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The competing roles of i-ZnO in Cu(In,Ga)Se₂ solar cells

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ABSTRACT

The electrical role of the highly resistive and transparent (HRT) i-ZnO layer in Cu(In, Ga)Se₂(CIGS) solar cells is investigated. By tuning the resistivity of atomic layer deposited (ALD) i-ZnO through the use of post-growth O₂-plasma treatments, it is shown that low i-ZnO carrier densities (i.e. high resistivities) actually restrict the performance of CIGS solar cells by reducing the extent of band-bending of the CdS/CIGS junction (the effect of series resistance is ruled out as the origin of any observed differences). This is the first evidence that i-ZnO has a negative electrical effect in CIGS solar cells (alongside the positive effect of shunt mitigation), and based on these results, attempts to maximise resistivity of the i-ZnO (typically sought-after for this HRT layer) are not recommended. Device efficiencies of 12.5% were obtained when using low resistivity as-grown ALD i-ZnO (resistivity, $\rho=0.6\ \Omega\text{ cm}$, carrier density, $n=3.5\cdot 10^{18}\text{ cm}^{-3}$, and work function, $\Phi=4.06\text{ eV}$), but this decreased to 11.5% when using high resistivity, plasma-treated ALD i-ZnO ($\rho=134\ \Omega\text{ cm}$, $n=0.2\cdot 10^{18}\text{ cm}^{-3}$, and $\Phi=4.21\text{ eV}$). SCAPS modelling revealed the reason for the difference to be the effect that the i-ZnO work function (controlled by carrier density) has on the band-bending and built-in voltage, V_{bi} , of the main junction. Capacitance-voltage experiments confirmed that the V_{bi} is lower ($\Delta V_{bi}\sim 0.1\text{ V}$) when using low carrier density, high resistivity i-ZnO. This general effect was also found when using RF-sputtered i-ZnO, whereby the inclusion of high resistivity i-ZnO similarly generated lower efficiencies (15.0%) than low resistivity i-ZnO (15.9%).

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1. Introduction

In parallel to the encouraging advances of the record efficiencies of CuIn_(1-x)Ga_xSe₂ (CIGS) based solar cells [1], a number of groups are also focussing on replacing the CdS ‘buffer’ layer with Cd-free alternatives, such as ZnS [2], Zn(O,S) [3,4], ZnSe [5], ZnMgO [6] or In₂S₃ [7]. This is understandable, given the desire for the CIGS technology to be an entirely Cd-free alternative to CdTe. It is noticeable though that regardless of the choice of buffer layer, CIGS device configurations (both lab- and industrial-scale) almost invariably maintain the inclusion of the i-ZnO ‘highly resistive and transparent’ (HRT) layer between the buffer and front electrode (typically, doped-ZnO). And yet, despite its ubiquity, there is a distinct shortage of understanding regarding exact role of the i-ZnO. In general, it is usually thought that the resistive i-ZnO acts only to minimise the detrimental effect of short-circuit pathways and weak diodes, which may develop in the presence of pinholes

in the CIGS or buffer layers [8], thereby increasing the shunt resistance, fill factor (FF) and open-circuit voltage (V_{oc}). This particular effect has been shown by several research groups [9–11]. Based on this mechanism, the i-ZnO layer is thought to be unnecessary in devices that are not limited by low shunt resistances (e.g. for some lab-scale processes), but it should increase the performance uniformity for large-area processes (e.g. modules) for which pinholes are difficult to eliminate. Additional effects of the i-ZnO layer have been alluded to – for example, overly thick i-ZnO layers are thought to introduce parasitic series resistance [10] or increase reflectivity [12]. Indeed, there are reports on the correlation of device efficiency with i-ZnO thickness [9,10,12–14], but few reports can be found describing the correlation of device efficiency with the electrical properties of i-ZnO. In particular, the effect that this layer has on the energy band structure of the device, and therefore on the peak efficiency, is not fully understood. The band structure of any photovoltaic device is, of course, highly definitive of its final working behaviour. In one contribution, Nguyen et al. [15] suggested that the combined properties of the window layers (e.g. i-ZnO/CdS) should be chosen such that: a) band-bending in the CIGS layer itself is maximised; and b) the

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defect densities at the interfaces are minimised, but in that case different window layer combinations were compared, and the properties of the i-ZnO layer were not changed. Jiang et al. [16] and Chaisitsak et al. [17] used different deposition conditions to change i-ZnO resistivity, but in both cases, the change in growth process made it challenging to decouple the effects of resistivity, substrate temperature, growth time and film thickness (the extent of thermal budget delivered to a CIGS device during window layer deposition is known to strongly influence efficiency [18]).

In this work, we present a controlled study whereby the effect of the resistivity and carrier density of the i-ZnO layer on device behaviour, and the obtainable efficiency, is evaluated (whilst keeping the i-ZnO deposition temperature fixed) for the baseline device structure ZnO:Al/i-ZnO/CdS/CIGS/Mo/glass. Atomic layer deposition (ALD) was used to generate the i-ZnO layers, primarily owing to the high batch-to-batch reproducibility of the electrical properties that is achievable with ALD. High reproducibility is paramount for this study, and can be challenging to achieve given the sensitivity of ZnO resistivity to small process variations, with incremental shifts of stoichiometry (e.g. O/Zn ratio and the associated concentration of various compensating native defects, or the extent of unintentional H-doping) being particularly influential [19,20]. ALD also provides unrivalled thickness control and conformality [21]. The necessary tuning of the i-ZnO resistivity was achieved via a short (3 min) post-growth O₂-plasma treatment (again, using the same substrate temperature as during deposition), so that the deposition parameters could be kept constant in order to not introduce additional variables. CIGS device behaviour was studied in detail using: i) dark and light current-voltage measurements; ii) device simulations by SCAPS [22]; iii) capacitance-voltage profiling; and iv) transmission electron microscopy, in order to closely examine the exact role of i-ZnO. We demonstrate that small variations in i-ZnO carrier density (one order of magnitude) can affect device efficiency significantly (1.1% absolute), and this is discussed in terms of the extent of band bending of the i-ZnO/CdS/CIGS junction. Ultimately, we show that the higher i-ZnO resistivities limit the best achievable efficiency by reducing the built-in voltage of the device (although the higher resistivity also narrows the distribution of efficiencies within a single batch). As a result, we indicate that lower i-ZnO resistivities should be sought in cases whereby device quality is not hindered by high occurrences of shunts. Secondly, we prove this concept by utilising lower resistivity sputter-grown i-ZnO to yield maximum efficiencies of 15.9%. However, upon complete omission of the i-ZnO layer, device efficiency was not further improved (efficiencies agreed within error).

Where possible, these results are aligned with those from previous works on i-ZnO found in the literature in an attempt to further the general understanding of the HRT layer. These insights should be highly useful to enable further optimisation and efficiency enhancement of state-of-the-art CIGS devices.

2. Experimental

2.1. Standard cell fabrication procedure

ZnO:Al/i-ZnO/CdS/CIGS/Mo solar cells were fabricated on soda-lime glass. The (400 nm thick) Mo layer was generated by DC sputtering, the CIGS (1.5 μm) by co-evaporation (Ga/(Ga+In)=0.3), the CdS (80 nm) by chemical bath deposition, the i-ZnO (60 nm) by either thermal-ALD or RF sputtering (see below), and the ZnO:Al (200 nm, resistivity, $\rho=5 \cdot 10^{-4} \Omega \text{ cm}$, and sheet resistance, $R_{\text{sheet}}=25 \Omega/\square$) by RF sputtering at room temperature. This fabrication process is the same as has been reported before [8], besides the introduction of ALD i-ZnO. All cells reported here

were completed by evaporation of Ni/Ag/Ni finger contacts, and defined by scribing into individual cells (5 mm $\times$ 10 mm).

