Two-terminal Perovskite silicon tandem solar cells with a high-Bandgap Perovskite absorber enabling voltages over 1.8 V

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Abstract
Perovskite silicon tandem solar cells are a promising technology to overcome the efficiency limit of silicon solar cells. Although highest tandem efficiencies have been reported for the inverted p-i-n structure, high-efficiency single junction perovskite solar cells are mostly fabricated in the regular n-i-p architecture. In this work, regular n-i-p perovskite solar cells with a high-bandgap mixed cation mixed halide absorber suitable for tandem solar cells are investigated by compositional engineering and the open-circuit voltage is improved to over 1.12 V using a passivating electron contact. The optimized perovskite solar cell is used as a top cell in a monolithic perovskite silicon tandem device with a silicon heterojunction bottom cell allowing for voltages up to 0.725 V. The tandem solar cells with an active area of 0.25 cm² achieve record open-circuit voltages of up to 1.85 V and have efficiencies over 20%. Analyzing the perovskite absorber by spatially resolved photoluminescence measurements shows a homogenous and stable emission at ~ 1.7 eV which is an optimal value for tandem applications with silicon. The tandem solar cells are mainly limited due to a low current. A spectrometric characterization reveals that the perovskite solar cell is current limiting which could be improved by a thicker perovskite absorber.

KEYWORDS
high-bandgap perovskite absorber, perovskite silicon tandem solar cells, spectrometric characterization

1 | INTRODUCTION

Increasing efficiency of solar cells is a key issue to further decrease the levelized costs of electricity (LCOE) of photovoltaics (PV) as the main part of the LCOE are area related costs like module and installation costs.

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Here, silicon solar cells are by far the dominating PV technology. Especially silicon heterojunction solar cells that allow for high voltages over 0.7 V reach high efficiencies above 26%.1 However, the efficiency of single junction silicon solar cells is limited. The Shockley Queisser limit for a bandgap of 1.1 eV is ~ 30%,2 taking Auger recombination into account the maximum efficiency for silicon solar cells is 29.4%.3 With tandem...
solar cells, thermalization losses can be reduced. In consequence, for an optimal top cell bandgap of 1.72 eV, the Shockley Queisser limit for a silicon based tandem solar cell is increased to over 42%.\textsuperscript{6}

Perovskite solar cells are promising as a tandem partner for silicon. Since their emergence in PV in 2006\textsuperscript{5} efficiency has continuously improved and has reached more than 20%,\textsuperscript{6-14} with a record efficiency of 25.2%.\textsuperscript{15} They can be fabricated using solution-\textsuperscript{16,17} as well as vacuum-\textsuperscript{18,19} and hybrid\textsuperscript{20-22} deposition techniques. Low-temperature processes are available for all layers,\textsuperscript{23-25} making perovskite solar cells also interesting in combination with a silicon heterojunction bottom solar cell which would degrade at temperatures over 200°C. Annealing above 200°C results in the effusion of hydrogen, thereby depassivating interface defects at the amorphous/crystalline silicon interface and thus, increasing recombination losses of the silicon heterojunction bottom cell.\textsuperscript{26,27} With a strong absorption coefficient and a sharp absorption edge,\textsuperscript{28} also the optical properties of perovskites are highly suitable for tandem application. Additionally, the bandgap can be adjusted in a wide range by compositional engineering.\textsuperscript{29-31}

Since the report of the first monolithic perovskite silicon tandem device in 2015 with an efficiency of 13.6%\textsuperscript{32} tandem performance was substantially increased up to a certified efficiency of 28% reported by Oxford PV in the end of 2018.\textsuperscript{33} The highest efficiency with published solar cell structure is 26.0%.\textsuperscript{34} The decisive factors for reaching high efficiencies with perovskite silicon tandem solar cells are the overall device structure, the absorber material and the adaptation of the contact layers.

