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The path towards efficient wide band gap thin-film kesterite solar cells with transparent back contact for viable tandem application

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ABSTRACT

Wide band gap thin-film kesterite solar cell based on non-toxic and earth-abundant materials might be a suitable candidate as a top cell for tandem configuration in combination with crystalline silicon as a bottom solar cell. For this purpose and based on parameters we have extracted from electrical and optical characterization techniques of $\text{Cu}_2\text{ZnGeSe}_4$ absorbers and solar cells, a model has been developed to describe the kesterite top cell efficiency limitations and to investigate the different possible configurations with transparent back contact for four-terminal tandem solar cell application. Furthermore, we have studied the tandem solar cell performance in view of the band gap and the transparency of the kesterite top cell and back contact engineering. Our detailed analysis shows that a kesterite top cell with efficiency $> 14\%$, a band gap in the range of 1.5–1.7 eV and transparency above 80% at the sub-band gaps photons energies are required to achieve a tandem cell with higher efficiency than with a single silicon solar cell.

1. Introduction

Kesterite materials have been widely investigated as potential absorber layers for thin-film solar cell technology with a record efficiency of 12.6% reported for CZTSSe based devices [1]. The band gap of these absorbers can be tuned either by varying the S/Se content or by partially replacing tin (Sn) atoms by silicon (Si) or germanium (Ge) atoms. The development of wide-band gap kesterite solar cells based on abundant and low-cost materials might be beneficial for tandem solar cell applications, if used as a top cell with the existing high efficiency crystalline silicon solar cells in a four-terminal configuration.

However, since most of the earth abundant materials have strong absorption and poor electronic properties due to their chemical and structural defects, further development of both absorber material and device architecture are required to achieve high-efficiency devices.

Germanium incorporation in CZTSSe kesterite based solar cells has been studied before and device efficiencies up to 9–12 % have been reported with band gaps in the range of 1.2–1.1 eV [2,3]. Also, kesterite solar cells with a band gap of 1.4–1.5 eV were fabricated with pure Ge substitution [4–7]. However, the efficiency of Ge based kesterite solar cells is still below the record efficiency obtained in CZTSe cells. Thus, further and significant improvement of both absorber materials and device structure have to evolve to achieve high-efficiency solar cells based on these compounds.

The current challenge with kesterite based solar cells is the growth of the kesterite phase without secondary phases which are known to limit the solar cell performance. The most commonly reported secondary phases (binary and ternary) are Zn(S)Se , Cu(S)Se_2 , Sn(S)Se_2 , $\text{Cu}_2\text{Sn(S)Se}_3$ [8–11] and has been reported even in devices with high efficiency. Their effect on the solar cell performance strongly depends on their

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position in the kesterite film and their electrical and optical properties. They could form at the front, in the bulk and at the back side of the thin film, therefore it is important to track down their location in the film and understand the conditions of their formation during the film growth in order to avoid or minimize their effect.

However, despite the availability of several wet chemical etchants to remove the secondary phases, only the ones located at or near the surface of the film can be etched away during the device preparation.

The use of earth abundant and low toxic material as a top cell on a crystalline Si bottom cell in a tandem configuration is an alternative layout suggested to boost the solar cell efficiency and reduce the production costs. In tandem structure, photocurrent matching is one of the requirements that should be considered in the design of series-connected tandem solar cells, which is usually obtained by adapting the thickness of the top cell and the band gaps of both top-cell and bottom-cell. In a four-terminal mechanically stacked tandem structure, current matching is not necessary, since the two cells are independently connected. However, because of the mechanical stacking approach, a top-cell with transparent electrodes and good transparency at long wavelengths is mandatory.

In this work, $\text{Cu}_2\text{ZnGeSe}_4$ (CZGSe) absorbers and ZnO/CdS/ $\text{Cu}_2\text{ZnGeSe}_4$ /Mo/Glass solar cells with an optical band gap of $E_g \sim 1.5\text{eV}$ and an efficiency up to 7% are studied using various electro-optical characterization techniques to investigate the device performance. Furthermore, we present a model based on realistic parameters extracted from the measurements to discuss in detail the efficiency limitation in these wide band gap materials.

In addition, numerical simulations are used to determine some of the cell requirements and the best configuration for the kesterite based solar cell with transparent back contact if to be used as a top cell on a c-Si bottom cell in a four-terminal tandem structure.

2. Experimental

2.1. Device preparation

The solar cells were prepared by DC-sputtering of Cu and Zn layers and e-beam evaporation of Ge layer on $5 \times 5 \text{ cm}^2$ Soda-Lime Glass (SLG)/SiON/Mo substrate. The SiON barrier layer thickness is about 120 nm and is used to inhibit excessive diffusion of Na and other impurities from the glass into the absorber. The precursor layers were then selenized at 470°C in a 10% H_2Se atmosphere for 15 min. The absorbers were etched in a HCl solution with a concentration 12 wt% and at a temperature 80°C for 15–20min to remove ZnSe secondary phases from the surface of the CZGSe absorber.

For the solar cell preparation, a thin *n*-type CdS buffer layer was deposited using chemical bath deposition, followed by RF-sputtering of *i*-ZnO (120 nm) and Al doped ZnO (350 nm) layers. For the top contact, a 50 nm Ni - 1 μm Al finger grid pattern was evaporated through a shadow mask. Cells with an area about 0.5 cm^2 were isolated by needle scribing. More details about the cells preparation can be found in Refs. [4,5].

2.2. Device characterization

X-ray diffraction (XRD) was performed on thin film absorbers deposited on glass and on complete solar cells to study the structural properties of the films. The XRD patterns of the films were performed on a Bruker D8 Discover equipped with a LynxEye silicon strip detector in the Bragg-Brentano configuration with $\text{Cu K}\alpha$ radiation.

Fourier transform infrared spectroscopy was carried out using a Bruker Hyperion 2000 microscope coupled to a Bruker Vertex 80v. The measurements were recorded in reflection using the microscope under near normal incidence conditions to estimate the thickness of the films from the interference fringes. The IR absorbance was performed using the spectrometer to investigate the vibrational modes of the kesterite and any other phases which may be produced during the growth of the

films.

Transmission/Reflection spectra were measured on CZGSe absorber deposited on Quartz using a Varian Cary 500 UV/Vis spectrometer.

The mobility of the *p*-type CZGSe films deposited on glass was determined from AC Hall measurements in the VanderPauw configuration.

Capacitance voltage (*C-V*) and admittance spectroscopy *C-f-T* (AS) were carried out using a HP 4192 A LF impedance analyzer in the frequency range 10^2 – 10^7Hz . The doping density in the CZGSe absorbers was calculated from the *C-V* measurements, while the admittance spectroscopy technique allows us to identify and analyse the defects in these devices [12]. Temperature dependent measurement *C-f-T* and *J-V-T* were performed using a cold finger cryostat mounted on a nitrogen source.

The microstructure of the cells and the film morphology was further investigated using transmission electron microscopy (TEM) on samples prepared using the focused ion beam (FIB) technique, on a Be support. Prior to the sample preparation, a Pt/carbon layer was deposited on the films to protect the surface layer. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and energy dispersive X-ray (EDX) maps were acquired using a FEI Tecnai Osiris microscope equipped with a Super-X detector and operated at 200 kV.

The data were recorded using probes with convergence semi-angles in the 21–25 mrad range (with a probe size of about 1 Å) and the EDX maps were generated from the intensity of the Cu-K, In-L, Ga-K, Se-K, Cd-L, S-K, Zn-K, O-K, C-K, and Mo-K lines.

3. Results and discussion

3.1. Electro-optical characterization

Fig. 1 shows the XRD measurements performed on a bare CZGSe absorber and the complete solar cell. The JCPDS cards of tetragonal $\text{Cu}_2\text{ZnGeSe}_4$ (No. 00-052-0867) and ZnSe (No. 01-088-2345) were used to identify the different phases. The kesterite phase is formed in both cases with good crystallinity in a tetragonal lattice with $a = 5.606 \text{ \AA}$ and $c = 11.042 \text{ \AA}$. In Fig. 1(a), XRD peaks related to ZnSe phases can clearly be seen in the XRD patterns of the CZGSe absorbers grown on glass before the HCl chemical etch. These peaks are no longer detectable in the finished devices (Fig. 1(b)), as the absorbers underwent hot wet-chemical etch before the chemical bath deposition of the CdS buffer layer.

The optical band gap of the absorbers was deduced from the tauc-plot [13] of the absorption coefficient and has values between 1.45-1.49 eV in these CZGSe based solar cells as plotted in Fig. 2.

The CZGSe film thickness as determined from the interference fringes has values between 1.4 and 1.7 μm . A refractive index of 2.92 was used for the calculation of the film thickness, as estimated from the Moss equation [14]:

$$E_g n^4 = k \quad (1)$$

where E_g is the band gap of the material and k is a constant with values 95–108 eV.

The absorption coefficient α was calculated from the measured transmission and reflection of the films using UV-Vis spectroscopy given in the supplementary material (Fig. S1), as [15].

$$\alpha(\lambda) = \frac{1}{d} \ln \left[\frac{1 - R(\lambda)}{T(\lambda)} \right] \quad (2)$$

The doping density in these cells is quite low ($< 10^{15} \text{ cm}^{-3}$) plausibly caused by the use of the SiON barrier layer which inhibits diffusion of Na into the absorber layer. In their work on the beneficial incorporation of Ge into CZTSe absorber, Giraldo et al. [16] have demonstrated that during the reactive annealing there was a strong reaction between Ge and Na, which controls the doping density of the absorber.