2.2. i-ZnO deposition and electrical characterisation for the comparative studies

The thermal-ALD process (using diethylzinc and H₂O as the Zn and O precursors respectively, and previously reported in [23]) generates films with a high level of batch-to-batch reproducibility, i.e. resistivity, $\rho, \sim 10^{-1} \pm 10^{-2} \Omega \text{ cm}$ at a substrate temperature of 120 °C, and is therefore suitable for use in accurate comparative studies. In Section 3.2, CIGS devices with two different sets of ALD i-ZnO electrical properties are compared: A CdS/CIGS/Mo/glass plate was cut into two halves, and each was separately loaded into an Oxford Instruments OpAL ALD reactor. Prior to i-ZnO deposition, the CdS surfaces of the stacks were exposed to an O₂ inductively coupled plasma (ICP, 150W) for 30 s (for surface activation), and then 60 nm i-ZnO films were deposited with the substrates held at 120 °C (the deposition took 1 h and 10 min). One half was left as-grown, and the other was O₂-plasma-treated (ICP, 150W) for a further 180 s (the as-grown sample was held for a further 180 s at 120 °C to ensure that both samples were subject to the same thermal budget). For both i-ZnO depositions, SiO₂/Si substrates were also included in the reactor, and the resistivity, carrier density (n) and carrier mobility (μ) of the as-grown and O₂-treated i-ZnO films were each determined using the i-ZnO/SiO₂/Si stacks via four-point probe and Hall measurements (see Section 3.1). The work functions of these films were measured using X-ray photoelectron spectroscopy (XPS). All devices were completed with ZnO: Al, Ni/Ag/Ni and scribing as above. This particular experiment investigates the influence of i-ZnO resistivity on CIGS performance in the resistivity range $\rho=10^{-1}$ – $10^2 \Omega \text{ cm}$.

In Section 3.3, firstly, a proof-of-concept experiment evaluating the effect of using i-ZnO having even lower resistivities (down to $\rho=10^{-3} \Omega \text{ cm}$) on device efficiency is presented. For these i-ZnO films, RF-sputtering (at room temperature) was utilised.¹ The reproducibility of RF sputtering was poorer than that for ALD, and so the two different resistivities investigated ($\rho=2 \cdot 10^{-3}$ and $6 \Omega \text{ cm}$, corresponding to $R_{\text{sheet}}=3.5 \cdot 10^2 \Omega/\square$ and $10^6 \Omega/\square$ respectively) were acquired from the batch-to-batch variation of the i-ZnO resistivity (attributed to varying levels of O₂ background pressure prior to depositions) in two consecutive ZnO:Al/i-ZnO/CdS/CIGS/Mo stack depositions. Note the batch-to-batch variation of the other layers in consecutive depositions is considered to be small (average efficiency $\pm 0.5\%$), although fluctuations of the baseline CIGS quality, i.e. pin-hole density, does affect baseline reproducibility at a time-scale of months (average efficiency $\pm 3\%$). This accounts for the difference in efficiencies from experiment-to-experiment in this study, but this baseline variability is negligible within experiments since they are either conducted using the same CdS/CIGS/Mo stack (as for the ALD i-ZnO comparison) or with consecutive stacks (as here, for the RF-sputtered i-ZnO comparison).

Secondly, the effect of omitting the i-ZnO layer entirely was investigated, with ZnO:Al/i-ZnO/CdS/CIGS/Mo devices being compared to ZnO:Al/CdS/CIGS/Mo devices. Sputtering was used for the i-ZnO layer, in this case in order to avoid the higher temperature of the ALD process which could bias the comparison (here, i-ZnO

¹ The ALD process is currently only capable of producing equivalent resistivities (10^{-3} – $10^{-2} \Omega \text{ cm}$) at substrate temperatures of 200 °C or higher and it was desirable to minimise substrate temperature because temperatures exceeding 150 °C are thought to cause degradation of CIGS devices [18]. RF sputtering has the potential to produce these low resistivities at room temperature (nominal), but the process is less reproducible than that of ALD.

$\rho = 6 \cdot 10^{-3} \Omega \text{ cm}$ and $R_{\text{sheet}} = 10^3 \Omega/\square$ – the same CdS/CIGS/Mo stack was used for both samples.

It should be noted that we appreciate that ALD and RF-sputtering can yield significantly different film microstructures and this may add an extra variable to the experiment. However, the reader should understand that the primary investigation is that of the ALD as-grown vs. ALD plasma-treated samples. ALD was selected due to its reproducibility, and the method of modifying resistivity using post growth plasma treatments was selected in order to avoid microstructural differences that may arise from changing conditions during growth. In this way, the electrical properties are primarily modified simply by varying the O-content. The RF-sputtered i-ZnO experiment merely serves as a proof-of-concept to investigate if the trend in performance vs. i-ZnO resistivity is consistent. An in-depth comparison of the virtues of ALD and sputtering in this case is beyond the scope of this work.

2.3. CIGS device characterisation

Current density–voltage (J – V) data were recorded both under Air Mass (AM) 1.5 conditions and in the dark, at 25 °C (measurements were corrected for day-to-day fluctuations in lamp intensity, which was $\pm 4\%$ as determined using a Si reference cell). Simulations of J – V data and energy band diagrams were carried out using SCAPS, with the parameters used for the simulations being listed in the Supporting Information, Table S1. Capacitance–voltage profiles were generated by extracting capacitance values from fitting impedance spectra with an equivalent circuit model (a resistor component in series with a parallel combination of a resistor and a constant phase element) – this method is described by Guenther et al. [24] and examples of our fitted impedance spectra are shown in Fig. S1 in the Supporting Information. The impedance measurements were acquired (in dark conditions) with an Autolab PGSTAT302N potentiostat, polarising the device at DC voltages of -0.1 V to $+0.8 \text{ V}$ and applying an AC signal with an amplitude of 10 mV over the frequency range of 1 kHz – 1 MHz . Mott–Schottky plots ($1/C^2$ vs. V) were then used to determine the built-in voltage (V_{bi}) of the cells according to the method of Blood and Orton [25]; further information is deferred to Section 3.2.

For cross-sectional transmission electron microscope (TEM) imaging, FIB lift-out sample preparation was carried out in an FEI Nova 600iNanoLab dual-beam system. The cross-sections were then imaged in a Jeol ARM200F TEM in high-angle annular dark-field (HAADF) scanning TEM (STEM) mode.

