processed CZTSSe thin-film solar cells and mini-modules made by IMRA Europe, which can shed some light on the potential of these devices.

This will be followed by recently published data on durability tests made by crystalsol on CZTSe monograins powders and modules.

2.2. Stability data of solution-processed kesterite solar cells

Here we disclose as yet unpublished data on stability tests performed by IMRA Europe on CZTSSe cells where the absorber layer is fabricated by a solution-based method. This method consists of a non-pyrolytic spray of a colloidal-based ink in a water–ethanol mixed solvent [13–16]. The colloidal dispersion is made of CZTS nanoparticles synthesized by a fast precipitation method. A two-step annealing, first in a N₂ atmosphere followed by a Se-containing atmosphere, leads to a CZTSSe film of micron-sized particles with a typical S:Se ratio of approximately 35:65. A controlled tuning of the Cu–Zn–Sn concentrations (especially Sn) allows us to get cell conversion efficiencies of the order of 10%, with the champion efficiency being 11.5% (J_{sc} = 34.1 mA cm⁻², V_{oc} = 0.51 V, fill factor (FF) = 0.66, and area 0.244 cm², with an anti-reflection coating (ARC)). The rest of the device structure is similar to that of other CZTSSe cells: a commercial Mo glass (with Na barrier), a CdS buffer layer, and i-ZnO and ITO window layers. In some cases, an ARC of MgF₂ was added. Ni/Al fingers were deposited on the front contact. The tested cells reported here showed an initial efficiency in the range of 9.5% to 10.5%, without any need for heat or light soaking.
The indoor stability test was a continuous lamp illumination (equivalent to approximately 1 sun irradiance) in open-circuit conditions, run over a long period of time of more than 5200 h (about 7 months). The cell performance was periodically measured under a calibrated solar simulator, and after a short current–voltage measurement, the samples were positioned back under the lamp of the stability setup. The ambient humidity in the lab during the period of the stability test was on average about 30% relative humidity, and the cell temperature under the continuous illumination was about 45 °C–50 °C. Four different samples were tested, each one containing 16 cells of 0.5 × 0.5 cm² area. They correspond to CZTSSe films with a 35:65 S:Se ratio and the same Cu:Zn:Sn ratio film composition (in the Cu-poor, Zn-rich region). The Cu:Zn:Sn precursor ratio was 45.3:28.6:26.0. The average composition of the film after annealing is still a matter of discussion, but several techniques seem to indicate that it is quite close to the precursor composition for this type of colloidal spray process. Two samples were unsealed and in direct contact with ambient air. The two other samples (also unsealed) were placed in a gas-tight box with static dry N₂ gas mounted in a N₂ glove box, a situation which can be considered almost as sealed. The cells, though, were taken out into ambient air for the short current–voltage measurement, then put back into the box and re-filled with N₂.

For each of these two groups of samples, one sample had the ARC and the other did not. The evolution of the cell efficiency and the other performance parameters was very similar among the 16 cells within each sample, and among the four different samples (figure 1). The cell performance decreased by less than 10%–20% in the first 500 h and afterwards it stayed stable or even slightly increased. There was not a clear difference on the effect of the atmosphere in contact with the cells (ambient air or dry N₂), nor on the effect of having or not having an ARC in the cell. Therefore, these factors are likely not the cause of the initial decrease of efficiency. These results are quite promising, though additional tests, such as a higher cell temperature (up to 85°C) or cells connected to a load, should be carried out to confirm this tendency.