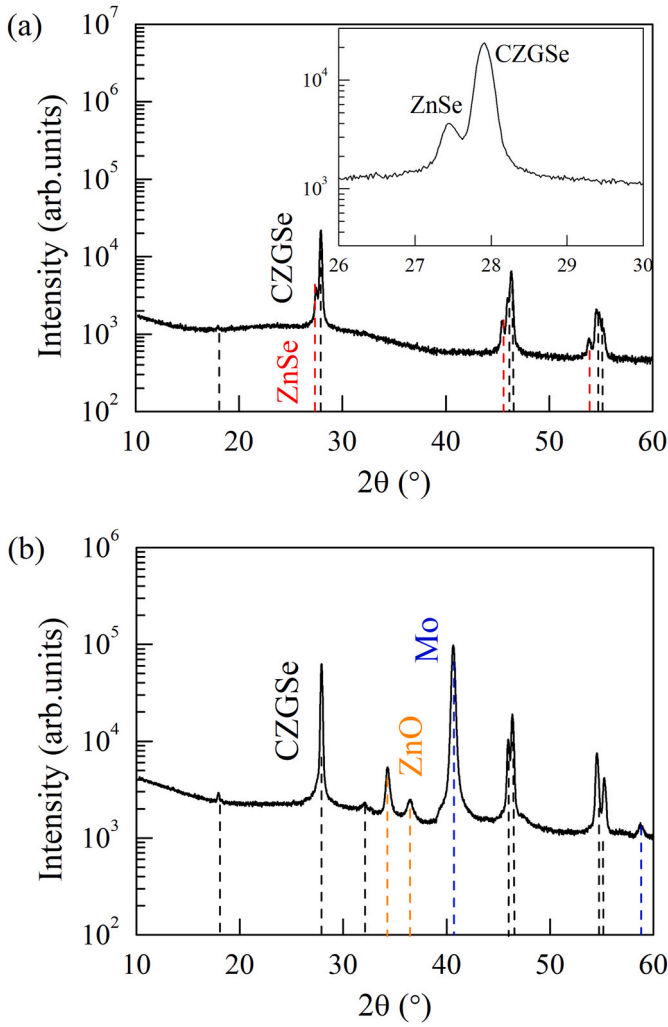


Fig. 1. XRD patterns measured on CZGSe absorber film deposited on Glass (a) and on the CZGSe solar cell (b). The JCPDS cards of $\text{Cu}_2\text{ZnGeSe}_4$ (00-052-0867) (black dash lines) and ZnSe (01-088-2345) (red dash lines) were used for the identification of the different phases. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The role of Na was well investigated in $\text{Cu}(\text{In,Ga})\text{Se}_2$ based solar cells [17] and its beneficial effect has also been reported in kesterite solar cells. It was shown that adding Na during the film growth either by diffusion from the SLG substrate or by using a Na precursor layer, enhances the grain growth and crystallization of the film [18] and increases the p -type doping of the absorber and the open-circuit voltage (V_{oc}) [19,20]. Note that the p -type concentration measured by the Hall measurements on these CZGSe films deposited directly on glass was quite high $\sim 10^{18} \text{ cm}^{-3}$ and we assigned this to a high diffusion of Na from the soda lime glass into the absorber. This leads us to conclude that using controlled Na precursor layers might be the best way to incorporate Na in these absorbers and use its beneficial effects. The average value of hole mobility measured in the films was $2.3 \text{ cm}^2/\text{V.s}$. Also, it is worth considering that the mobility measured by Hall-effect measurements is commonly limited by defect states and a high potential energy barrier at the grain boundaries where scattering of carriers plays an important role in the polycrystalline films.

Admittance spectroscopy (AS) and current-voltage measurements under different temperature and illumination (J - V - T) were performed to get more information about defects and recombination mechanisms governing the performance of these devices.

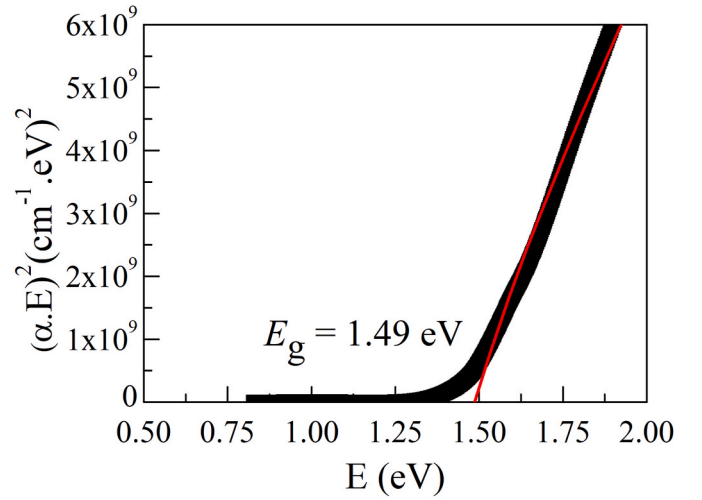


Fig. 2. Optical band gap of CZGSe absorber extracted from the Tauc plot of the absorption coefficient calculated from transmission/reflection measurements given in supplementary material (Fig. S1).

The admittance spectroscopy spectra C - f - T were converted into density of defect states using the theory and the analysis discussed in Ref. [21] to reduce the noise of the admittance spectra:

$$N_t(E_\omega) = -\frac{(V_{bi} - V)^2}{w[qV_{bi} - E_{F\infty}]} \frac{dC}{d\omega} \frac{w}{kT} \quad (3)$$

Where N_t is the defect density, w is the depletion width, V_{bi} the built-in voltage, V the applied voltage, q the elementary charge, $E_{F\infty}$ a Fermi energy level, C the capacitance and ω the angular frequency.

Admittance spectroscopy measurements unveil the presence of two defects: a shallow one around 100–150 meV and a deep defect with an energy level around 280 meV.

Fig. 3 shows the distribution of the defect energy levels as measured from admittance spectroscopy and approximated by a Gaussian distribution of deep states [12]. Although this technique cannot distinguish between acceptor and donor defect levels, it allows to determine the energy distribution within the band gap of the material with sufficient reliability. It was reported that the p -type conductivity in kesterite films is determined by both V_{Cu} and Cu_{Zn} antisites defects. According to the calculation of Chen et al. [22], these defects are formed in Kesterite under Cu -poor and Zn -rich growth conditions, with a shallow level at 0.01–0.02 eV for the V_{Cu} defect and a deeper level around 0.11–0.150 eV for Cu_{Zn} . Although the latter is in good agreement with the defect level measured here at 150 meV, a barrier-like signal, as it was reported in chalcogenide based solar cells on Mo/SLG substrates cannot be excluded [23,24]. The first-principles calculation of defect formation in CZGSe semiconductors done by Nishihara et al. [25] shows that Cu vacancies can be easily formed under Cu -poor condition in this compound, which makes it a p -type absorber for thin-film solar cells and antisite defects like Cu_{Zn} can hardly be formed under these conditions. The average composition of the CZGSe films as deduced from STEM-EDX measurements is $[\text{Cu}]/([\text{Zn}]+[\text{Ge}]) = 0.9$ and $[\text{Zn}]/[\text{Ge}] = 1.03$. The films are Cu -poor with Zn/Ge ratio nearly equal to 1 therefore the doping is most likely controlled by the presence of Cu vacancies V_{Cu} .

Current-voltage measurement performed at different temperatures is displayed in Fig. 4. This measurement technique provides an insight into recombination processes limiting the device performance, especially the open-circuit voltage V_{oc} . The diode current under dark is given by:

$$J = J_s \left[e^{\left(\frac{qV}{kT}\right)} - 1 \right] \quad (4)$$

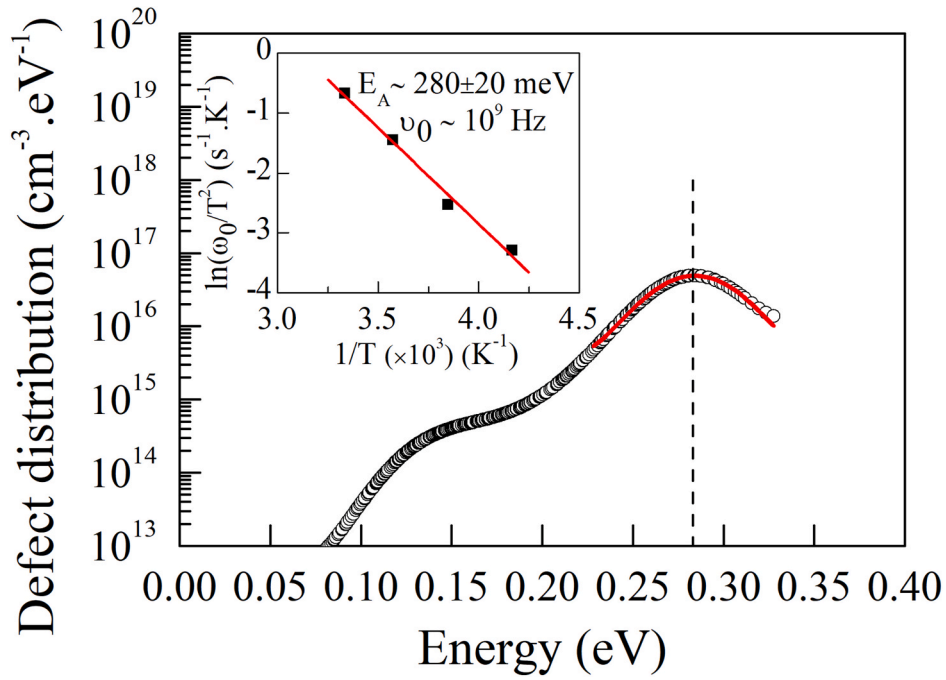


Fig. 3. Defect density in CZGSe solar cell calculated from admittance spectroscopy measurements (*C-f-T*). Symbols: measurements, solid lines: curve Fit using Gaussian distribution for defect states. The inset shows the Arrhenius plot of the defect at 280 meV and the attempt-to-escape frequency ν_0 used to calculate capture cross-section [12].