3. Results and discussion

3.1. Electrical properties of ALD i-ZnO

All electrical properties of as-grown and O_2 -plasma treated ALD i-ZnO are listed in Table 1; the resistivity of as-grown i-ZnO (defined as ‘low ρ ’ for the remainder of the manuscript) was $0.6 \Omega \text{ cm}$ ($R_{\text{sheet}} = 10^5 \Omega/\square$) and that of O_2 plasma-treated i-ZnO (‘high ρ ’) was $134 \Omega \text{ cm}$ ($R_{\text{sheet}} = 2 \cdot 10^7 \Omega/\square$). The ρ increase with plasma-treatment was a result of a reduction in both the carrier density

($3.5 \cdot 10^{18}$ to $0.2 \cdot 10^{18} \text{ cm}^{-3}$) and the mobility (3.0 – $0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). According to XPS data (not shown), whilst both as-grown and plasma-treated ZnO were sub-stoichiometric (i.e. $\text{O}/\text{Zn} < 1$), the plasma-treated ZnO had both: a) a higher O content in the ZnO form ($\sim 44.5\%$ compared to $\sim 43.5\%$ for as-grown); and b) a lower O content in the form of surface OH-groups (0.5% compared to 1.0%), throughout the 60 nm layer. This is consistent with the notion that, in general, a higher O content of the ZnO form leads to more resistive (lower n -type carrier density) ZnO since it is O-vacancies that are thought to compensate p -type behaviour and provide sites for n -type substitutional H-dopants [19,20]. As is the case here, even small variations in stoichiometry can significantly affect the final carrier density. As a result of the reduced carrier density following O_2 -plasma treatment, the work function accordingly increased by $\sim 0.1 \text{ eV}$ (from 4.06 eV to 4.21 eV), as determined from XPS measurements.

3.2. Effect of i-ZnO resistivity on obtainable CIGS efficiency

The light J – V curves of the best 9 cells (i.e. the upper quarter of the data set, 36 cells were measured for each sample here) from each of the two separate plates of ZnO:Al/i-ZnO/CdS/CIGS/Mo (i. as-grown i-ZnO, low ρ , ii. O_2 -treated i-ZnO, high ρ) are shown in Fig. 1. The device performance parameters (for the single best cell, and the average) of each are shown in Table 2. Throughout this manuscript, comparisons are primarily made between the best cells (upper quarters of data sets) in order to focus on the effect of the i-ZnO on the obtainable performance, and to exclude the influence of heavily shunted cells (the prevalence of which is discussed in Section 3.3), which are a result of randomly distributed CIGS defects (see Ref. [8]) – Cu-spitting during co-evaporation results in the formation and fall-off of CuSe_x particles. The spatial distribution of these across a $10 \text{ cm} \times 10 \text{ cm}$ sample appears to be random, and consecutive CIGS depositions show a negligible variation in the extent of Cu-spitting, but over the time scale of months, the prevalence can vary. Therefore, selection of the top 25% of cells from each sample ensures that averages are unaffected by the defected cells (i.e. those with $FF < 50\%$). For the reader's reference, a scatter plot of all efficiencies is shown in Fig. 2, and it can be immediately seen that cells can be grouped into 2 distinct populations for each sample, with the lower population denoted as heavily shunted cells. Box-plots of all performance parameters of the upper population are also included for both samples. However, as discussed, throughout the manuscript we maintain that quantitative analysis is based on the top 25% of cells as they are most unaffected by CIGS shunts, and can therefore more effectively demonstrate differences caused by i-ZnO layer electrical properties. A cross-sectional TEM image showing the thicknesses and microstructure of the window layers is shown in Fig. 3 – no microstructural differences could be seen between as-grown and plasma-treated samples.

The best and average efficiencies of cells with low ρ i-ZnO (12.6% and $11.7 \pm 0.6\%$ respectively) are higher than those of cells having high ρ i-ZnO (11.5% and $10.4 \pm 0.6\%$). The difference is primarily accounted for by the lower FF when using high ρ i-ZnO. The use of high ρ i-ZnO also results in lower V_{oc} and J_{sc} than for

Table 1
Electrical properties of i) as-grown (low ρ); and ii) O_2 -plasma treated (high ρ) ALD i-ZnO (on SiO_2/Si). The quoted values are averages of up to 4 measurements taken from different regions across the samples and the ranges are the standard deviations. For R_{sheet} , 4 replica samples of each condition were made and the values lied within the ranges in the table.

	T (°C)	O_2 -plasma	R_{sheet} ($\Omega \square^{-1}$)	ρ ($\Omega \text{ cm}$)	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	n (10^{18} cm^{-3})	Φ (eV)
Low ρ	120	No	$(1.0 \pm 0.1) \cdot 10^5$	0.6 ± 0.06	3.0 ± 0.3	3.5 ± 0.1	4.06 ± 0.04
High ρ	120	Yes	$(2.0 \pm 0.2) \cdot 10^7$	130 ± 10	0.2 ± 0.1	0.2 ± 0.1	4.21 ± 0.10

Fig. 1. Light J - V curves of the best 9 performing cells from each of the two separate plates of ZnO:Al/i-ZnO(ALD)/CdS/CIGS/Mo – i. O_2 -treated i-ZnO with high ρ (134 Ω cm, black lines), ii. as-grown i-ZnO with low ρ (0.6 Ω cm, red lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Device performance parameters for CIGS devices that include either low ρ (as-grown) or high ρ (O_2 -treated) ALD i-ZnO. See Table 1 for i-ZnO electrical properties. Averages are taken from the best 9 performing cells from each plate (the ranges are defined as the standard deviation of the individual cell values).

	Low ρ (best)	High ρ (best)	Low ρ (avg.)	High ρ (avg.)
η (%)	12.6	11.5	11.7 ± 0.6	10.4 ± 0.6
V_{oc} (mV)	642	636	639 ± 4	632 ± 6
J_{sc} (mA cm $^{-2}$)	30.8	30.4	30.7 ± 0.4	30.1 ± 0.4
FF (%)	63.6	59.8	59.5 ± 2.0	54.8 ± 2.0
R_s (Ω cm 2)	2.6	2.9	2.8 ± 0.2	3.2 ± 0.2
R_{sh} (Ω cm 2)	635	500	500 ± 180	350 ± 150
J_0 (mA cm $^{-2}$)	$8 \cdot 10^{-4}$	$4 \cdot 10^{-3}$	$4 \cdot 10^{-3} \pm 2 \cdot 10^{-3}$	$2 \cdot 10^{-2} \pm 1 \cdot 10^{-2}$

Fig. 3. HAADF-STEM cross-sectional image of the window layer region (ZnO:Al/i-ZnO/CdS) on a CIGS grain within a full CIGS cell.

low ρ i-ZnO cells, but the difference is not as significant as the difference in FF . It may be assumed that the lower FF is primarily caused by the higher resistance of i-ZnO contributing to a higher overall series resistance (R_s). However, the increase in R_s is minimal (from $2.8 \pm 0.2 \Omega$ cm 2 to $3.2 \pm 0.2 \Omega$ cm 2), and as a matter of fact, we should not expect i-ZnO resistivities in the range 10^{-1} – $10^2 \Omega$ cm to contribute significantly to the series resistance, since the resistance in the direction of carrier transport through a 60 nm i-ZnO layer would be negligible for such resistivities. Elsewhere, Ishizuka et al. [10] had to use much higher resistivities ($10^5 \Omega$ cm) to demonstrate that R_s increased with i-ZnO thickness

Fig. 2. a) A scatter plot of all 36 cells for each of the low ρ and high ρ ALD i-ZnO samples. The distribution shows 2 clear populations in each case, with the lower populations being heavily shunted and not suitable for comparisons. b) Box-plots of the device parameters of the upper populations, circled in (a), for both samples.