The highest efficiencies over 25%, so far, have been reached with an inverted p-i-n structure,\textsuperscript{34-38} but also more than 22% has been achieved with the regular n-i-p architecture.\textsuperscript{39,40} The actual top value for the open-circuit voltage ($V_{OC}$) of 1.83 V was first reported for a regular structure.\textsuperscript{41} In the meantime, 1.83 V have also been reported for the p-i-n structure.\textsuperscript{38} As highest efficiencies for single junction perovskite solar cells are reported for the n-i-p structure,\textsuperscript{7-10,14} tandem research on this device polarity remains a relevant research topic.

While the first publications on perovskite silicon tandem solar cells mostly used methylammonium lead triiodide (MAPbI$_3$) as perovskite absorber,\textsuperscript{32,42-45} recent studies propose perovskites with a higher bandgap approaching 1.7 eV as more suitable.\textsuperscript{37,41,46} However, for common high-bandgap compositions based on halide mixing, phase segregation under illumination and low $V_{OC}$ was reported.\textsuperscript{47-49} Better stability was reached with mixed cations using formamidinium (FA) and caesium (Cs).\textsuperscript{29,50,51} Bush et al. reached 17.5% efficiency in p-i-n perovskite cells using a 1.68 eV mixed cation mixed halide absorber containing FA and Cs (FA$_{0.75}$Cs$_{0.25}$Pb$_3$(I$_{0.8}$Br$_{0.2}$)$_3$) with improved photo-stability.\textsuperscript{52}

Furthermore, an enhanced $V_{OC}$ in n-i-p perovskite solar cells was reached by a passivation layer between the electron contact and the perovskite absorber. Peng et al. proposed a [6,6]-phenyl-C61-butyric acid methyl ester (PC61BM) and poly (methyl methacrylate) (PMMA) layer on a mesoporous TiO$_2$ electron transport layer (ETL) in solar cells with Cs$_{0.07}$Rb$_{0.20}$FA$_{0.765}$MA$_{0.135}$Pb$_{2.35}$Br$_{0.45}$ absorber and gained ∼80 mV compared to control devices without passivation.\textsuperscript{53}

In this work, we present monolithic perovskite silicon tandem solar cells combining the two technologies allowing for highest efficiencies in single junction solar cells: a silicon heterojunction solar cell and a perovskite solar cell with n-i-p architecture. We use a top solar cell absorber with a tandem-relevant optical bandgap around 1.7 eV. As high-bandgap mixed cation mixed halide perovskites usually face voltage losses due to halide segregation, we focus on voltage improvement as a first step towards high efficiencies in this paper. First, we present tandem-relevant high-bandgap absorbers with varying Cs to Br ratios and implementing a PCBM/PMMA passivation layer in single junction perovskite solar cells. Combining the optimized top solar cell with a silicon heterojunction bottom solar cell with passivating contacts leads to a new record $V_{OC}$ of 1.85 V and an efficiency over 20% on an active area of 0.25 cm$^2$. A detailed examination of our tandem device using spatially resolved photoluminescence confirms a homogeneous and remarkably photo-stable perovskite absorber. However, the current of the cells is still relatively low. We further analyze our tandem devices with spectrometric characterization revealing that the perovskite top solar cell limits the current and has a low parallel resistance and discuss issues of the front side contact limiting the overall current.