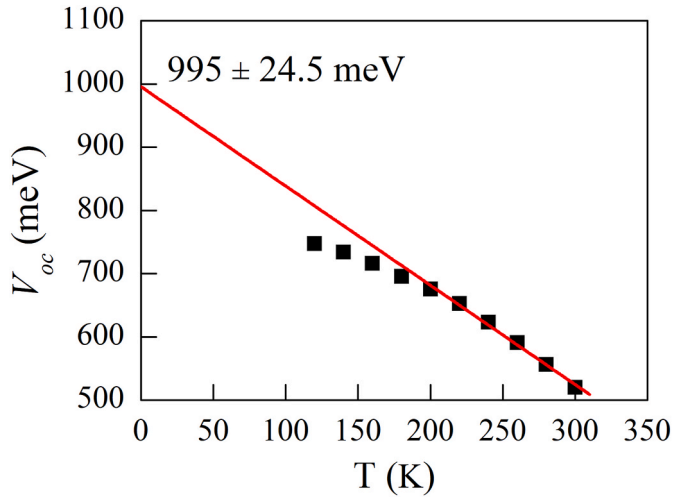


Fig. 4. Temperature dependence of V_{oc} measured in CZGSe cell and extrapolated at 0K giving an activation energy $E = 995 \pm 24.5$ meV.

Where n is the diode ideality factor and kT/q the thermal voltage. J_s is the saturation current and is expressed as:

$$J_s = J_0 e^{-\frac{E_a}{nkT}} \quad (5)$$

Where E_a is an activation energy or a barrier governing recombination under dark condition and J_0 is a prefactor weakly temperature dependent.

Under open-circuit condition $J = J_{sc}$ (J_{sc} the short-circuit current), V_{oc} is then given by

$$V_{oc} = \frac{E_a}{kT} - \frac{nkT}{q} \ln\left(\frac{J_0}{J_{sc}}\right) \quad (6)$$

From Eqs. (5) and (6) one can see that a decrease in E_a increases the

dark current and lowers V_{oc} . When the activation energy E_a is equal to the absorber band gap E_g , bulk recombination is dominant. When interface recombination is dominant, the activation energy E_a is lower than E_g and represents a barrier at the interface. It is worth mentioning here that E_a lower than E_g could be due to the presence of secondary phases in the absorber or band gap fluctuation. In this case the main recombination loss takes place at the area with lower energy and a higher saturation current at the secondary phase areas may occur as well.

The extrapolation of the V_{oc} to 0K using Eq. (6) gives an activation energy of 995 ± 24.5 meV which is below the CZGSe absorber band gap energy in these devices. Also, current-voltage curves at different temperatures displayed a strong roll-over at low temperature as shown in Fig. 5, which may be caused by the presence of a barrier limiting the

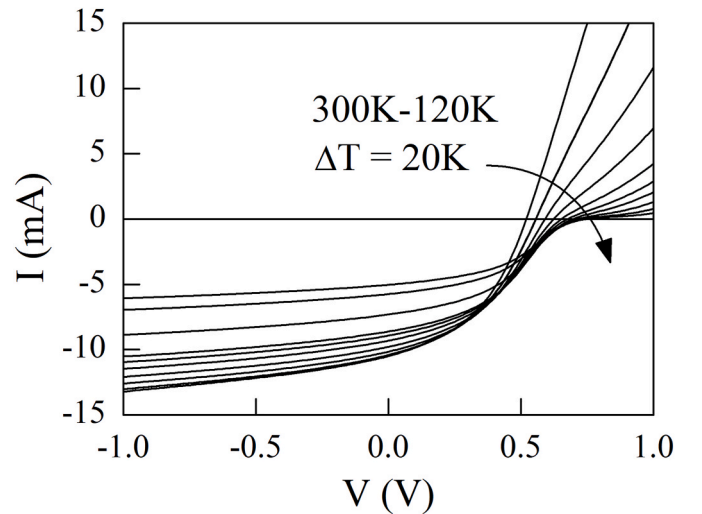


Fig. 5. Current-voltage curves of CZGSe cell, measured in a temperature range 300-120K and a step of $\Delta T = 20$ K.

device performance.

3.2. Films morphology

Fig. 6 shows the HAADF-STEM image of the CZGSe solar cell as well as a STEM-EDX mixed map. The sample consists of a CZGSe layer of a thickness about 1.0–1.7 μm with grain sizes about 200–400 nm. The structure and composition of the CZGSe absorber is not uniform, as one can see in the map. There are regions of admixture phases which are attributed to inclusions of ZnSe at the top of the absorber layer, Cu_{2-x}Se phase which is present at the grain boundaries and at the interface with the Mo back contact and Cu_2GeSe_3 at the back of the CZGSe absorber. The Cu_2GeSe_3 phase is rather thick and has a thickness between 120 and 160 nm. The average of Cu:Zn:Ge:Se atomic ratios taken on 38 spectra measured at different locations in the film, is found to be 27.4:13.2:12.8:49.6 giving a composition of $\text{Cu}_{1.95(0.07)}\text{Zn}_{1.06(0.06)}\text{Ge}_{1.02(0.05)}\text{Se}_{3.97(0.11)}$. Note that close to the Mo back contact, other elements like Si, N, O and C are also detected and their presence is related to the SiON barrier layer at the back contact.

FTIR spectroscopy was performed in absorbance on lifted-off CZGSe absorbers and is presented in Fig. 7. The IR active modes in the kesterite lattice have B and E symmetry [26,27]. They are also Raman active and their labelling in Fig. 7 is based on earlier results reported using Raman spectroscopy [28], where the IR active modes appear with weak intensity. Note that the ZnSe secondary phases on the top of the CZGSe were not detected in the absorbers after the HCl chemical etch. However, the vibrational mode at 215 cm^{-1} which corresponds to the (LO) mode of Cu_2GeSe_3 phase [29] is detected which confirms the presence of

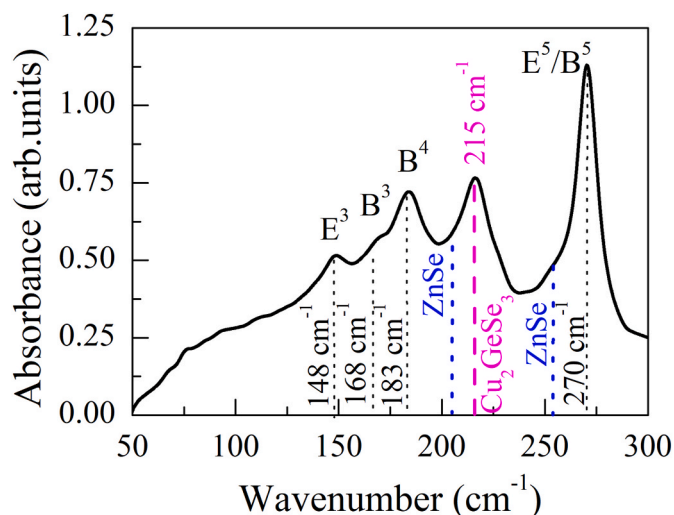


Fig. 7. FTIR measured in absorbance on lifted-off CZGSe absorbers. The IR active modes of the kesterite lattice having E and B symmetry are shown (black dot lines). The labelling is based on early reported Raman peaks [28]. The peak related to the Cu_2GeSe_3 phase can be seen at 215 cm^{-1} wavenumber (pink dash line). Peaks related to ZnSe secondary phase were not detected. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