Fig. 4. Experimental data of the J - V curves of the best cells for low ρ (open red circles) and high ρ ALD i-ZnO (black circles), along with the curves simulated by SCAPS. In the SCAPS simulation, only the i-ZnO carrier density was changed, and all other material properties are shown in Table S1 in the supporting information. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(to 110 nm), and Sheer et al. [12] saw no R_s effect when using resistivities of $10^1 \Omega \text{ cm}$ for films as thick as 210 nm. In this work, it is interesting to note that the higher i-ZnO resistance also results in a lower shunt resistance (R_{SH} , from $500 \pm 180 \Omega \text{ cm}^2$ to $350 \pm 150 \Omega \text{ cm}^2$) – the R_{SH} values are taken from the slope around the zero bias region as is protocol, but the difference between the two samples is particularly clear in Fig. 1 in the bias range of 0.1–0.4 V – so evidently, the reduction in FF induced by the higher i-ZnO resistivity must be associated with a separate mechanism.

To investigate this further, device electrical behaviour was simulated using SCAPS: For the simulations, band-gap values, thicknesses and carrier densities were taken from prior in-house UV–VIS, ellipsometry, electron microscopy, Hall and capacitance-voltage measurements of the materials. Unknown parameters (carrier mobilities, electron affinities, densities of states and interface defects) were taken from Refs. [26–28] and then incrementally adjusted (within acceptable ranges according to literature values) to obtain a suitable fit to the best measured J - V curves of the low- ρ i-ZnO cells – the SCAPS fit (red line) and the experimental data (open red circles) are both shown in Fig. 4. Here, the carrier density of i-ZnO was fixed to $3.5 \cdot 10^{18} \text{ cm}^{-3}$, as was measured for as-grown i-ZnO (all other material properties used are shown in the supporting information in Table S1). Then, to fit the best measured J - V curve (black circles) of the low- ρ i-ZnO cell, all parameters were kept constant, aside from the i-ZnO carrier density which was changed to $2 \cdot 10^{17} \text{ cm}^{-3}$, i.e. that measured for the high- ρ samples. Note that the fit (dashed black line, Fig. 4) is excellent in this latter case, showing that the reduction of FF is well replicated simply by reducing i-ZnO carrier density. To evaluate whether the reduction in FF could simply be caused by an increase in R_s , then rather than reducing i-ZnO carrier density in the simulation, the series resistance was increased by the ratio measured for these two cells (i.e. from $2.6 \Omega \text{ cm}$ to $2.9 \Omega \text{ cm}$). However, this only caused a 0.1% decrease in efficiency, and could not replicate the reduction in shunt resistance or V_{oc} .

Instead, the likely mechanism that is responsible for the dependence between FF , V_{oc} , and i-ZnO carrier density is illustrated in Fig. 5a–c: Fig. 5a shows the energy band diagrams at the i-ZnO/CdS/CIGS interface region, also generated using SCAPS, for the cases of high ρ ($n = 2 \cdot 10^{17} \text{ cm}^{-3}$) and low ρ ($n = 3.5 \cdot 10^{18} \text{ cm}^{-3}$) i-ZnO, under AM1.5 illumination and at a bias voltage of 0.5 V (i.e.

Fig. 5. a) Energy band-diagrams under AM1.5 illumination at a bias voltage of +0.5 V for ZnO:Al/i-ZnO/CdS/CIGS/Mo solar cells; b) electron and hole depth-profiles in the CIGS layer; and c) Shockley-Read-Hall recombination rate profiles in the CIGS layer, all of which were generated by SCAPS for the case of low ρ i-ZnO (red) and high ρ i-ZnO (black). E_c , E_v , E_{Fp} and E_{Fn} refer to the conduction band, valence band, electron quasi-Fermi level and hole quasi-Fermi level positions respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

close to the maximum power points). It can be seen that while the low ρ i-ZnO is essentially degenerate (i.e. with the electron quasi-Fermi level, E_{Fn} , at the same energy as the conduction band edge, E_c), the high ρ i-ZnO is not. The associated higher work function of the high ρ i-ZnO (confirmed with XPS measurements, see Table 1) results in a lesser extent of band bending in the first few hundred nm of the CIGS layer – i.e. a lower built in voltage, V_{bi} . As discussed in the introduction, the properties of the window layers should be chosen to maximise the band bending [15]. Fig. 5b and c show that upon this reduction of the band bending (when the high ρ i-ZnO is used), the carrier density and recombination profiles within the CIGS are changed: The onset of hole density (p) depletion towards the CdS/CIGS interface is shifted such that in the region 50–400 nm from the interface, p is larger (e.g. $2.1 \cdot 10^{13} \text{ cm}^{-3}$ at 150 nm from the interface for high ρ i-ZnO, compared to $0.7 \cdot 10^{13} \text{ cm}^{-3}$ for low ρ i-ZnO) and this causes a higher rate, R , of Shockley-Read-Hall recombination in the junction region – R is dependent on both n and p and also the extent of Fermi-level splitting. It is the increased rate of recombination in forward bias – when using a higher resistivity, lower carrier density, and higher work function i-ZnO – which raises the J - V curve upwards thereby lowering FF and ultimately efficiency. A

Fig. 6. $1/C^2$ - V plots for full devices with a) low ρ i-ZnO and b) high ρ i-ZnO. For each, the built-in voltage, V_{bi} , is determined by extrapolation from the linear response in region 1 (i.e. from the low forward and low reverse bias range). Inset in (b) shows a close-up of the high bias region (indicated in (a) and (b)) for both cells. c) C - V plots for both cells, fit with Eq. (3) in order to extract V_{bi} as a fitting parameter. d) Energy band-diagrams for both cells, as simulated by SCAPS at 0 V in the dark; V_{bi} is a summation of V_{bi1} and V_{bi2} .

reduction of V_{bi} should also be responsible for the reduction in V_{oc} . Dark J - V measurements confirmed that the recombination in cells with high ρ i-ZnO is higher than in cells with low ρ i-ZnO (according to the reverse saturation currents, J_0 , listed in Table 2).

To further validate the mechanism outlined above, the V_{bi} – which is the upper limit to the achievable V_{oc} [29] – should be directly measured. The typical method is to use capacitance-voltage profiling; V_{bi} is taken as the x -axis intercept of $1/C^2$ - V plots, according to the method of Blood and Orton [25], based on Eq. (1),

$$\frac{1}{C^2} = \frac{2}{A^2 \epsilon \epsilon_0 e N} (V_{bi} - V) \quad (1)$$

where A is the device area, ϵ is the relative permittivity, ϵ_0 is the permittivity of free space, e the electron charge, and N the carrier density of the less doped side of the junction, i.e. the CIGS layer in this case – note that N can be determined from the slope of $1/C^2$ - V . Fig. 6a and b show the $1/C^2$ - V plots for representative cells having low and high ρ i-ZnO respectively. For both plots, there are three regions of differing slope, which indicates non-uniform doping depth-profiles through the CIGS layers: 1) the low reverse and low forward bias range, having a shallow slope ($N \sim 4 \cdot 10^{15} \text{ cm}^{-3}$); 2) the mid-forward-bias range; having a steeper slope