### 2 RESULTS AND DISCUSSION

#### 2.1 Device architecture

The realized tandem solar cells consist of a mesoscopic n-i-p perovskite solar cell on top of a rear-side textured heterojunction silicon solar cell (Figure 1a). The bottom solar cell features boron and phosphorous doped amorphous silicon (a-Si) as selective contacts and intrinsic a-Si as passivation layers. Due to this passivation the bottom cells show high open-circuit voltages of up to 0.725 V in Suns$V_{OC}$ measurements (Figure S1).\textsuperscript{34} In the tandem device, this value is slightly lowered to ∼0.69 V – 0.70 V as not the whole light intensity reaches the silicon bottom solar cells and a shadow mask is used to define active cell areas in current – voltage (IV) measurements (Figure S2). The bottom solar cell is connected to the top via an indium doped tin oxide (ITO) recombination layer. The ETL of the perovskite solar cell consists of compact and mesoporous TiO$_2$, both processed at low temperature in order not to degrade the bottom solar cell. The low-temperature process is described in our previous publications.\textsuperscript{24,55} PCBM/PMMA is used as a passivation layer. The perovskite absorber is FA$_{0.75}$Cs$_{0.25}$Pb$_3$(I$_{0.8}$Br$_{0.2}$)$_3$. As hole transport layer (HTL) doped 2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spiribifluorene (Spiro-OmMeTAD) was used. An ITO front side contact was directly sputtered on the Spiro-OmMeTAD without any buffer layer. A magnesium fluoride (MgF$_2$) layer was applied to reduce front side reflection. Both ITO layers (interconnection and front side contact) are sputtered through a mask with four openings of 6 mm x 6 mm defining 4 individual solar cells per substrate (photograph in Figure 1b). For current – voltage measurements a shadow mask with an opening of 5 mm x 5 mm is used. The scanning electron microscope (SEM) cross section of a tandem solar cell (Figure 1c) illustrates the difference in size of the two sub-cells (200 μm thick silicon wafer and ∼1 μm thick perovskite solar cell). Zooming to the perovskite shows a pinhole free absorber with large crystal grains.
2.2 | Perovskite absorber composition and electron contact passivation

The top cell absorber is a FA$_{1-x}$Cs$_x$Pb(I$_{1-y}$Br$_y$)$_3$ mixed cation mixed halide perovskite. Before fabricating tandem solar cells, x and y values were systematically varied and tested in single junction perovskite solar cells with n-i-p architecture. Three suited perovskite compositions (17% Cs and 27% Br, 25% Cs and 20% Br, 31% Cs and 17.5% Br) are presented here. The bandgap reduction effect of lower Br amount was successfully counterbalanced by increasing Cs with a bandgap widening effect. All compositions therefore show an optical bandgap around 1.7 eV determined from Tauc plots (Figure S3). Additionally we tested a PCBM/PMMA passivation layer on the ETL for all three compositions. Further film characterization is given in the SI (Figure S4).

The composition with 25% Cs and 20% Br shows a ~ 1.5 mA cm$^{-2}$ higher short-circuit current density ($J_{SC}$) than the other compositions. With PCBM/PMMA, a clear passivation effect can be seen for all absorbers resulting in a significantly higher voltage for the solar cells (Figure 2). High $V_{OC}$ values of up to 1.126 V are reached for 17% Cs and 27% Br as well as 25% Cs and 20% Br compositions. The latter also shows the highest fill factor (FF). Thus, solar cells with the composition of 25% Cs and 20% Br combined with a PCBM/PMMA passivation layer reach highest efficiencies and were therefore applied in tandem devices.

In parallel with the tandem solar cells, semi-transparent perovskite single junction solar cells were fabricated reaching even higher voltages of >1.15 V. Exemplary IV curves of these cells are shown in Figure S5.

Even 1.15 V is a decent $V_{OC}$ value for a perovskite with an optical bandgap ~ 1.7 eV compared to literature, and 50 mV higher than published by Bush et al. for a p-i-n device structure, there is still room for improvement towards its theoretical detailed balance limit of 1.40 V. For further improvement of the $V_{OC}$, an additional passivation layer on the hole contact side between the perovskite absorber and Spiro-OMeTAD could be used. Several groups already reported on improvement by passivating the hole contact using ultra-thin PMMA, dopant free Spiro-OMeTAD mixed with poly(3,4-ethylenedioxythiophene) (PEDOT), or a 2D perovskite layer.