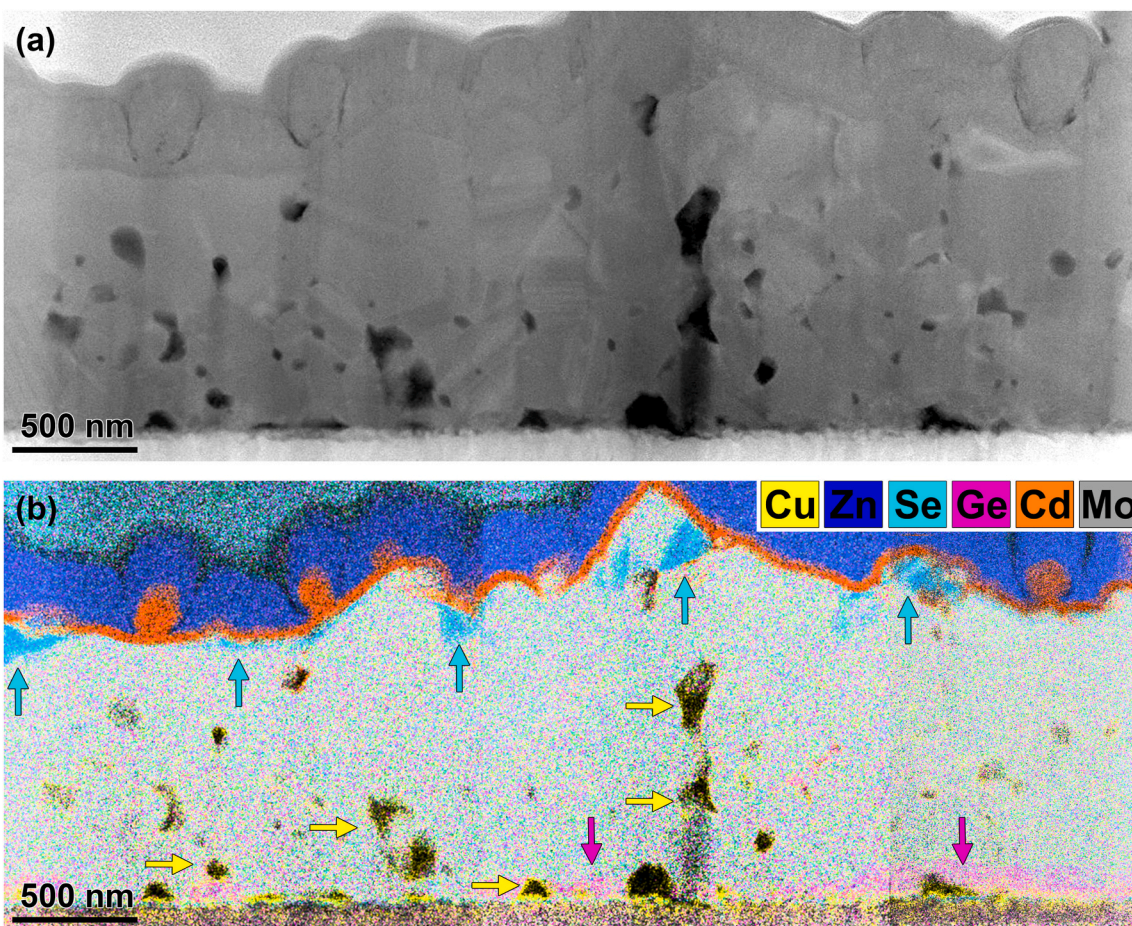


Fig. 6. HAADF-STEM image of the complete CZGSe solar cell (a) and corresponding Cu/Zn/Se/Ge/Cd/Mo mixed map (b). Secondary phases regions are shown in arrow: ZnSe (blue arrows), Cu_2GeSe_3 (pink arrows) and Cu_{2-x}Se (yellow arrows). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the ternary phase at the back of the CZGSe absorber, in accordance with the results of the TEM analysis. Raman spectroscopy has been widely used to determine the kesterite and secondary phases in earth abundant based solar cells but to the best of our knowledge these are the first reported results on FTIR performed on kesterite materials showing the IR active vibrational modes and the presence of the Cu_2GeSe_3 ternary phase in these CZGSe wide band gap devices.

4. Modelling and simulations

In the first part of this section, we present a model which is developed to explain the CZGSe solar cell performance using SCAPS software [30]. In the second part, the parameters limiting the cell performance are analyzed and discussed. Then, a model for a transparent back contact (TBC) based on optimized cell parameters which can be used for tandem applications is presented and compared with the standard configuration of a cell with Mo/SLG back contact. Finally, a model for the kesterite-Si tandem structure is presented and discussed in depth as a function of the kesterite top cell band gap and transparency.

The starting parameters used in the simulations were obtained by a set of electrical and optical characterization techniques performed on the $\text{Cu}_2\text{ZnGeSe}_4$ (CZGSe) thin-film absorber and the complete solar cell as given in section 2.2.

The enhancement of kesterite solar cells performance through back contact optimization has been predominantly related to the presence and the control of a $\text{Mo}(\text{S,Se})_2$ layer reported in most thin-film solar cells grown on Mo-coated soda-lime glass, such as CIGSe [31], CZTSe [32]. The presence of this layer determines the selective electrical back contact for the absorber layer. It is quite difficult to detect the presence of MoSe_2 secondary phase in these devices and the reason could be the presence of the barrier layer which blocks Na diffusion towards the Mo layer. It was demonstrated by Caballero et al. [33] that Na acts as catalyst and enhances the formation of MoSe_2 layer at the back contact of the solar cells. However, the presence of SiON barrier layer in the CZGSe devices limits Na diffusion towards the Mo, which may inhibit the formation of MoSe_2 layer at the back contact.

On the other hand, the interface between the CZGSe absorber and Mo back contact in the devices is rather complicated and contains several inclusions, but the main feature is the formation of a big inclusion of crystalline Cu_2GeSe_3 phase at the bottom of the absorber. Therefore, the selective back contact is defined by the presence of this ternary phase.

Cu_2GeSe_3 is reported to be a ternary p -type semiconductor with a direct band gap of 0.78–0.94 eV [34,35]. In the work of Endo et al. [36], the Hall mobility and concentration measured at room temperature are $0.5 \text{ cm}^2/\text{V}\cdot\text{s}$ and 10^{19} cm^{-3} , respectively and are quite dependent on the annealing temperature of the samples.

In our calculation, a Cu_2GeSe_3 ternary phase with a thickness of 120–150 nm as determined by TEM measurements was included in the

model with the material properties given in Table 1.

Reflectance loss on the kesterite cell surface was considered in all calculations and no internal reflections at the top/bottom cell or optical parasitic loss were included. All the other parameters used in the simulations are summarized in Table 1.

4.1. Model for a CZGSe based solar cell with $\eta \sim 7\%$

In virtue of the complicated structure of thin-film solar cells, there is no straightforward method that can be used to model all the measurements data. However, one can always start with a partial model which can describe a specific behavior or a measurement but has a marginal effect on the other measurements and consequently helps to understand or describe the complete cell behavior. In our case, we started by a first set of parameters to describe the doping profile (from capacitance-voltage measurements) and current-voltage measurements under dark and illumination conditions.

The p -type doping in the CZGSe absorber was introduced as a shallow acceptor level at 0.02 eV above the valance band with low capture cross section, considering the presence of V_{Cu} as discussed in section 2. In this case, the defect acts as dopant but does not contribute to the recombination. The deep defect with an activation energy of 280 meV was introduced as an acceptor level with a concentration in the range of 10^{15} cm^{-3} and a hole capture cross section $\sigma_p \sim 10^{-17} \text{ cm}^2$ as deduced from the attempt-to escape frequency ν_0 [12] of the Arrhenius plot shown in the inset of Fig. 3. There is no information about the charge states that could form at the interface between the CdS buffer layer and the CZGSe absorber layer, due to secondary phases or any other species which might be introduced after the chemical etching treatment. Thus, recombination at the CdS/CZGSe interface is added assuming charge-free SRH recombination.

The current-voltage and capacitance-voltage curves were calculated using our model for the CZGSe solar cell with 7% efficiency. A good agreement between the simulations and the measurements is obtained as shown in Figs. 8 and 9 and the solar cell outputs given in Table S1 in supplementary material. The non-uniform doping profile was reproduced by assuming an exponentially graded doping profile in the absorber which gives quite a decent fit with the measurement as can be seen in Fig. 9(b).

As stated before, the presence of the ternary phase Cu_2GeSe_3 will define the selective back contact with the Mo layer. Mo has a low metal work function of 4.9 eV therefore a Schottky barrier is expected at the back $\text{Cu}_2\text{GeSe}_3/\text{contact}$. However, the presence of this ternary phase with a band gap (0.9 eV) lower than the band gap of the CZGSe absorber

Table 1

Parameters used in the simulations at standard solar cell test conditions. The values marked by $(^*)$ are the optimized parameters after the simulations.

Parameter	ZnO	CdS	CZGSe	Cu_2GeSe_3 [34–36]	MoO_x [37]
$d(\mu\text{m})$	0.150	0.045	1.4	0.125	0.04
E_g (eV)	3.3	2.4	1.5	0.9	2.85
χ (eV)	4.4	4.2	4.41	4.13	2.6
μ_n ($\text{cm}^2/\text{V}\cdot\text{s}$)	100	100	100	20	100
μ_p ($\text{cm}^2/\text{V}\cdot\text{s}$)	25	25	2	2	20
N_d (cm^{-3})	10^{18}	1×10^{17}	–	–	–
N_A (cm^{-3})	–	–	$2 \times 10^{14}/10^{16}$ (*)	10^{19}	10^{17}
ϕ_b (eV)	0.130				
R_s ($\Omega\cdot\text{cm}^2$)	$5/1.5$ (*)				
R_{sh} ($\Omega\cdot\text{cm}^2$)	$370/900$ (*)				

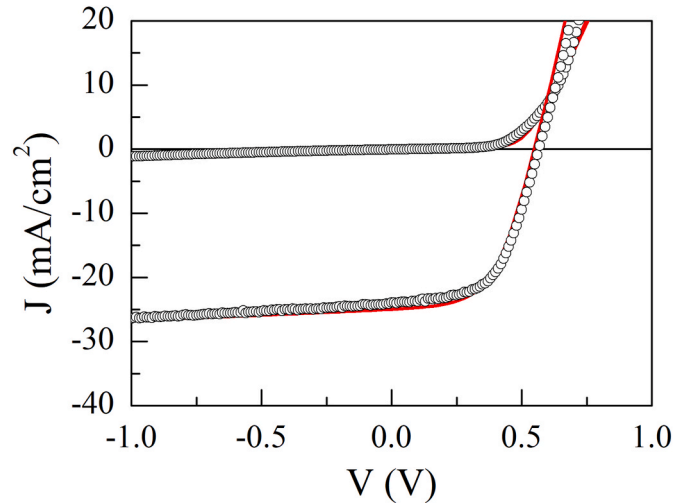


Fig. 8. Dark and light current-voltage curves. Symbols: measurements, Solid lines: simulations.