($N \sim 2 \cdot 10^{15} \text{ cm}^{-3}$); and 3) the high-forward-bias region, also having a shallow slope ($N \sim 4 \cdot 10^{15} - 6 \cdot 10^{15} \text{ cm}^{-3}$). The applied voltage corresponds to a depth into the CIGS layer into which the space-charge region, from which the capacitive behaviour is generated, extends. This depth, x_d , is given by:

$$x_d = \frac{\epsilon \epsilon_0 A}{C} \quad (2)$$

Indeed, this is the basis upon which carrier density depth-profiles are constructed; i.e. by computing N from the local $1/C^2$ - V slope and, x_d , from Eq. (2) [30–32]. From our data, region 1 corresponds to a depth of 0.65–0.75 μm , region 2 to $x_d \sim 0.35$ –0.6 μm , and region 3 to $x_d \sim 0.01$ –0.1 μm . In such a case of non-uniform doping, there is some inconsistency in the literature as to whether region 1 [33] or region 2 [34] should be used to extrapolate for V_{bi} . However, Mauk and Sites [35] explicitly state that region 1 should be used, and that the fall in the inverse squared capacitance in region 2 is related to the increase in capacitance caused by extraneous band-gap states in the space-charge region. Indeed, both Mingebach [36] and Kirchartz [37] report that V_{bi} is underestimated when extrapolating from region 2. This is also observed here; extrapolating from region 2 yields a V_{bi} ($\sim 0.48 \text{ V}$)

that is lower than all V_{oc} 's measured (> 0.6 V), which cannot be the case. The use of region 1 however (as shown in Fig. 6a and b) generates realistic V_{bi} values and reveals a clear difference between the two samples; for low ρ i-ZnO, $V_{bi} = (0.84 \pm 0.04)$ V, and for high ρ i-ZnO, $V_{bi} = (0.75 \pm 0.04)$ V. Close inspection of region 3 (Fig. 5b inset for both cells), which corresponds to a space-charge region depth close to the CdS/CIGS interface also suggests that V_{bi} is larger for the low ρ i-ZnO cell (and this was consistently seen for other pairs of cells). Alternatively, Khelifi et al. [31] proposed a method to determine V_{bi} in the case of non-uniform doping densities, by fitting C-V data with the following expression;

$$C = \frac{C_0'}{\left(1 - \frac{V}{V_{bi}}\right)^{\frac{1}{\beta}}} \quad (3)$$

where C_0' is a constant, and β is a measure of the non-uniformity of the doping density. Note that when the doping is uniform $\beta=2$ and Eq. (3) becomes identical to Eq. (1). Here, this method yields $V_{bi} = (0.89 \pm 0.02)$ V for low ρ i-ZnO, and $V_{bi} = (0.76 \pm 0.02)$ V for high ρ i-ZnO (see Fig. 6c for the fits to the C-V data), these values being highly comparable to those determined via extrapolation from region 1 of $1/C^2$ -V plots. From the band-diagrams generated by SCAPS at 0 V in the dark (Fig. 6d), for low ρ i-ZnO the V_{bi} is expected to be 0.08 V higher than for high ρ i-ZnO.

These results suggest that the use of i-ZnO with a lower carrier concentration and therefore higher resistivity does indeed result in reduced band-bending towards the CdS/CIGS interface, as predicted by SCAPS modelling. This appears to lead to a higher recombination rate and therefore higher reverse current and lower FF. It should also account for the small reduction in V_{oc} that was observed. Note that we believe the presence of the conduction band offset at the CdS/CIGS interface causes the extent of band-bending to primarily influence FF (much like the J-V distortion behaviour described by Kanevce et al. [38]), since if the offset is removed from the simulation then the extent of band-bending is most influential over V_{oc} (not-shown). However such a positive band-offset of up to 0.25 eV can indeed be expected at this interface [39,40]. We also note that according to the model of Nguyen et al. [15], who also discussed the effect of window and buffer layer electrical properties on CIGS device performance, a reduction in the band-bending could also be associated with: a) an increase in the Fermi level to conduction band distance at the CdS/CIGS interface (as seen in Fig. 6d), which can hinder electron extraction; and b) a decrease in the Fermi level to valence band distance at this interface, which can promote holes to recombine with electrons (also seen in Fig. 6d). This increased interfacial recombination may add to the increased space-charge-region recombination that has been elucidated by SCAPS modelling.

We have also considered the possibility that any difference in the measured J-V curves between high and low resistivity i-ZnO could merely be an artefact introduced by the second O_2 -plasma treatment, i.e. by an increased defect density within i-ZnO or underlying layers (CdS) via plasma-damage. In terms of the i-ZnO layer, we tested the influence of i-ZnO defect density in SCAPS simulations and observed that even when the i-ZnO defect density is increased by up to 6 orders of magnitude, no effect on device performance was observed, therefore i-ZnO plasma-damage is not thought to influence the results. In terms of the CdS layer, we should reiterate that both samples were subject to an O_2 -plasma pre-treatment (i.e. directly incident on the CdS layer for surface activation) which should conceivably be more damaging to CdS properties than the treatment after i-ZnO (60 nm) deposition, and yet, in preliminary experiments this pre-treatment was empirically proven to not degrade cell η , V_{oc} , or, crucially, FF (see Table S2 in the supporting information, which compares cells with ALD

i-ZnO and RF-sputtered i-ZnO having resistivities on the order of $10^{-1} \Omega \text{ cm}$). Therefore, any plasma damage to CdS during pre-treatments and post-growth treatments of i-ZnO are also not thought to influence results. These arguments support the correctness of our attribution of the observed differences entirely to the i-ZnO electrical properties, and we highlight the strong agreement among: a) the expected V_{bi} difference from SCAPS simulation (~ 0.08 V); b) the expected V_{bi} difference based on the measured work function difference (~ 0.1 V); and c) the measured V_{bi} difference (~ 0.09 V).

A short discussion of the roles of window layer interfacial states remains prudent however. In the model of Nguyen [15], three possible recombination pathways are described: a) at the i-ZnO/CdS interface; b) at the CdS/CIGS interface; and c) in the CIGS space-charge region. In Nguyen's model, the importance of the Fermi level position at the CdS/CIGS interface for defining which of these recombination pathways dominate is highlighted. It is consistent with our model in stating that it is more favourable for the Fermi level position to be closer to the conduction band at this interface. However, whereas we state that the i-ZnO doping density is the governing factor for defining the Fermi level position, Nguyen states that the i-ZnO/CdS defect density is the governing factor. Nevertheless, it is clear from Nguyen's model that a reduction in i-ZnO doping would have a similar negative effect on the band diagram as that of an increase in i-ZnO/CdS defect density, and would therefore affect recombination pathways in a similar way – i.e. they would both increase the Fermi level to conduction band distance and therefore lead to increased hole recombination and reduced electron extraction at the CdS/CIGS interface. The question therefore remains as to which effect is strongest in defining the Fermi level in our case. We do not expect i-ZnO/CdS interface state density to differ too greatly between the two sample sets – defect density at this region may be increased by the pre-plasma treatment before ALD i-ZnO deposition, but this step was identical for both samples. Moreover, as discussed above, from SCAPS simulations, increasing defect density at this interface by many orders of magnitude had no effect on the simulated J-V curves. For these reasons, we maintain that the i-ZnO doping density is the more influential parameter.

3.3. Recommendations for i-ZnO material properties

In light of the results shown in Section 3.2, it could be concluded that the i-ZnO layer is detrimental to the device performance, particularly if its resistivity is too high. This may be true for the best performing cells, but note that the higher resistivity i-ZnO also resulted in a narrower distribution of the cell efficiencies taken from all cells across the plates (36 each). Whilst the peak efficiencies (and average efficiencies of the upper quarter) are lower for high ρ i-ZnO, the number of cells with $\eta < 5\%$ was also lower (5 cells compared to 9 for low ρ i-ZnO). This is almost certainly as a result of the higher capability of the high ρ i-ZnO to diminish the effect of shunts in underlying layers. With this in mind, it is clear that the suitable choice of i-ZnO properties is highly process-dependent, i.e. if the given process is highly afflicted with pinholes in CIGS or CdS layers then a higher resistivity i-ZnO should be chosen (this is particularly relevant when upscaling the technology to large area). On the other hand, if the given process yields high quality shunt-free device stacks, then the i-ZnO may be limiting to peak device efficiency via the mechanism outlined in Section 3.2, and either lower resistivities or complete omission of the i-ZnO should be sought.