2.3 | Tandem solar cell results

The overall best performing tandem device achieves a stabilized efficiency of 21.6% obtained from fixed voltage measurement applying the maximum power point voltage for 30 min and has open-circuit voltages between 1.83 V and 1.84 V in the IV characteristics (Figure 3). The highest $V_{OC}$ values are 1.841 V and 1.850 V obtained from reverse and forward scan direction, respectively (Figure S6). To the best of our knowledge these are the highest $V_{OC}$ values reported for perovskite silicon tandem solar cells so far. The overall performance of this device is a little lower compared to the champion device due to a lower FF and slightly more pronounced hysteresis. The stabilized value, measured over 6 min in this case, is 21.1% (Figure S6). Photovoltaic parameters of all tandem solar cells fabricated in this batch are shown in Figure S7.

The values shown so far were obtained from laboratory measurements using a non-spectrally adjusted LED sun simulator. After six weeks storage in a nitrogen filled glovebox, the best performing tandem solar cell presented in Figure 3a was measured in the accredited solar cell calibration laboratory at Fraunhofer ISE, CalLab PV Cells. The stabilized efficiency has been determined to (19.91 ± 0.65)% (Figure 4a). The corresponding calibration report can be found in the SI. This value is clearly lower than in the results presented above. The difference is originating from a by ~ 0.6 mA cm$^{-2}$ lower $J_{SC}$ and a by ~ 3% reduced FF. As the CalLab PV Cells measurements were carried out over one month later than the measurements shown before, one
can assume that the solar cell slightly degraded over that time. We noticed the same trend (lower FF and lower $J_{SC}$) also for perovskite single junction solar cells after a few weeks (Figure S5). To ensure that no significant mistake was made in the laboratory measurements shown in Figure 3 we measured the tandem cell again at the laboratory setup after the CalLab PV Cells measurements and retrieved similar values than the CalLab values shown in Figure 4 (Table S1). This shows that our internal laboratory measurements are well aligned with the calibration standard and thus that the initially measured efficiency of 21.6% is reliable.

From the IV curves one can see that the tandem solar cell has a comparatively low parallel resistance $R_p$. For further investigation a spectrometric characterization was carried out (Figure 4c). A detailed description of this method which is known from the characterization of III-V multijunction cells can be found in literature.\textsuperscript{60,61} Basically the spectrum used for IV scans is varied from a red rich to a blue rich spectrum, while the overall effective irradiance is constant, which means that the photo-currents of the individual sub-cells change, but their sum remains constant. For the red-shifted spectrum the top cell is expected to limit the current of the tandem device, and for the blue-shifted spectrum the bottom cell. At each measurement point a value can be defined for both sub-cells by the corresponding ratio of the photo current density under the actual spectrum $J_{photo, subcell}$, actual to the photo current density under the reference spectrum $(AM1.5g$ spectrum) $J_{photo, subcell}$. During the spectrometric characterization the simulator spectrum is varied in a way that the sum of the two subcell ratios $J_{photo, subcell, actual}/J_{photo, subcell, AM1.5g}$ always equals 2.