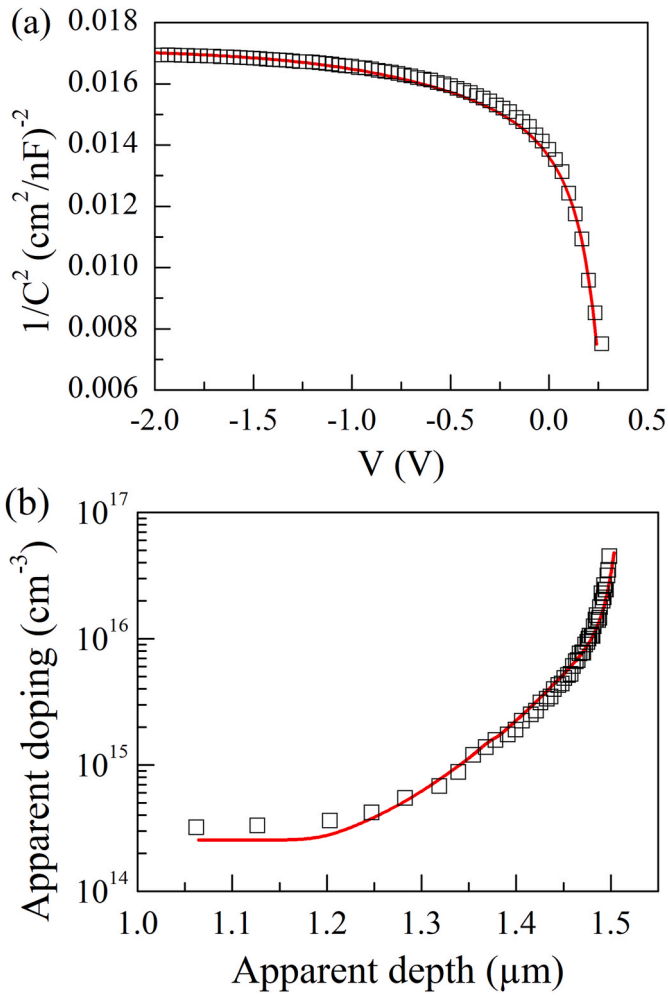


Fig. 9. (a) Mott-Schottky plot from capacitance voltage ($C-V$) at frequency $f=10^5$ Hz and (b) Doping profile extracted from the Mott-Schottky plot. Symbols: measurements, Solid line: simulations.

(1.5 eV) creates a large blocking barrier for the majority carriers (holes) as illustrated in the energy band diagram in Fig. 10. The effect of these barriers on the solar cell performance is discussed in the next section. Also, to our knowledge, this is the first time the effect of a ternary phase formed at the back surface of a kesterite absorber, not directly related to the Mo back contact layer, is taken into account in numerical modelling

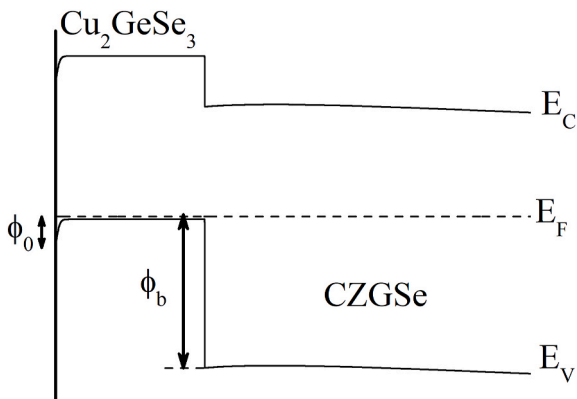


Fig. 10. Band energy diagram at the CZGSe back surface/Mo back contact showing the contact barrier ϕ_0 at the Mo contact and the formation of a blocking barrier ϕ_b induced by the presence of Cu_2GeSe_3 ternary phase.

based on experimental observations.

According to the measurements and simulations, the solar cell performance limitations are caused by several parameters such as deep defect assisted recombination, low doping and carrier mobility in the absorber, a blocking barrier and parasitic effects due to high series resistance and low shunt resistance. Each of these parameters will be studied and discussed in more detail in the next section.

4.2. Optimization of solar cell parameters

In this section, we analyse the effect of each loss mechanism on the performance of the CZGSe based solar cells in order to optimize the cell parameters and increase the solar cell efficiency.

4.2.1. Effect of doping and deep defects in the CZGSe absorber

In these compounds, we found that high diffusion of Na from the SLG into the CZGSe absorber was detrimental for the solar cell performance, while using a barrier layer such as SiON inhibits diffusion of Na into the absorber. Consequently, this leads to low doping in the absorber and decreases the open-circuit voltage.

Based on admittance spectroscopy, a deep acceptor defect with a level around 229 meV was reported in CZTSe solar cells deposited on alkali-free borosilicate glass, which became shallower with sodium incorporation [20]. The defect agrees well with the one measured in our devices around 280 meV and could be related to an insufficient amount of Na in the absorber. The role of Na on the enhancement of the device performance is still under debate and it seems more likely that its beneficial effect is related to the removal or redistribution of native point defects in the absorber, as has also been suggested for CIGSe and CZTSe based solar cells [20,38].

The solar cell efficiency was calculated as function of the concentration of the deep acceptor trap at 280 meV and the results are displayed on Fig. 11(a). It shows that the presence of this deep defect has a strong effect on the solar cell efficiency, when its concentration is higher than 10^{15} cm^{-3} . However, the effect is less severe if we could consider that the deep defect becomes shallower with an energy level at 100 meV above the valence band. To explain the effect of this defect on the cell behavior, we calculate the internal recombination in the absorber at a voltage $V = 0.5$ V, in order to compare the recombination around the open-circuit voltage. As shown in Fig. 11(b), the loss in the device performance is caused by an increase of recombination in the absorber when the defect level gets deeper in the band gap and/or is present with concentration $N_t > 10^{15} \text{ cm}^{-3}$.

Therefore, due to the strong reaction between Ge and Na from the SLG during the CZGSe absorber deposition, strategies to introduce Na into Ge based absorbers are required during device preparation. The use of thin Na precursor layers during the absorber growth could be the best strategy to control the diffusion of Na into the absorber and increase both the doping and the open-circuit voltage. For tandem applications, this may be a practical way to enhance the crystallization and optimize the doping in the absorber, since growing absorbers directly on a transparent back contact may lead to poor electrical properties and device performance [39]. Another way to introduce Na into kesterite absorber was proposed by Espindola-Rodriguez et al. [40], where a Mo or Mo:Na nanolayer was inserted between the CZTSSe absorber and the FTO transparent back contact and device efficiency above 7 % was achieved.

We showed in the experimental part that the doping in these devices was quite low and below 10^{15} cm^{-3} . There are several downsides of low doping in the absorber layer which directly influence the open-circuit voltage. First, it leads to low built-in voltage and consequently to low open-circuit voltage. Moreover, an absorber layer with low doping increases the space charge region and the recombination rate in it. Which further reduces the open-circuit voltage. Simulated open-circuit voltage and efficiency versus the doping N_A in the CZGSe absorber shows that the optimum value of the p -type doping in these devices should be in the

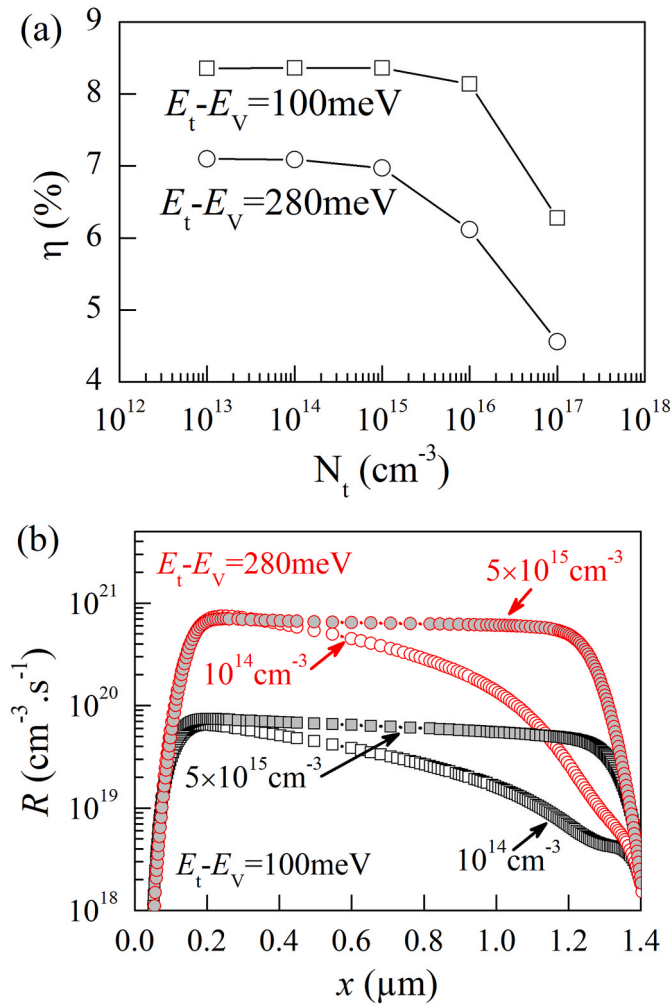


Fig. 11. (a) Effect of deep trap concentration N_t on the solar cell efficiency. The case of the defect $E_t = 280 \text{ meV}$ shifting to a shallow level $E_t = 100 \text{ meV}$ is considered. (b) The Calculated recombination $R(x)$ at $V = 0.5 \text{ V}$ in the absorber for $E_t = 100 \text{ meV}$ and $E_t = 280 \text{ meV}$ with different defect concentrations $N_t = 10^{14} \text{ cm}^{-3}$ and $N_t = 5 \times 10^{15} \text{ cm}^{-3}$.

range $10^{15} \leq N_A \leq 10^{17} \text{ cm}^{-3}$ (see Fig. S2 in supplementary material).