A more detailed insight into the other performance parameters is shown in figure 2 for one of the samples, namely the sample inside the box with N₂, and with ARC, the other samples showing similar tendencies. The initial loss of efficiency is mainly due to a loss in \( J_{sc} \) (initial average \( J_{sc} \) of approximately 32 mA cm⁻² for that sample) and FF (initial average FF of approximately 0.63 for that sample). The variation of the series resistance \( R_s \) with time seems quite small and likely does not affect the FF. The causes of these initial losses on \( J_{sc} \) and FF are still unknown. After the first 500 h, the performance parameters were not degraded. On the other hand, the \( V_{oc} \), which showed a negligible loss in the first 500 h (initial average \( V_{oc} \) of ~0.51 V for that sample), slightly increased with time, surpassing even the initial value. This behavior could be explained by the slow increase of the Cu/Zn cation order degree on the kesterite structure [17]. Indeed, it has been shown in [16] that cells heated at temperatures around 80 °C–100 °C for several days lead to a small increase of the band gap, and, in turn, to some increase of \( V_{oc} \) and some decrease of \( J_{sc} \), the decrease in FF being less evident to explain. Since the cell temperature in this stability test was about 45 °C–50 °C, the possible Cu/Zn ordering would be much slower, so it is not certain whether this phenomenon occurred in the time framework of this test.

In summary, these long stability tests of continuous illumination carried out on quite efficient (~10%) CZTSSe cells fabricated by solution process have shown good stability with less than 10%–20% loss versus the initial performance.

Concerning outdoor tests under a real environment, IMRA devices of large area are being tested in the framework of the European STARCELL project (H2020-NMBP-03-2016-720907). The first results are described in the next paragraph.

2.3. Field testing of mini-modules made of solution-processed kesterite

The testing of a kesterite mini-module under a real environment was carried out in the industrial solar plant co-owned by Ayesa, located in La Rinconada, Córdoba (Spain), where the company performs maintenance and supervision works. The control system collects field irradiance, device temperatures and generated power continuously. Some other weather parameters were also recorded (ambient temperature, humidity and wind speed). The kesterite mini-module was placed next to large commercial solar panels mounted on two-axis trackers. Trackers are used to ‘track the sun’ and always find the best tilt of the PV panel with the aim of having the greatest amount of solar irradiance, which means more energy production. Some of the control system levels were implemented for monitoring the performance of the kesterite mini-module. The sealed mini-module (see description below) was placed in a box for placing the connections and sealed with silicone paste to avoid water entering, the front glass of the sealed mini-module being in direct contact with the ambient environment and light. A regulator and measurement system was in charge of maintaining the cell at the maximum power point. A basic regulator was implemented in order to reach the maximum power point of the device with a methodology of trial–error and different attempts to reach it according to the environmental conditions. Due to the small impedance of the kesterite mini-module, some shift on the
Figure 1. Evolution of normalized cell efficiency under continuous lamp irradiation (~1 sun) and open circuit condition for four types of samples (each one having 16 cells of 0.5 × 0.5 cm$^2$ area). CZTS:Se thin films with a 35:65 S:Se ratio.

maximum power point could occur, but this does not prevent following the evolution of the measured device power with time. “GridPilot”, a supervisory control and data acquisition (SCADA) system based on web and developed by Ayesa has been customized and configured to monitor the in-field data of production, current, voltage, weather and other parameters.

The initial period shown here covers three and a half months, from the hot summer to the autumn, comprising cloudy days as well as some days of strong rain. Hence, this gives a very first idea of the behavior of the device in real and hard conditions. The kesterite mini-module of 5 × 10 cm$^2$ was made by IMRA Europe by scaling up its wet deposition method (colloidal ink spray), using two large cells 5 × 5 cm$^2$ (finger configuration) connected in series, as described below.
Figure 3 shows the evolution of the device power delivered continuously as well as the in-field irradiance. It can be clearly seen that the device power has remained basically constant during this period, knowing that the changes in device temperature and diffuse light can change the power for the same irradiance. The average of irradiance taking into account 24 h a day was around 370 W cm\(^{-2}\) in this very illuminated region over the summer period. In the zoom of figure 3 it can be seen how closely the device follows the changes of irradiance on the same day. Device temperatures have changed from less than 10 °C to over 40 °C.

For a better evaluation, a daily power output statistic has been carried out. Power values have been filtered first for irradiances between 900 and 1100 W m\(^{-2}\) each day in order to show homogeneous data. Then, as shown in figure 4, a boxplot for each day gives the median, a confidence interval of about 95% for the power output and ‘outlying’ points. This further confirms that the delivered power at around 1 sun remained constant over this period.

In summary, for the first time outdoor tests under a real environment of a kesterite mini-module were carried out and show potentially good durability in real environmental conditions.