A clear current mismatch with the top cell limiting the device can be seen from this evaluation as the maximum $J_{SC}$ is reached for a spectrum with an increased blue part $J_{photo, bottom, actual}/J_{photo, bottom, AM1.5g} = 0.9$ and $J_{photo, top, actual}/J_{photo, top, AM1.5g} = 1.1$. The $V_{OC}$ is only slightly affected by the spectral variation. The FF shows an asymmetric behavior with a strong increase with increasing blue part of the spectrum and only a slight increase for red rich spectra. While normally a rather symmetric behavior would be expected, an asymmetry occurs when the current limiting sub-cell has a comparatively low $R_p$.\textsuperscript{61} Thus, from the spectrometric characterization it can be concluded that the perovskite solar cell has the lower $R_p$. The photo current of the perovskite solar cell $J_{photo, top}$ is therefore slightly lower than the $J_{SC}$ of the tandem solar cell. This difference is schematically illustrated in Figure S8. More details are available in the publication by Meusel et al.\textsuperscript{61} A rough estimation assuming a $V_{OC}$ of 1.13 V for the perovskite solar cell leads to a 1.2% lower $J_{photo, top}$ of 14.4 mA cm$^{-2}$ at standard testing conditions (STC). From the spectrometric characterization it can be seen that the spectrum must be shifted to the blue by almost 10% for current matching. Adding 10% to $J_{photo, top}$ would result in 15.8 mA cm$^{-2}$. From the external quantum efficiency ($EQE$) shown in Figure 4b the silicon current is 17.7 mA cm$^{-2}$, reducing it by 10% would result in a value of 15.9 mA cm$^{-2}$. So far the results are consistent. For the perovskite solar cell, the integration over the as measured EQE multiplied by the AM1.5g spectrum only results in 12.0 mA cm$^{-2}$ compared to a photo current of 14.4 mA cm$^{-2}$. As all the other values are matching, we assume that the EQE of the perovskite cell is underestimated. A possible reason might be a low time constant for dynamic processes in the perovskite cell so that it cannot follow the chopper frequency used for the EQE measurement or a dependency of the EQE from bias illumination. Additionally, reversible degradation might occur when keeping the perovskite solar cell under short-circuit conditions. The dashed line in Figure 4b shows the EQE scaled to the more reasonable value of 14.4 mA cm$^{-2}$. The measurement report for the spectral response of CalLab PV Cells can be found in the SI.

Looking at the power output at maximum power point $P_{MP}$ in the spectrometric characterization, one can see that the highest power is generated for current matching conditions. Thus, to improve the tandem solar cell it would be necessary to enhance the current in the
perovskite top cell. This could be achieved by increasing the absorber thickness. The EQE shows that for wavelengths between 550 nm and 700 nm the silicon solar cell absorbs a significant part of the light (~ 1.4 mA cm\(^{-2}\)) above the perovskite bandgap. With a thicker perovskite, this could be partly absorbed in the top cell, lowering the bottom cell current and resulting in a better current matched tandem device. Yin et al. calculated that a thicker absorber layer leads to better perovskite solar cell performance.\(^62\) In a recent study on optical simulation, Tucher et al. showed that in a similar n-i-p architecture than presented in this work, a perovskite absorber thickness of over 1.2 \(\mu\)m would be beneficial for a bandgap of 1.7 eV in perovskite silicon tandem devices.\(^63\) Another option would be lowering the perovskite bandgap. This also would increase the top cell current. On the other hand, it might lower the voltage. However, this is not necessarily the case as 1.5 eV - 1.6 eV perovskite absorbers generally show less \(V_{OC}\) loss relatively to their theoretical Shockley-Queisser limit \(V_{OC}\).\(^49\) Very recently, a \(V_{OC}\) of 1.18 V was achieved for a n-i-p perovskite solar cells with a 1.53 eV perovskite absorber by Jiang et al.\(^64\)

Compared to other tandem devices with n-i-p structure, our device performs similarly to the tandem cell presented by Hou et al. who also achieved a \(V_{OC}\) over 1.8 V using a 1.67 eV perovskite absorber.\(^41\) The current of their device (almost 16 mA cm\(^{-2}\)) is significantly higher, but the FF (~70%) is lower. Other n-i-p tandem cells reached between 22% and 23% efficiency with a lower \(V_{OC}\) ~ 1.75 V but a significantly
higher $J_{SC}$ up to 17.6 mA cm$^{-2}$.$^{35-38}$ With a $p$-$i$-$n$ structure tandem efficiencies over 25% were achieved.$^{35-38}$ It is noticeable that in all these cases the $V_{OC}$ is indeed lower (between 1.75 V and 1.80 V) than in our case, but the $J_{SC}$ is again clearly higher with values between 17.8 mA cm$^{-2}$ and 19.5 mA cm$^{-2}$.$^{35-38}$ although Bush et al. also used a high-bandgap absorber (1.68 eV).$^{37}$ Thus, in comparison, the overall current of our tandem devices is rather low, even if current matching could be reached. Here, the front side contact with Spiro-OMeTAD and ITO is the main reason: incoming light first faces the ITO with a refractive index $n$ of $\sim 2$ determined by spectral ellipsometry, afterwards the Spiro-OMeTAD ($n \sim 1.6$)$^{65}$ before entering the perovskite absorber with $n \sim 2.4$.$^{56}$ The reflectance can significantly be lowered in a wide spectral range with the MgF$_2$ antireflection coating used in our samples (Figure 5). The integrated reflected current density decreases from 8.1 mA cm$^{-2}$ to 5.0 mA cm$^{-2}$. However, the unfavorable order of refractive indices still leads to strong front side reflection. To further lower front side reflection, a textured foil could be used as in the case of other publications about perovskite silicon tandem solar cells.$^{40,42,43,67,68}$ Another option would be the use of silicon bottom solar cells with a textured front side.$^{69}$ However, the top cell cannot be deposited by solution processes anymore, but vacuum techniques like evaporation or hybrid processes would be required for all layers.