Since the hole mobility is expected to vary with the p -type doping of the absorber and a lower doping density should lead to a higher hole mobility, the device performance can be improved with absorbers having higher grain quality. The efficiency is plotted as a function of doping and hole carrier mobility in the CZGSe absorber (Fig. S3 in supplementary material), showing that an increase in device efficiency of 1–2% absolute can be achieved with doping density $10^{16} \leq N_A \leq 10^{17} \text{ cm}^{-3}$ and hole mobility values higher than $40 \text{ cm}^2/\text{V}\cdot\text{s}$. While the doping of the absorber can be increased by using alkali precursor layers, improvement of the bulk grain quality in order to increase the mobility of the films is still a big challenge, knowing that the highest hole mobility measured in kesterite materials till now was about $39.7 \text{ cm}^2/\text{V}\cdot\text{s}$ with a doping of $p = 2 \times 10^{17} \text{ cm}^{-3}$ in CZTSe films grown at substrate temperature of 400°C [41]. Note that a mobility of minority carriers “electrons” of about $100 \text{ cm}^2/\text{V}\cdot\text{s}$ was considered in our calculations consistent with the values of $70\text{--}140 \text{ cm}^2/\text{V}\cdot\text{s}$ reported in p -type kesterite absorbers [42,43].

4.2.2. Effect of series and shunt resistance

Another major factor limiting the CZGSe cell performance is the parasitic series and shunt resistances. The high series resistance reported in most kesterite solar cells was mainly attributed to the presence of a

blocking back contact barrier induced by the presence of a thick $\text{Mo}(\text{S}, \text{Se})_2$ layer at the back contact [44,45], and/or secondary phases near the heterojunction such as $\text{Zn}(\text{S}, \text{Se})$, which act as interface recombination centers [46]. On the other hand, low shunt resistance was related to the presence of voids and secondary phases in the absorber. In these CZGSe cells, the parasitic resistances are possibly produced by several factors including the presence of secondary phases in the absorber (ZnSe), (Cu_{2-x}S) and voids as revealed by the TEM measurements. Moreover, the presence of a Cu_2GeSe_3 ternary phase at back of the CZGSe absorber creates a barrier for the majority carriers and a non-ideal Schottky contact and may increase the parasitic resistance effect.

Till now all the record efficiencies in kesterite based solar cells were reported for devices with series resistance below $2 \Omega \text{ cm}^2$ [1,47]. To analyse the effect of high series resistance and low shunt resistance on the device performance, the efficiency of the CZGSe cell is calculated as a function of the parasitic resistances. We found that the optimum device performance is reached for series resistance below $2 \Omega \text{ cm}^2$ and shunt resistance above $800 \Omega \text{ cm}^2$ (see Fig. S4 in supplementary material).

4.2.3. Effect of band alignment and interface states at CdS/CZGSe

The presence of interface states and the type of conduction band alignment (conduction band offset) at the CdS/CZGSe interface may be both responsible for the large open-circuit deficit commonly observed in kesterite devices. In the case of CdS/CZGSe with n^+p structure (with low absorber doping $N_D \gg N_A$), electrons are majority carriers at the interface and the interface recombination is governed by holes of the absorber. Note that, there are two distinguished paths for the recombination at the interface depending whether the heterojunction is of type (I) or of type (II) [48]:

- In a type (I) heterojunction where $\Delta E_c > 0$, with a spike like conduction band offset (CBO), and electrons recombine with holes of the absorber.

- In a type (II) heterojunction where $\Delta E_c < 0$, with a cliff-like conduction band offset (CBO), electrons in the buffer recombine with holes in the absorber.

The properties of the interface are evaluated by the interface recombination velocity S_i and the number of interface states as follow:

$$S_i = N_i \sigma_{n,p} v_{thn,p} \quad (7)$$

Where N_i is the concentration of the interface states, $\sigma_{n,p}$ is the thermal capture cross section of electrons/holes and $v_{thn,p}$ is the thermal velocity of electrons/holes.

The interface recombination current is given by

$$J_i = q S_i (p - p_0) \quad (8)$$

with $p - p_0$ the excess of minority carriers at the absorber side.

In Fig. 12, V_{oc} and η are plotted as a function of the interface recombination velocity S_i and the conduction band offset ΔE_c . A device efficiency in a range of 8–10 % is obtained for conduction band offset in the range $-0.1 < \Delta E_c < 0.3 \text{ eV}$ and interface recombination velocity $S_i \leq 10^4 \text{ cm/s}$. In the same range of ΔE_c , the open-circuit voltage reaches maximum values above 600 meV and is quite independent of the interface quality for positive band offset ΔE_c where inversion layer occurs at the interface. In case of negative band offset ΔE_c the open-circuit voltage decreases with higher interface velocities. As one can deduce from Eq. (6), the decrease in V_{oc} for cliff-like band alignment is directly related to a decrease of the barrier at the interface.

These findings reveal that the limitation of the device performance and especially the V_{oc} deficit are only slightly affected by the band alignment ΔE_c and the quality of the buffer/absorber interface in these wide band gap kesterite devices. Hence, the open-circuit deficit is most likely due to an internal barrier in the CZGSe absorber layer created by secondary (or ternary) phase segregation with low band gap inside the absorber such as the Cu_2GeSe_3 phase.

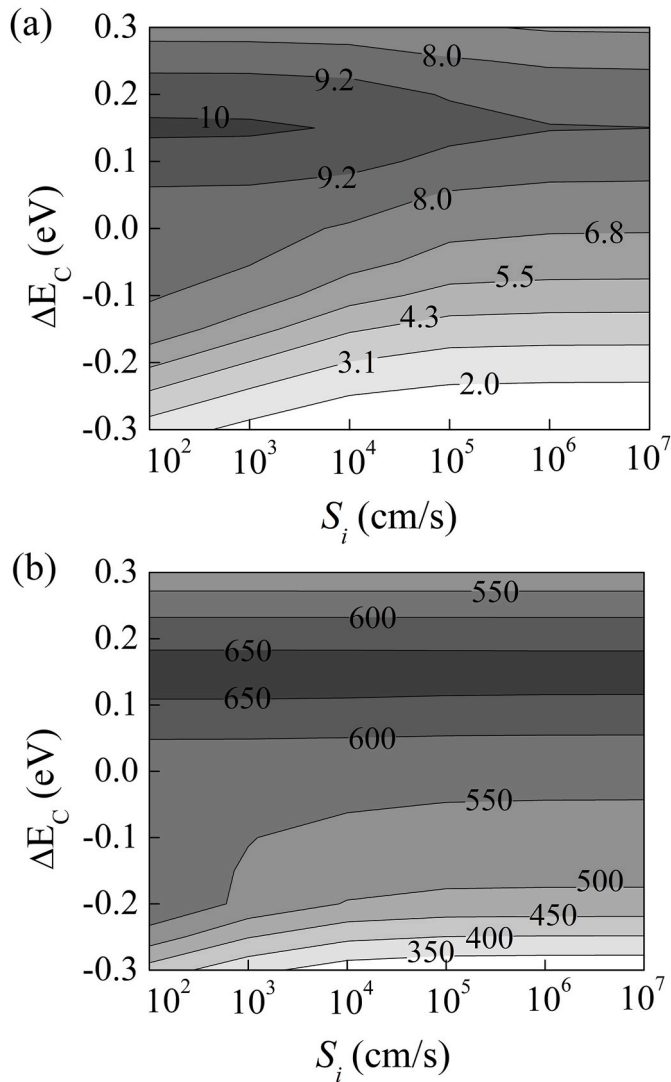


Fig. 12. (a) Efficiency (η) and (b) open-circuit voltage (V_{oc}) calculated as a function of CdS/CZGSe interface recombination velocity (S_i) and conduction band offset (ΔE_c).

4.2.4. Effect of blocking barrier

The non-idealities observed in thin-film solar cell characteristics have been reported to be instigated by non-ohmic back contact [49,50]. In CIGSe and kesterite, where molybdenum is commonly used as back contact material, device performance limitations were attributed to the formation of Mo(S,Se) layer at the interface due to the reaction of absorber elements (e.g., S or Se) with Mo contact. Replacing Mo by another material contact is advisable but finding an alternative back contact with high metal work function and stable ohmic contact for kesterite solar cells is quite challenging especially for an absorber material with wide band gap and low p -type doping density.