As a proof of concept, one set of cells (ZnO:Al/i-ZnO/CdS/CIGS/Mo) having a very low resistivity RF-sputtered i-ZnO layer ($2 \cdot 10^{-3} \Omega \text{ cm}$) was compared to a set having a sputtered i-ZnO with a resistivity of $6 \Omega \text{ cm}$ (note that there are not intentional

Table 3

Device performance parameters for CIGS devices with sputtered i-ZnO resistivity of $2 \cdot 10^{-3} \Omega \text{ cm}$ and $6 \Omega \text{ cm}$. The ranges are taken as the standard deviation around the averages of the individual cell values.

	$\rho = 2 \cdot 10^{-3} \Omega \text{ cm}$ (best)	$\rho = 6 \Omega \text{ cm}$ (best)	$\rho = 2 \cdot 10^{-3} \Omega \text{ cm}$ (avg.)	$\rho = 6 \Omega \text{ cm}$ (avg.)
η (%)	15.9	15.0	15.6 ± 0.2	14.6 ± 0.2
V_{oc} (mV)	660	656	663 ± 5	652 ± 5
J_{sc} (mA cm^{-2})	31.1	30.7	30.7 ± 0.4	30.4 ± 0.3
FF (%)	77.4	74.3	76.5 ± 1.0	73.8 ± 1.0
R_s ($\Omega \text{ cm}^2$)	1.3	1.5	1.4 ± 0.3	1.5 ± 0.2
R_{sh} ($\Omega \text{ cm}^2$)	2890	1580	3060 ± 1650	1750 ± 350

Fig. 7. Light J - V curves of the best 11 performing cells from each of the two separate plates of ZnO:Al/i-ZnO(RF-sputtered)/CdS/CIGS/Mo, for which the i-ZnO resistivity was $\rho = 6 \Omega \text{ cm}$ (black lines) and $\rho = 2 \cdot 10^{-3} \Omega \text{ cm}$ (red lines) respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

O_2 -plasma treatments in this comparison). The results of the best cell from each plate (and the average of the best 11 cells—44 cells were measured in total) are shown in Table 3 – the light J - V curves of the best cells are shown in Fig. 7 and scatter and box plots of all cells' parameters are shown in Fig. 8 (the box plots discount the heavily shunted cells, which are circled in Fig. 8a). Note that the absolute efficiencies of these cells are higher than those shown in Section 3.2 since the baseline CIGS quality was higher (i.e. a lower macro-scale pin-hole density, the cause of which is described in Ref. [8]), and possibly due to the lower substrate temperature used in the sputtering process. As predicted, the use of the lower resistivity i-ZnO indeed yielded higher efficiencies, owing to an increase in FF , but also to V_{oc} and J_{sc} . Once again, R_{SH} increases as the i-ZnO resistivity is decreased, which, whilst unexpected, agrees with the mechanism outlined in Section 3.2. Indeed, in the absence of intentional O_2 -plasma treatments in this proof-of-concept experiment, the consistency with Section 3.2 further supports the earlier attribution of the performance differences solely to i-ZnO properties, as opposed to variations in the extent of plasma damage. Note that the improved J - V characteristics of this sample set (relative to those in Section 3.2) could be reproduced in SCAPS (Fig. 9) by using lower values for the shunt resistance and recombination rates in the CIGS layer, and moreover, the difference between the cells having high and low resistivity i-ZnO could again be replicated (this time using i-ZnO resistivities of $5 \cdot 10^{17}$ and $5 \cdot 10^{20} \text{ cm}^{-3}$, estimated from the sheet resistance values).

Next, a set of cells with no i-ZnO layer (i.e. ZnO:Al/CdS/CIGS/Mo) was compared to a set with an RF sputtered i-ZnO layer ($\rho = 6 \cdot 10^{-3} \Omega \text{ cm}$) – the former set effectively has a ZnO resistivity of $5 \cdot 10^{-4} \Omega \text{ cm}$ (the ZnO:Al layer) directly in contact with the CdS. No further improvements were observed upon complete omission of the i-ZnO layer (see Table 4), the average efficiencies being $13.8 \pm 0.2\%$ and $13.6 \pm 0.1\%$ for the best cells with and without i-ZnO respectively. The removal of the i-ZnO actually leads to marginally lower FF and V_{oc} . It is possible that any potential further improvements gained from removing the i-ZnO layer (i.e. by maximising the built-in voltage) are negated by the enhanced effect of shunting and/or weak diodes in this case. Alternatively,

Fig. 8. a) A scatter plot of all 44 cells for each of the low ρ and high ρ RF-sputtered i-ZnO samples. The distribution shows 2 clear populations in each case, with the lower populations being heavily shunted and not suitable for comparisons. b) Box-plots of the device parameters of the upper populations, circled in (a), for both samples.

Fig. 9. Experimental data of representative J - V curves (taken from Fig. 7) for low ρ (open red circles) and high ρ RF-sputtered i-ZnO (black circles), along with the curves simulated by SCAPS. In the SCAPS simulation, only the i-ZnO carrier density was changed between the two data sets. Relative to the SCAPS simulations shown in Fig. 4, the chosen CIGS defect density was lower ($3 \cdot 10^{13} \text{ cm}^{-3}$) and the shunt resistance was increased. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 4

Device performance parameters for CIGS devices with a sputtered i-ZnO layer ($\rho = 6 \cdot 10^{-3} \Omega \text{ cm}$) and without. The ranges are taken as the standard deviation around the averages of the individual cell values.

	With i-ZnO (best)	Without (best)	With i-ZnO (avg.)	Without (avg.)
η (%)	14.1	13.7	13.8 ± 0.2	13.6 ± 0.1
V_{oc} (mV)	650	638	641 ± 4	637 ± 2
J_{sc} (mA cm^{-2})	31.1	30.8	30.6 ± 0.3	31.0 ± 0.3
FF (%)	71.0	69.6	70.2 ± 0.4	68.6 ± 0.6
R_s ($\Omega \text{ cm}^2$)	2.0	2.0	1.9 ± 0.2	2.1 ± 0.1
R_{sh} ($\Omega \text{ cm}^2$)	1110	1090	1040 ± 161	1250 ± 118

Shi et al. [41] propose that the presence of an i-ZnO layer results in the resistivity of the subsequently deposited ZnO:Al electrode to be lower than in the absence of i-ZnO (since the i-ZnO ‘seed layer’ promotes the growth of larger grains in ZnO:Al), which may account for the lower R_s when i-ZnO is included here. Future works will investigate the development of lower resistivity ALD-grown i-ZnO at lower substrate temperatures ($< 100^\circ \text{C}$) to maximise the obtainable efficiency of CIGS devices.