Additionally, parasitic absorption, especially in the Spiro-OMeTAD featuring the highest extinction coefficient of the whole layer stack,$^{65}$ lowers the current of the tandem device. Thus, for significant decrease of optical losses, the hole transport material has to be exchanged. Also current matching could be improved by replacing Spiro-OMeTAD as most of its parasitic absorption occurs in the short-wavelength range.$^{69}$ A promising candidate might be copper thiocyanate (CuSCN) which was used in dye-sensitized solar cells before.$^{70}$ Perovskite single junction solar cells in the regular $n$-$i$-$p$ structure with CuSCN as HTL were reported to achieve 20% efficiency.$^{71}$ Pattanasattayavong et al. published a refractive index of $~1.9$ and an extinction coefficient $< 10^{-4}$ for this material,$^{72}$ which is more promising than Spiro-OMeTAD considering both values. The implementation of CuSCN in our perovskite solar cells is currently under investigation.

### 2.4 Photoluminescence measurements

To further characterize the tandem solar cells, subcell-selective and spatially resolved photoluminescence (PL) measurements were carried out on all four solar cells (cells 1–4) of one substrate. The approach has been reported before$^{73}$: Using different excitation wavelengths, charge carriers are generated selectively in either the top or the bottom cell. The spectrally resolved detection of the PL signal additionally ensures the unambiguous separation of the two cells. The peak photon energy of the emitted light from the perovskite solar cells is directly correlated to the optical bandgap of the perovskite absorber.$^{74-78}$ The perovskite shows a laterally homogenous peak position of 1.69 eV across the substrate on all four cells (Figure 6a, first row). This is a noteworthy result as the bandgap of solution-processed perovskite solar cells is often non-uniform.$^{79-81}$ The spatially averaged PL spectra for the perovskite show again the PL peak position of 1.69 eV for all four cells (Figure 6b). Tracking the PL emission spectrum over time reveals photo-stable behavior of the perovskite. During 80 s constant illumination (532 nm, 0.5 $\mu$W $\mu$m$^{-2}$) the peak position does not change significantly, indicating that no photo-induced halide segregation is occurring (Figure 6c). Photo-instable high-bandgap perovskites would change their PL peak position exponentially towards lower energies within a few seconds under constant illumination,$^{77}$ accompanied by a $V_{OC}$ loss,$^{52}$ which is not the case for our samples (Figure 3).

Concerning the PL intensity corresponding to the perovskite, a distinct difference can be observed between the four cells. One cell (cell 1) shows a higher intensity than the others (Figure 6a, second row; Figure 6b) whereas the PL intensity corresponding to the silicon solar cell shows the reverse trend (Figure 6a, third row). The difference correlates with the IV parameters as follows: the FF is reduced for cell 1 mainly due to a higher series resistance compared to the other three cells, resulting in a $\eta_{abs}$ lower efficiency (see Figure S7). An anti-correlation between PL intensity and performance of perovskite solar cells has been reported before.$^{24,82}$ In case of contacts with sufficient carrier selectivity, generated charge carriers might be extracted from the perovskite absorber lowering the PL signal. However, we do not see a difference in the current, only in FF, while in previous publications the PL signal was compared to the current obtained by light beam induced current measurements.$^{24,82}$