The hole barrier height is defined by the difference between the Fermi energy level and the valence band edge as:

$$\phi_b = E_{F_p} - E_V \quad (9)$$

In Fig. 13 the barrier for holes ϕ_b is calculated using Eq. (9) as a function of the doping of the layer in contact with the Mo layer. Thus, the doping is varied in the Cu_2GeSe_3 ternary phase present between the CZGSe absorber layer and the Mo contact. The height of the barrier calculated at the Mo contact is constant and equal to $\phi_0 = 130$ meV, which is in accordance with the value deduced from AS measurements and assigned to a barrier signal response at the back contact. On the

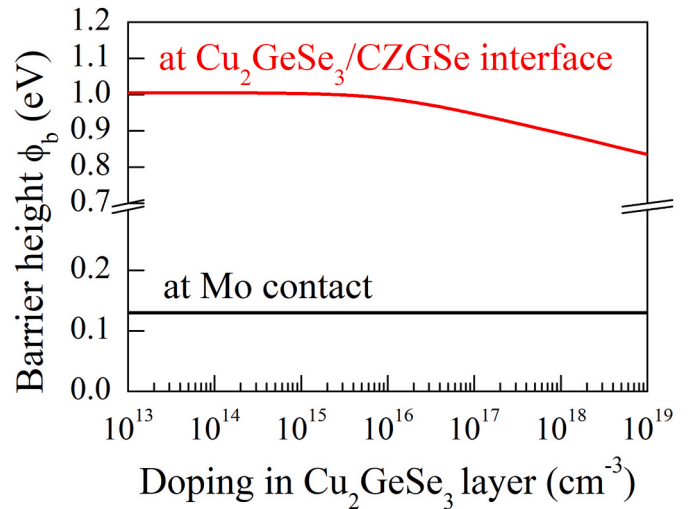


Fig. 13. Barrier height calculated at the Mo contact (ϕ_0) (black solid line) and at $\text{Cu}_2\text{GeSe}_3/\text{CZGSe}$ back surface (ϕ_b) (red solid line) as a function of the p -type doping in the Cu_2GeSe_3 ternary phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

other hand, the barrier for holes induced by the presence of Cu_2GeSe_3 is quite dependent on the doping and decreases when the p -type doping in this layer increases. This is because the valence band edge E_V shift up when increasing the doping in the Cu_2GeSe_3 layer. Note that the value calculated for a high doping concentration is very close to the activation energy E_a deduced from the $V_{oc}(T)$ plot extrapolated to 0 K in Fig. 4. The simulations corroborate that the high open-circuit voltage deficit recorded in the devices is engendered to a large extent by an internal hole blocking barrier created by the presence of a Cu_2GeSe_3 ternary phase at the back of the CZGSe absorber. The open-circuit deficit is calculated assuming different back contact type (Schottky or Ohmic), with and without the presence of the ternary phase and the results are presented in Fig. 14. It is readily apparent that a high V_{oc} deficit is recorded in the presence of the Cu_2GeSe_3 ternary phase independent of whether the back contact is Schottky- or Ohmic-type. While without the ternary phase the deficit is reduced from 900 meV to 600 meV with a device efficiency in a range 14–15%.

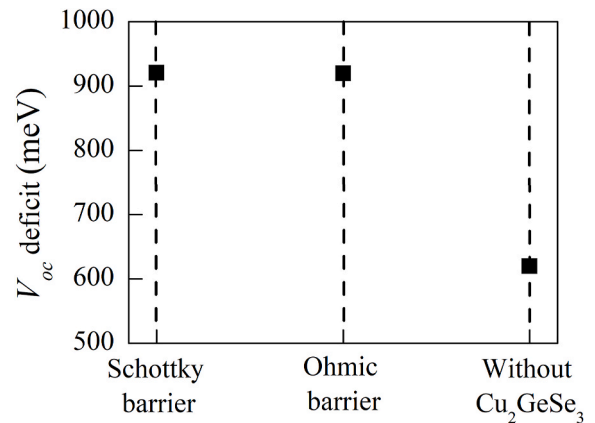


Fig. 14. Open-circuit (V_{oc}) deficit calculated for different back contact-type with and without Cu_2GeSe_3 ternary phase.

4.3. CZGSe solar cells on a transparent back contact (TBC) for tandem applications

As stated before, a conducting back contact with good transparency is indispensable for the CZGSe cell when it is to be used as a top-cell in tandem applications. In this section, different structure configurations are tested and discussed based on the model developed and using optimized parameters of the doping in the CZGSe absorber and the parasitic resistances. The optimized parameters are cited in Table 1.

4.3.1. Molybdenum (Mo) back contact versus transparent back contact (TBC)

Fig. 15 displays the open-circuit voltage deficit and efficiency of a CZGSe solar cell with two different back contact configurations: CZGSe on transparent back contact (TBC) and CZGSe on TBC using molybdenum oxide (MoO_x) as an intermediate layer. The calculations were performed using the realistic cell parameters extracted from measurements and using the optimized parameters for doping density in the absorber and parasitic resistances given in Table 1, without the presence of Cu_2GeSe_3 layer. Practically, the removal of the ternary phase at the back surface of the absorber layer could be achievable by exfoliation process to remove the Mo back contact as it has been successfully realized for CIGSe and CZTSe solar cells [51,52], followed by chemical etching to remove the ternary phase or any other phases or elemental residues [53,54]. Another advantage of the exfoliation process is that it allows the deposition of the kesterite cell on a transparent back contact at low temperature avoiding the degradation of the latter during a high temperature deposition and selenization processes of the kesterite absorber.

However, when using a transparent back contact the main loss in the device performance will be provoked by a drop in the V_{oc} , which is a consequence of the low metal work function of the TBC leading to non-ideal band alignment with the CZGSe absorber. Moreover, most of the conductive transparent oxides used in solar cell technology have a low metal work function in the range of 4.7–4.9 eV [55] and may not be suitable as back contact materials in CZGSe devices. In this case, the use of an intermediate layer such as MoO_3 is recommended to overcome this problem. As one can see in Fig. 15, the V_{oc} deficit in the solar cell can be reduced when using an intermediate layer with high band gap such as MoO_3 . For the record, MoO_3 has already been used as interfacial layer between TBC (ITO) and the $\text{Cu}(\text{In,Ga})\text{Se}_2$ absorber in a superstrate configuration [56] and between $\text{Cu}_2\text{ZnSnSe}_4$ and Mo contact to improve the back contact properties, and further as a primary back contact in kesterite solar cells [57,58]. Furthermore, the thickness of the MoO_x layer needs to be optimized to reduce the light absorption loss in this

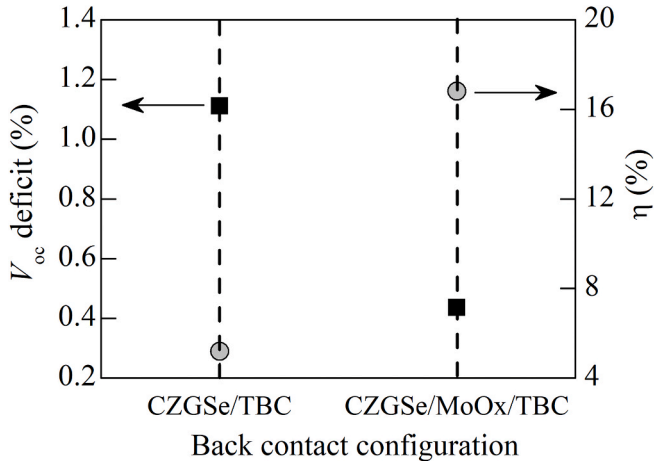


Fig. 15. Open-circuit deficit (V_{oc}) and efficiency (η) calculated for different back contact configurations, CZGSe/TBC and CZGSe/ MoO_x /TBC.

layer and maintain good transparency of the top cell for tandem application.

4.4. Kesterite-Si tandem structure

To calculate the efficiency of a four terminal tandem solar cell, we used the CZGSe with the optimized parameters obtained in section 3.2 as a top cell on a Si bottom cell. For the bottom Si solar cell, a SCAPS model which was developed for a PERL Si cell with 25 % efficiency is used [59]. In the model we consider a n^+pp^+ structure with a wafer thickness (absorber layer) of 300 μm and a ZnS/MgF_2 double anti-reflection layer as described in Ref. [60]. The light trapping was included using the Lambertian scattering scheme [61–63]. Then, the effect of the top cell band gap and long-wavelengths transmission is studied and discussed for various cell structures.

4.4.1. Effect of the top cell band gap

The band gap of the CZGSe absorbers prepared in this work with pure Ge substitution was about 1.5 eV, which is not high enough for efficient tandem applications. Not only a wide band gap material is mandatory but also good transparency at long wavelengths together with a high cell efficiency are required for the top cell to be used on a Si bottom cell in tandem applications. Therefore, it is essential to know the efficiency limitations in these devices. For this purpose, the efficiency of the kesterite solar cell was calculated as a function of the absorber band gap. Theoretical studies have shown that the band gap of $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{Se}_4$ and $\text{Cu}_2\text{ZnSn}_{1-x}\text{Si}_x\text{Se}_4$ alloys as function of the x composition for both ‘Ge’ and ‘Si’ substitute [64] varies from 1 to 1.5eV and from 1 to 2.3eV respectively.

We started from a device efficiency of up to 10% for the standard kesterite cell with the presence of the Cu_2GeSe_3 phase at the back of the absorber and up to 15% for a cell without the ternary phase and an intermediate MoO_x layer between the absorber and the TBC back contact, as suggested in section 4.3.1, and then varied the band gap of the absorber from 1.45 eV to 2.3 eV. In this way, the effect of a wide range of band gaps either based on Ge/Sn or Si/Sn compounds are analyzed using realistic device parameters.

Indubitably, varying the band gap also induces a change in the band alignment at the conduction and valence bands. Shu et al. [64] reported in their first-principles calculations study, that the substitution of Sn by Ge or Si does not significantly change the valence band maximum (VBM) energies, because they consist of Se 4p and Cu 3d orbitals. Thus, we assumed that changes in the band alignment occur predominantly in the conduction band and that the conduction band offset (CBO) varies between 0.2 and -0.65 eV in the range of the band gaps given above. We used the absorption coefficient as measured for the CZGSe absorber and we varied the band gap accordingly. The calculated efficiency of the top cell versus the absorber band gap and the conduction band offset (CBO) is displayed in Fig. 16 for a standard cell and a cell with a MoO_x layer, respectively. The efficiency drops in these devices from 10% to 3% when the band gap of the absorber increases from 1.45 eV to 2.3 eV due to the large negative cliffs. Nevertheless, device efficiencies higher than 8 % can still be maintained for absorber band gaps $1.4 \leq E_g \leq 1.8$ eV and $-0.15\text{eV} \leq \text{CBO} \leq 0.2$ eV. The advantage of an exfoliation and the use of MoO_x intermediate layer in case of a TBC contact can clearly be seen in the band gap range $1.40 \leq E_g \leq 1.85$ eV and conduction band offset range $-0.20\text{eV} \leq \text{CBO} \leq 0.25\text{eV}$, where device efficiency up to 16% could be achieved.