2.4. Stability of monograin kesterite powders, solar cells and modules

Another type of CZTSSe-based solar cell is that based on monograin technology, developed by crystalsol. Details of the technology are explained in section 3.1. The main tests carried out by crystalsol were heat tests.
in dry atmosphere in contact with air without illumination, either on grains alone, grains coated with CdS, or unsealed modules.

The stability of powders and modules has been investigated in detail [10, 11, 18, 19]. A critical parameter that was found to be important for the long-time stability of the grains used for this technology (up to 3000 h at 85 °C) is the exact ratio of anions (S\(^{2-}\) and/or Se\(^{2-}\)) to cations (Cu\(^{+}\), Zn\(^{2+}\), Sn\(^{4+}\)) and their relative content and real oxidation state in the precursor material. The final composition of the crystals, the impurities and vacancies may vary and with it also the stability of the powder material. In particular, a too large copper deficit with respect to the crystal unit cell determining tin ions seems to lead to non-stable CZTSSe materials. In the Estonian part of the company crystalsol, CdS-coated CZTSSe powders are routinely tested for their long-time stability by keeping them in air at 105 °C for a few days before finishing cells to test the possibility of shipping them to Austria without losses. In these tests, stable powders do not lose efficiency.
Even storing the single-crystalline powders in general does not decrease the efficiency of cells made even after a few years.

For efficiency and also for stability, the exact composition of the material plays a key role. As shown in figure 5 for CZTSSe with S/Se ratios of 80/20 and 60/40, the copper content in particular plays a key role. Crystalsol’s internal classification defines as ‘stable’ cells losing less than 5% of their starting efficiency in the 1000 h accelerated aging test at 85 °C (many of them being ‘completely stable’, i.e. without any loss of efficiency). Other classes are ‘promising’ for those with less than 10% loss (91%–95% of initial efficiency), ‘possible’ (51%–90% remaining efficiency), and ‘unstable’ those with less than 50% but still measurable efficiency after 1000 h testing.

Whereas the Zn:Sn ratio seems to have no or little influence on the stability of kesterite, the copper content seems to be critically important. For monograins with higher sulfur content (80%), the Cu:(Zn + Sn) ratio should be between 94 and 98%. For a higher content of selenium the range of Cu:(Zn + Sn) ratio leading to a stable material may even be smaller and around an even lower concentration, between 93% and 94%.

The humidity test mainly aims at testing the module sealing since all contact materials (mainly TCOs, but also metal (Al, Ag, Cu) films) corrode in humid surroundings. However, the solar cell materials also need to be stable at these temperatures. So crystalsol tested the CZTSSe powders and modules without sealing, mainly in a dry atmosphere at 85 °C as shown in figure 6. Here, different modules were prepared mainly from 80:20 S:Se ratio powders with Cu/(Zn + Sn) = 0.97 and Zn/Sn = 1.06, and measured in a standard solar simulator after different amounts of time in an oven at 85 °C in the presence of a silica gel drying agent (circles, squares and diamonds). For comparison, also a 50:50 S:Se ratio module (triangles) with similar metal composition is included, which here showed slightly lower stability.

Although crystalsol’s stoichiometric CZTS monograins are very stable even in air, powders can also be produced with much less stability. Such powders have been investigated in detail [10–12] using several techniques such as performance parameters and serial resistance variations, EQE, PL, LBIC and EBIC. Crystalsol’s aging or degradation investigations on unstable CZTS and CZTSSe powder-based solar cells show two main degradation processes. One is short-term and temporary back-side degradation with a non-Ohmic barrier built up. The second is a long-term permanent front-side degradation leading to an increase of resistance and recombination. As a main reason for this, copper diffusion from CZTS to the
buffer layer of CdS is identified. Copper in CdS leads to a well-known increase of dark resistance, effective charge carrier recombination processes and pronounced photocurrent effects.

Interesting results were obtained in outdoor tests of modules protected only by polyethylene terephthalate (PET) foils, permeable for water, as shown in figure 7. Parallel accelerated aging tests (85 °C in dry air, no sealing) showed a continuous decrease of efficiency by about 50% within 1000 h (assumed to simulate a use of about ten years).