In the supporting information (Fig. S2), the data from all experiments (i. ALD i-ZnO; ii. RF-sputtered i-ZnO; and iii. inclusion vs. exclusion of i-ZnO) are collated together – note that the resistivity for the sample with no i-ZnO is taken to be $5 \cdot 10^{-4} \Omega \text{ cm}$ which is the resistivity of the ZnO:Al layer. Admittedly, the fluctuation of CIGS quality between sample sets introduces an extent of scatter to the trends, but nevertheless, a dependence of η and FF on i-ZnO resistivity can be identified. A strong trend between J_{sc} and resistivity is also notable (albeit within a narrow J_{sc} range), however, one should appreciate that the J_{sc} for the sample with no i-ZnO is primarily influenced by the fact that there is less parasitic ZnO absorption.

4. Conclusions

The intention of this study was to interrogate the effect of i-ZnO electrical properties on the behaviour of CIGS solar cells, and to thereby learn more of the role of the HRT i-ZnO layer in these

devices. Atomic layer deposition was the method of choice for the generation of i-ZnO layers owing to its high run-to-run reproducibility and unrivalled thickness control. Using a post-growth O_2 -plasma, the resistivity of the i-ZnO layer could be increased by decreasing the carrier concentration, and the effect of these electrical properties could be studied. It was shown that higher i-ZnO resistivities lead to lower efficiencies, primarily via decreased FF (and to a lesser extent, V_{oc}). Device modelling demonstrated that the mechanism responsible for this is that the lower i-ZnO carrier concentration associated with the high resistivity corresponds to a higher work function, and the resulting band-bending of the i-ZnO/CdS/CIGS junction is therefore reduced. This reduces the built-in voltage of the cell, which firstly leads to lower V_{oc} , but more significantly, affects the hole and electron carrier density in the shallow CIGS region, ultimately resulting in higher recombination and therefore higher forward current and lower FF . The lower built in voltage was confirmed using capacitance-voltage profiling.

The trend was also seen when RF-sputtered i-ZnO was used instead of ALD – i.e. higher values of η (up to 15.9%), FF and V_{oc} being obtained for the low resistivity i-ZnO ($\rho = 6 \cdot 10^{-3} \Omega \text{ cm}$). However, the use of lower resistivity i-ZnO layer can also lead to a wider distribution of cell efficiency across a single batch, and the complete omission of the i-ZnO layer did not lead to further improvements (marginally lower V_{oc} and FF); these two observations indicate that the i-ZnO is still responsible for minimising shunting to some extent. Evidently, the optimal application of the i-ZnO layer is clearly dependent on the quality of the underlying stack (for instance, pinhole density in CIGS and CdS layers), but we have demonstrated that the absolute peak efficiency is limited by an overly high i-ZnO resistivity. We believe that these insights remain highly relevant to state-of-the-art CIGS devices (for which efficiencies are enhanced by the use of anti-reflective coatings and post-growth potassium treatments) and in particular in view of large-area processing which necessitates i-ZnO buffer layer inclusion as a result of the higher likelihood of macro-defect formation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.solmat.2016.07.049>.

References

- [1] P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T.M. Friedlmeier, M. Powalla, Properties of Cu(In,Ga)Se₂ solar cells with new record efficiencies