4.4.2. Effect of the top cell band gap and transmission at long wavelengths

In a tandem configuration, the light incident on the bottom cell is limited by the band gap of the top cell since only photons with energies $E < E_g$ will reach the bottom cell. In the ideal situation, this requires a top cell with sub-band gap transmission $T = 1$, which is not possible in practice due to parasitic absorption losses.

The efficiency of the tandem solar cell is assessed by varying both the

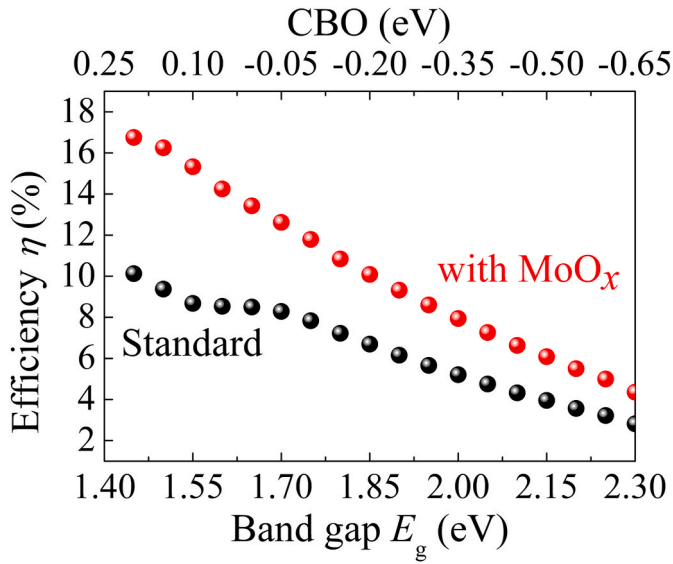


Fig. 16. Efficiency of the kesterite top cell versus its band gap E_g and the conduction band offset (CBO) for a standard cell (black symbols) and cell with MoO_x (red symbols). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

band gap, the conduction band offset and the transparency of the top cell, for a standard top cell and for a cell with MoO_x . Note that the efficiency decreases when the band gap increases, as it was shown previously and $T \neq 0$ for sub-band gap wavelengths. The results are given in Fig. 17. In the case of a standard cell with higher band gap and transparency higher than 80%, the efficiency is still not enough to retrieve the loss from the filtered Si-bottom cell. On the other hand, using a top cell with an efficiency between 15% and 13%, a band gap between 1.55 and 1.7 eV and $T > 85\%$ already leads to an increase in the efficiency of 0.4–1.5%, compared to the Si-bottom cell alone.

4.4.3. Example of a $\text{Cu}_2\text{ZnGeSe}_4/\text{Si}$ tandem cell

We use the specifications obtained in the previous sections for the thin film top cell to evaluate the performance of the four terminal tandem cell. The Si bottom cell efficiency was calculated assuming a CZGSe cell with a band gap $E_g = 1.5$ eV on top of it which is optically active and absorbs a significant fraction of the light. Another essential parameter which is required for the design of the top cell in a tandem configuration is the thickness of the CZGSe absorber. The thickness should be optimized in a way to maintain a good transparency and at the same time minimize the absorption loss by the top cell. Fig. 18 presents the calculated EQE for the CZGSe/ MoO_x top cell ($\eta = 17\%$) with a thinner absorber $d = 1 \mu\text{m}$ and the Si-bottom cell being filtered by the top cell ($\eta = 9.4\%$). The efficiency of the four-terminal tandem cell in this case is 26.4% and an increase of 1.4% is obtained compared to the Si PERL cell alone.

5. Conclusions

The highest efficiency reported in CZGSe with pure Ge is above 7% and there is still room for further enhancement regarding the device performance. At this stage, there are several cell parameters limiting the device efficiency which are quite below the parameters found in state of art CIGSe solar cells, such as the low doping of the absorber and the low mobility. However, the main loss in the device performance is caused by the presence of a Cu_2GeSe_3 ternary phase at the back of the absorber surface which creates an internal hole blocking barrier and increases the V_{oc} deficit. Device efficiency in a range of 14–15% can be reached if the ternary phase is removed, which could be realized by exfoliation of the back contact and using a selective chemical etching.

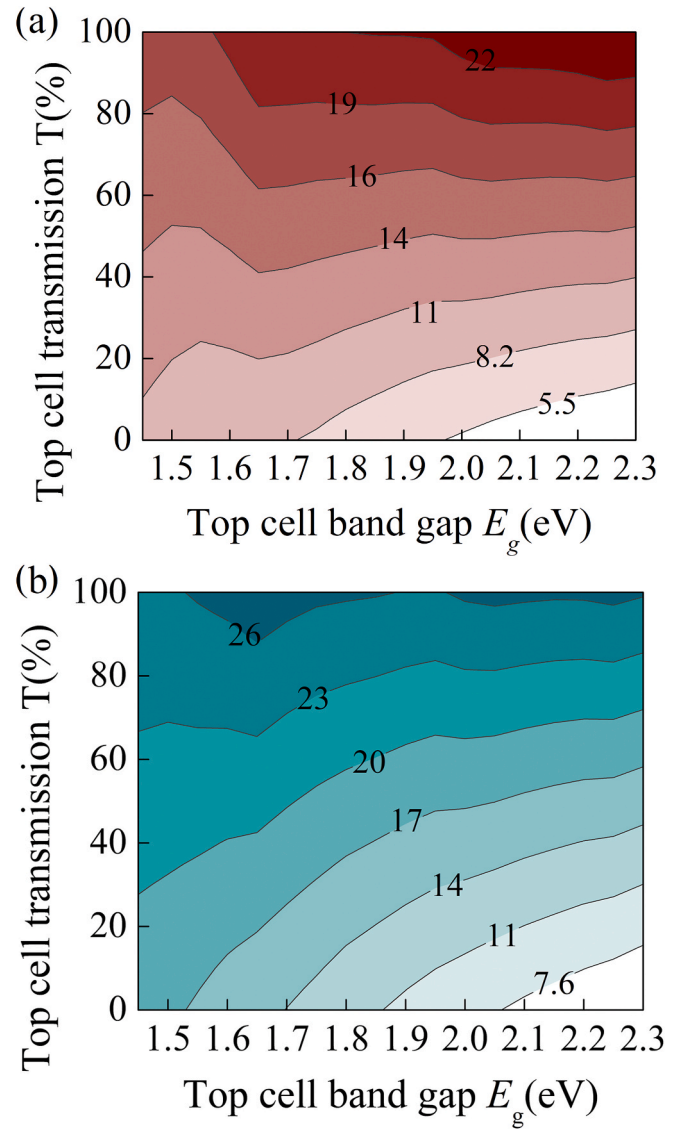


Fig. 17. Efficiency of the tandem cell as a function of band gap E_g and transmission (T) of the top cell. (a) for a standard cell; (b) for a cell with MoO_x .

Kesterite thin-film solar cells might be a good candidate as a top cell in combination with a Si crystalline bottom cell in a four-terminal tandem structure. However, the kesterite device performance is still below the requirements regarding the absorber band gap, efficiency and transparency. The band gap of $\text{Cu}_2\text{ZnSn}_{1-x}\text{Ge}_x\text{Se}_4$ and $\text{Cu}_2\text{ZnSn}_{1-x}\text{Si}_x\text{Se}_4$ alloys can easily be tuned by Si or Ge substitution in a range of 1–2.3 eV which is compatible with the recommended band gaps for the top cell in tandem structure when used with a Si bottom cell. However, increasing the band gap will be at the cost of decreasing the device efficiency in cells based on these alloys. Hence, further developments should be focused on cell layer engineering especially at the front and back contact to improve the device performance. Our calculations show that a cell with an efficiency above 14%, band gaps in a range of 1.5–1.7 eV and a transparency above 85% at long wavelengths are required to reach an efficiency gain of about 1–2% compared to the record Si cell efficiency of 25%.

CRediT authorship contribution statement

Samira Khelifi: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft, Writing - review

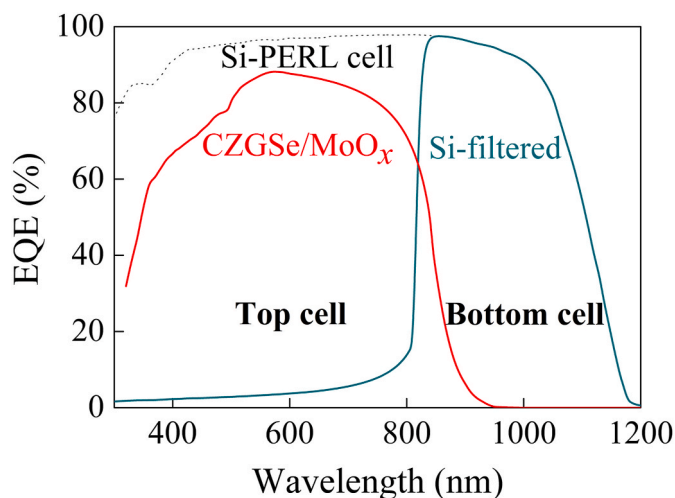


Fig. 18. External quantum efficiency (EQE) of the CZGSe/MoO_x top cell (red solid line) and the Si filtered bottom cell (green line). The calculated (EQE) of the PERL-Si cell bottom cell is also shown (black dot line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solmat.2020.110824>.

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