However, as demonstrated here, the modules in humid outdoor conditions show additional efficiency losses during the summer months, partly recovering until the following March. Such a climate effect has to our knowledge not been reported before. It is assumed to be due to changes in the junction behavior of the devices. Further investigations of this effect need to be performed.

In summary, long heat tests (in dry air) on powders and modules for crystalsol’s monograin technology have shown very good stability potential for CZTSSe compositions with a Cu/(Zn + Sn) content in a narrow interval comprised in the range ~0.90–0.98. Especially for higher Cu concentrations the degradation mechanisms are related to the degradation of the back and the front junctions most probably related to Cu ion diffusion.

3. Technological applications of kesterites

3.1. CZTS powder-based non-vacuum-produced and fully roll-to-roll monograin solar modules

The company crystalsol, founded in 2008 in Tallinn as OÜ and a year later in Austria as GmbH (both meaning a limited liability company), developed a very low cost powder and roll-to-roll (R2R) module production based on CZTSSe single crystals, [20] as shown in figure 8.

As a first step, powder grains with diameters starting from about 25 µm are grown in Tallinn, Estonia. The elemental precursors copper, zinc, tin, sulfur and selenium, or the binary precursors such as Cu2Se, ZnSe and SnSe, are mixed with an inert salt (mainly an alkali halide) and heated at small scale in evacuated quartz
Figure 8. SEM image of a kesterite single-crystalline grain (a) and a photograph of kesterite monograin powder (b) as produced in crystalsol OÜ in Tallinn, Estonia. The bright-looking spots are light reflexes from crystal planes directly reflecting the light of the sun into the camera. All particles in this image have diameters between 50 and 60 µm.

Figure 9. Prototype R2R printing line for the production of up to 30 cm wide active layers for endless monograin modules including wires and threads for structuring.

ampoules, as described in detail in [21–23], or, for larger amounts (currently up to a few kilograms), in graphite containers in inert atmosphere to temperatures above the melting point of the salts. Thereby, these salts act as a solvent for the metal ions and facilitate the growth of the powder grains. After cooling, the salt cake is dissolved in water and the CZTS powder separated by sieving. Too large grains are milled and, together with too fine powders, used for other growth processes. Thereby, very high overall yields can be obtained. After cleaning the surface, e.g. by etching followed by annealing, nice and often perfectly tetrahedral-shaped grains (see figure 4) are obtained. In order to protect the surface, a CdS layer about 30 nm thick is deposited all around the crystal in a classical chemical bath deposition process, thereby coating the p-type material already with the intrinsic or n-type buffer layer, as needed to finally form the photovoltaically active heterojunction front contact. Such protected powders are then stored or transported in air in order to print PV modules at crystalsol GmbH in Vienna, Austria. Even a few very old powders have been used to yield cells with the previously measured efficiency.

Figure 9 shows a photograph of crystalsol’s pilot R2R printing line for the active layer including the wires for series connection of the cells and threads for structuring the front contact (see also [24]).

The module production starts with printing a thin polymer layer on a re-usable substrate, into which first metal wires for the series connection of cells, and then a single layer of powder particles, are embedded [22, 23]. Every grain is already a small solar cell, since the p-type kesterite single crystals are already coated with an n-type buffer layer (e.g. cadmium sulfide or zinc oxysulfide) [25].

All grains are then contacted on the front side with printed ZnO contact stripes [26], and on the back side, after mechanical abrasion (thereby removing the buffer layer and opening the p-type core), with thin graphite stripes and a standard metal-based or a second transparent TCO back contact for transparent modules. These contacts connect the grains in parallel to each other, forming endless stripes of about 6 mm wide cells, interrupted by metal wires, which separate the cells and provide a highly conductive pathway from the front to the back side. The wires are in contact on one side with the TCO front contact of a cell on one side of the wire, and on the other side with the back contact stripe of the neighboring cell, so that all cells of
the (endless) module are connected monolithically (see figure 10). A front contact stripe on one side of the module and a back contact stripe on the opposite side of the module provide the outside contacts of such series-connected cell stripes. The voltage of the module is then determined by the number of cells within the module, currently about 20 V. Nearly all production steps of this module production are unique and were developed in-house.