- up to 21.7%, *Phys. Status Solidi (RRL) – Rapid Res. Lett.* 9 (2015) 28–31.
- [2] J.-Y. Baek, S.-R. Park, T.-Y. Yun, H.-J. Han, K.-B. Kim, C.-W. Jeon, Effects of the modified TCO sputtering condition on ZnS/CIGS solar cell, *Mol. Cryst. Liq. Cryst.* 586 (2013) 76–81.
 - [3] S. Mendes, F. Ziem, T. Lavrenko, T. Walter, I. Lauermann, M. Klingsporn, S. Schmidt, F. Hergert, R. Schlattmann, Above 16% efficient sequentially grown Cu(In,Ga)(Se,S)₂-based solar cells with atomic layer deposited Zn(O,S) buffers, *Prog. Photovolt.: Res. Appl.* 23 (2015) 1493–1500.
 - [4] T. Kobayashi, Z. Jehl Li Kao, T. Kato, H. Sugimoto, T. Nakada, A comparative study of Cd- and Zn-compound buffer layers on Cu(In_{1-x}Ga_x)(S_ySe_{1-y})₂ thin film solar cells, *Prog. Photovolt.: Res. Appl.* 24 (2015) 389–396.
 - [5] S. Siebentritt, P. Walk, U. Fiedeler, I. Lauermann, K. Rahne, M.C. Lux-Steiner, T. P. Niesen, F. Karg, MOCVD as a dry deposition method of ZnSe buffers for Cu(In,Ga)(S,Se)₂ solar cells, *Prog. Photovolt.: Res. Appl.* 12 (2012) 333–338.
 - [6] D. Hariskos, B. Fuchs, R. Menner, N. Naghavi, C. Hubert, D. Lincot, M. Powalla, The Zn(S,O,OH)/ZnMgO buffer in thin-film Cu(In,Ga)(Se,S)₂-based solar cells part II: Magnetron sputtering of the ZnMgO buffer layer for in-line co-evaporated Cu(In,Ga)Se₂ solar cells, *Prog. Photovolt.: Res. Appl.* 17 (2009) 479–488.
 - [7] K. Kim, L. Larina, J.H. Yun, K.H. Yoon, H. Kwon, B.T. Ahn, Cd-free CIGS solar cells with buffer layer based on the In₂S₃ derivatives, *Phys. Chem. Chem. Phys.* 15 (2013) 9239–9244.
 - [8] B.L. Williams, S. Smit, B.J. Kniknie, K.J. Bakker, W. Keuning, W.M.M. Kessels, R.E. I. Schropp, M. Creatore, Identifying parasitic current pathways in CIGS solar cells by modelling dark J-V response, *Prog. Photovolt.: Res. Appl.* 23 (2015) 1516–1525.
 - [9] Y. Nagoya, B. Sang, Y. Fujiwara, K. Kushiya, O. Yamase, Improved performance of Cu(In,Ga)Se₂-based submodules with a stacked structure of ZnO window prepared by sputtering, *Sol. Energy Mater. Sol. Cells* 75 (2003) 163–169.
 - [10] S. Ishizuka, K. Sakurai, A. Yamada, K. Matsubara, P. Fons, K. Iwata, S. Nakamura, Y. Kimura, T. Baba, H. Nakanishi, T. Kojima, S. Niki, Fabrication of wide-gap Cu(In_{1-x}Ga_x)Se₂ thin film solar cells: a study on the correlation of cell performance with highly resistive i-ZnO layer thickness, *Sol. Energy Mater. Sol. Cells* 87 (2005) 541–548.
 - [11] B. Misić, B.E. Pieters, J.P. Theisen, A. Gerber, U. Rau, Shunt mitigation in ZnO:Al/i-ZnO/CdS/Cu(In,Ga)Se₂ solar modules by the i-ZnO/CdS buffer combination, *Phys. Status Solidi A* 212 (2015) 541–546.
 - [12] R. Scheer, L. Messmann-Vera, R. Klenk, H.W. Schock, On the role of non-doped ZnO in CIGSe solar cells, *Prog. Photovolt.: Res. Appl.* 20 (2012) 619–624.
 - [13] C. Kim, H.-J. Jo, D.-H. Kim, D.-H. Son, D.-H. Lee, I. Rhee, Effect of ZnO layer thickness on efficiency of Cu(In,Ga)Se₂ thin-film solar cells, *Mol. Cryst. Liq. Cryst.* 565 (2012) 52–58.
 - [14] A.H. Jahagirdar, A.A. Kadam, N.G. Dhere, Role of i-ZnO in optimizing open circuit voltage of CIGS₂ and CIGS thin film solar cells, in: *Proceedings of the Conference Record of the 4th IEEE World Conference on Photovoltaic Energy Conversion*, 2006, pp. 557–559.
 - [15] Q. Nguyen, K. Orgassa, I. Koetschau, U. Rau, H.W. Schock, Influence of heterointerfaces on the performance of Cu(In,Ga)Se₂ solar cells with CdS and In(OH_xS_y) buffer layers, *Thin Solid Films* 431–432 (2003) 330–334.
 - [16] M. Jiang, K. Tang, X. Yan, Characterisation of intrinsic ZnO thin film deposited by sputtering and its effects on CuIn_{1-x}Ga_xSe₂ solar cells, *J. Photonics Energy* 2 (2012) 028502.
 - [17] S. Chaisitsak, T. Sugiyama, A. Yamada, M. Konagai, Cu(In,Ga)Se₂ thin-film solar cells with high resistivity ZnO buffer layers deposited by atomic layer deposition, *Jpn. J. Appl. Phys.* 38 (1999) 4989–4992.
 - [18] K. Sharma, B.L. Williams, A. Mittal, H.C.M. Knoops, B.J. Kniknie, N.J. Bakker, W. M.M. Kessels, R.E.I. Schropp, M. Creatore, Expanding thermal plasma chemical vapour deposition of ZnO:Al layers for solar cells, *J. Photoenergy*. 2014 (2014) 253140.
 - [19] O. Fumiyasu, C. Minseok, T. Atsushi, T. Isao, Point defects in ZnO: an approach from first principles, *Sci. Technol. Adv. Mater.* 12 (2011) 034302.
 - [20] A. Janotti, C.G. Van de Walle, Native point defects in ZnO, *Phys. Rev. B* 76 (2007) 165202.
 - [21] R.W. Johnson, A. Hultqvist, S.F. Bent, A brief review of atomic layer deposition: from fundamentals to applications, *Mater. Today* 17 (2014) 236–246.
 - [22] M. Burgelman, P. Nollet, S. Degraeve, Modelling polycrystalline semiconductor solar cells, *Thin Solid Films* 361 (2000) 527–532.
 - [23] Y. Wu, S.E. Potts, P.M. Hermkens, H.C.M. Knoops, F. Roozeboom, W.M. M. Kessels, Enhanced doping efficiency of Al-doped ZnO by atomic layer deposition using dimethylaluminum isopropoxide as an alternative aluminum precursor, *Chem. Mater.* 25 (2013) 4619–4622.
 - [24] K.M. Guenther, T. Gimpel, W. Schade, S. Kontermann, Using impedance spectroscopy for enhanced capacitance-voltage measurements on solar cells with multiple space charge regions and a structured surface, in: *Proceedings of the Conference Record of the 39th IEEE Photovoltaic Specialists Conference*, 2013, pp. 956–959.
 - [25] P. Blood, P. J.W. Orton, *The Electrical Characterisation of Semiconductors: Majority Carriers and Electron States*, Academic Press, London, 1992.
 - [26] C. Salame, M. Aillerie, P. Papageorgas, M. Mostefaoui, H. Mazari, S. Khelifi, A. Bouraiou, R. Dabou, Simulation of high efficiency CIGS solar cells with SCAPS-1D software, *Energy Procedia* 74 (2015) 736–744.
 - [27] B. Vermang, V. Fjällström, J. Pettersson, P. Salomé, M. Edoff, Development of rear surface passivated Cu(In,Ga)Se₂ thin film solar cells with nano-sized local rear point contacts, *Sol. Energy Mater. Sol. Cells* 117 (2013) 505–511.
 - [28] S. Oudraogo, F. Zougmore, J.M. Ndjaka, Numerical analysis of copper-indium-gallium-diselenide-based solar cells by SCAPS-1D, *Int. J. Photoenergy* 2013 (2013) 9.
 - [29] K. Schwanitz, S. Klein, Anti-reflective silicon oxide p-layer for thin-film silicon solar cells, in: X. Wang, Z.M. Wang (Eds.), *High Efficiency Solar Cells: Physics, Materials, and Devices*, Springer, London, 2014.
 - [30] T. Unold, T. Enzenhofer, C.A. Kaufmann, R. Klenk, A. Neisser, K. Sakurai, H.W. Schock, Analysis of defects in coevaporated high-efficiency Cu(In,Ga)Se₂ solar cells, in: *Proceedings of the Conference Record of the 4th IEEE World Conference on Photovoltaic Energy Conversion*, 2006, pp. 356–359.
 - [31] S. Khelifi, J. Marlein, M. Burgelman, A. Belgachi, Electrical characteristics of Cu(In,Ga)Se₂ thin films solar cells on metallic foil substrates, in: *Proceedings of the 23rd European Photovoltaic Solar Energy Conference*, 2008, pp. 2165–2169.
 - [32] M. Cwil, M. Igalson, P. Zabierowski, C.A. Kaufmann, A. Neisser, Capacitance profiling in the CIGS solar cells, *Thin Solid Films* 515 (2007) 6229–6232.
 - [33] P.J. Dale, A.P. Samantilleke, G. Zoppi, I. Forbes, L.M. Peter, Characterization of CuInSe₂ material and devices: comparison of thermal and electrochemically prepared absorber layers, *J. Phys. D: Appl. Phys.* 41 (2008) 085105.
 - [34] B. Qi, Z.-G. Zhang, J. Wang, Uncovering the role of cathode buffer layer in organic solar cells, *Sci. Rep.* 5 (2015) 7803.
 - [35] P.H. Mauk, H. Tavakolian, J.R. Sites, Interpretation of thin-film polycrystalline solar cell capacitance, *IEEE Trans. Electron Devices* 37 (1990) 422–427.
 - [36] M. Mingeback, C. Deibel, V. Dyakonov, Built-in potential and validity of the Mott-Schottky analysis in organic bulk heterojunction solar cells, *Phys. Rev. B* 84 (2011) 153201.
 - [37] T. Kirchartz, W. Gong, S.A. Hawks, T. Agostinelli, R.C.I. MacKenzie, Y. Yang, J. Nelson, Sensitivity of the Mott-Schottky analysis in organic solar cells, *J. Phys. Chem. C* 116 (2012) 7672–7680.
 - [38] A. Kanevce, M. Gloeckler, A.O. Pudov, J.R. Sites, Conduction-band-offset rule governing J-V distortion in CdS/Ci(G)S solar cells, *MRS Proc.* 865 (2005) F5.32.1–F5.32.6.
 - [39] H. Sim, J. Lee, S. Cho, S.J. Kwon, A study on the band structure of ZnO/CdS heterojunction for CIGS solar-cell application, *J. Semicond. Technol. Sci.* 15 (2015) 267–275.
 - [40] A.O. Pudov, A. Kanevce, H.A. Al-Thani, J.R. Sites, F.S. Hasoon, Secondary barriers in CdS-CuIn_{1-x}Ga_xSe₂ solar cells, *J. Appl. Phys.* 97 (2005) 064901.
 - [41] J.H. Shi, S.M. Huang, J.B. Chu, H.B. Zhu, Z.A. Wang, X.D. Li, D.W. Zhang, Z. Sun, W.J. Cheng, F.Q. Huang, X.J. Yin, Effect of ZnO buffer layer on AZO film properties and photovoltaic applications, *J. Mater. Sci.: Mater. Electron.* 21 (2010) 1005–1013.