For building integration applications, these flexible non-encapsulated modules can be used directly by companies producing facade or window elements. For outdoor applications, the modules need usual front- and back-side protection against water and mechanical impacts.

3.2. Upscaling of thin-film CZTS technology

3.2.1. All in-line vacuum process.

Vacuum processes have demonstrated great potential for producing high-performance thin-film solar cells for CIGS and CdTe technologies [27]. Next to the traditional production technology of CIGS and CdTe by combining vacuum and solution processes, a complete all in-line process has even higher advantage to enhance the throughput for the solar cell fabrication from an industrial perspective. Such an all in-line sputtering process was realized in CIGS technology by Midsummer with good cell uniformity, decent performance as well as high throughput [28, 29]. Nevertheless, for new materials such as kesterite, several improvements have to be made to the technology before bringing it to large industrial scale. In the case of Midsummer technology, which uses stainless steel as the cell substrate for a fast all in-line sputtering process, remaining challenges need to be tackled in kesterite technology, like improving the uniformity of the substrate heating.
An entire CZTS device was processed in a UNO-type home-design research and development in-line sputtering tool, i.e. a re-built SMO unit from Ulvac, for processing steps including annealing. Firstly, a 6 inch (15.6 × 15.6 cm$^2$) stainless-steel substrate was automatically loaded into the loadlock chamber and pumped down. Then the substrate was indexed to the first sputtering station for a conductive diffusion barrier deposition in order to prevent Fe diffusion towards the absorber material. The process continued with the deposition of a Mo-containing back contact layer. CZTS precursors of less than 1 µm were then DC pulse sputtered from compound CZTS targets of different composition. For the samples presented here, a single CZTS compound target with the composition of Cu/Sn = 1.76 and Zn/Sn = 1.24 was sputtered at the power density of 2–3 W cm$^{-2}$ under the pressure of 6 × 10$^{-2}$ to 4 Pa. During the sputtering, the substrate was not intentionally heated. Next, the as-prepared CZTS precursor was directly automatically transferred into an annealing chamber station for rapid thermal treatment in a mixture of Ar and H$_2$S at a pressure of about 5 × 10$^4$ Pa. After the annealing temperature of 550 °C was ramped up in 5 min, the annealing started and lasted for another 10 min. In the end, a natural cooling process down to below 150 °C was employed with the same gases in the annealing station before moving to other sputtering chambers in-line. Solar cell devices were finalized by sputtering an In-based buffer layer of less than 50 nm thickness and then a ZnMgO/ITO-based window layer. A top contacting grid was deposited by screen printing of low-temperature silver paste and subsequent curing at 200 °C. CZTS cells of 1 cm$^2$ were then mechanically scribed.

As seen in figure 11, the high to low cell performance is consistent with the high to low temperature distribution on the substrate. This temperature distribution has been shown to impact the distribution of CZTS composition, CZTS grain growth and secondary phase formation. CZTS solar cells with a n average of about 3% efficiency with a top performance of 5.1% have been achieved with 1 cm$^2$ total area devices on a 225 cm$^2$ size stainless-steel substrate [30].

### 3.2.2. Wet deposition process.

In addition to the scaling up of vacuum technologies, research has been carried out at IMRA Europe to scale up its wet deposition method (colloidal ink spray), and this is in the framework of the European STARCELL project (H2020-NMBP-03-2016-720907). The non-pyrolytic spray of the colloidal-based ink explained in section 2.1 can be applied onto 10 × 10 cm$^2$ areas with small variations of the spray parameters. The Cu:Zn:Sn ratios of the precursors were also slightly changed to a more Zn-rich composition (43.6:31.3:25.1), which led to a higher reproducibility when testing small cells, therefore a higher homogeneity on large areas is expected. The annealing step could also be scaled up, leading to quite homogeneous CZTSSe films. The deposition process of the front layer ZnO/ITO was already scaled up to 10 × 10 cm$^2$ areas. A finger configuration was designed to make large cells of either 5 × 5 or 5 × 10 cm$^2$ sizes, with 1 or 3 bus bars, respectively. The fingers were deposited by e-beam through a mask made of Ni(50 nm)/Al(4 µm)/Ni(10 nm). Sn-based current collectors were soldered on the bus bars and around the edge to the Mo back contact. The absorber areas were ~16–18 cm$^2$ or ~36–40 cm$^2$ for the 5 × 5 and 5 × 10 cm$^2$ cells, respectively. The best
performances (versus absorber area) were 6%–7% at irradiances of 0.5 to 1 sun. Mini-modules were fabricated with two series-connected large cells of 5 × 5 cm$^2$. The best efficiency at 1 sun was 7.0%, without sealing, showing practically no loss with respect to the performance of the individual large cells. A comparison of the performance of the different devices and those of small cells is shown in table 1.

(a) Current of mini-module divided by area of individual cell
(b) $V_{oc}$ of mini-module divided by two, the number of cells in series

When corrected by the dead area due to the fingers, it appears that $V_{oc}$ does not change with upscaling, and $J_{sc}$ is very close to the average values of small cells. The main loss in upscaling at this moment is the FF. Comparing with other parameters like the series and shunt resistance, as well as the ideality factor and saturation current (extracted by fitting to a single-diode model), it appears that it is the series resistance, and to some extent the shunt resistance, which will be the cause of the loss in the FF. The increase in series resistance is likely due to the soldering of the current collectors to the bus bars and the Mo back contact, which is at present a delicate manual operation, and/or some resistance coming from the Mo layer, and from the fine Al grid lines. On the other hand, the step from large cells to mini-modules does not represent any significant loss since the performance and sizes of the individual large cells were quite similar.

The mini-modules were sealed with a piece of soda-lime glass and a Torr-Seal epoxy adhesive (figure 12). A loss of about 6% in performance took place due to the reflection of the front glass. This sealing method was used as a proof of concept, but plastic encapsulation methods are other alternatives. One of these sealed mini-modules was sent to the in-field tests of the Ayesa group for durability tests in a real environment. The results of these tests have been explained above.

In summary, these upscaling results show that the absorber layer deposited by this colloidal ink spray method should be quite homogenous since the $J_{sc}$ after the dead finger area is removed and the $V_{oc}$ are very similar to those of small sister cells of 0.25 cm$^2$ area. The upscaling shows a loss of about 2 percentage points versus the small cells.

### 3.3. CZTS for water splitting

Another possible application for kesterite solar cells would be as electrodes in photoelectrochemical water-splitting devices. Using earth-abundant kesterite absorber for these applications would also keep the costs down, even at the large production rates necessary for large-scale hydrogen production. Ros et al used kesterite-based solar cells as a photocathode and achieved good efficiencies using an atomic layer-deposited (ALD) TiO$_2$ protection layer [31]. Large differences have been found in performance between CZTS and CZTSe, mainly due to the sensitivity of CZTS to long ALD processes, degrading the device.

Here, crystalsol’s monograin technology also proved to be very promising, allowing production of monograin membranes separating the hydrogen-evolving electrolyte from the oxygen-evolving one [32]. Very recent results even demonstrate membranes including ionically conductive spots resembling biological thylakoid membrane [33].

### 4. Conclusions

We have reviewed the stability, reliability, upscaling and technological applications of kesterite material, and disclosed some unpublished data. Long stability tests on wet-processed kesterite cells both under continuous...
indoor irradiance and in outdoor field tests showed no or small initial efficiency loss. In addition, long accelerated heat tests on monograin-based kesterite cells did not show any large degradation for certain CZTS compositions. The monograin technology is quite advanced, and in particular ready for indoor flexible applications. The thin-film technologies are under investigation, with two main types: an all in-line vacuum process, or a wet process based on colloidal ink spraying. The latter already showed >7% efficiency in the first test, which is less than 20% loss with respect to small cells of the same structure and composition. Possible technological applications of kesterite-based solar cells have been identified in the fields of photovoltaics and water splitting, both technologies largely taking advantage of the relative low cost and abundancy of the starting materials, allowing long-term mass production at relatively low cost.

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