Regarding the layer homogeneity, the PL intensity maps for both the perovskite and the silicon cells reveal local features. The points with a low PL intensity in both materials correspond to the areas with a high reflectance. The spatially resolved reflectance of the laser used for exciting the silicon shows a clear pattern originating from a spin coating process (Figure 6a, fourth row). Thus, non-uniform reflectance and transmittance in a spin coated layer such as Spiro-OMeTAD might be responsible for the local features in the PL intensity maps.
3 | CONCLUSION

Suitable perovskite compositions $\text{FA}_{1-x}\text{Cs}_x\text{Pb(I}_{1-y}\text{Br}_y)_3$ with optimum bandgap for tandem application around 1.7 eV were tested in single junction solar cells. Here, small changes in the composition, i.e. of the $x$ and $y$ values influence the performance with highest efficiencies found for 25% Cs and 20% Br. Moreover, we fabricated two-terminal perovskite silicon tandem solar cells with high open-circuit voltages up to 1.85 V which is, to the best of our knowledge, the highest reported value for monolithic perovskite silicon tandem solar cells. To reach these high values, we combined silicon heterojunction bottom solar cells with an implied $V_{OC}$ of up to 0.725 V and mesoscopic n-i-p perovskite top cells with open-circuit voltages up to 1.126 V including a PCBM/PMMA passivation layer. PL measurements showed that the mixed cation mixed halide perovskite absorber has a photo-stable and spatially homogenous optical bandgap close to 1.7 eV.

Our tandem solar cells reached efficiencies exceeding 21%. They are mostly limited by a low overall short-circuit current and current limitation by the perovskite solar cell as revealed in spectrometric characterization. While the current mismatch could be mitigated by adapting the absorber thickness or the bandgap, the overall $J_{SC}$ could be increased with optimized front side optics. Especially, the Spiro-OMeTAD needs to be replaced by a material with less parasitic absorption and a more suitable refractive index. Alternative hole transport materials are currently under investigation. Front-side textured silicon solar cells could increase the current even further. Finally, in such an adapted configuration, also n-i-p perovskite tandem solar cells might be able to exceed 25% efficiency, currently being reached by p-i-n devices.

4 | EXPERIMENTAL SECTION

4.1 | Device fabrication

4.1.1 | Silicon bottom cell fabrication

Silicon solar cells were fabricated from 200 μm thick silicon wafers (Siltronic, n-type, float zone, base resistivity 1 Ω cm). A pyramidal texture was etched using potassium hydroxide (KOH) on one side of the wafer. After RCA cleaning the silicon surface an intrinsic amorphous silicon passivation layer was deposited on both sides using plasma
enhanced chemical vapor deposition (PECVD) in an Oxford Instruments cluster tool. The thickness was ~8.5 nm on the planar and the textured side. (The thickness is defined via the deposition time which was longer for the textured side to account for the increased surface area compared to the planar side.) Afterwards a 21 nm n-doped amorphous silicon layer was deposited on the textured side followed by a p and p++ layer of 8 nm and 9 nm, respectively, on the planar side. The amorphous silicon deposition was performed in a parallel-plate PECVD reactor powered at 13.56 MHz, at 200°C, 500 mTorr using mixtures of silane (SiH₄), hydrogen (H₂), phosphine (PH₃) and diborane (B₂H₆). Subsequently, ITO (In₂O₃/SnO₂ = 90/10 wt%, target size 507 cm²) was DC sputtered in the same Oxford Instruments cluster tool on both sides using mixtures of argon and oxygen. Substrate holder temperature was 100°C, chamber pressure was 0.3 Pa and sputter power was 200 W. On the textured side 195 nm of ITO was deposited on the full area, on the planar side 80 nm of ITO was sputtered through a shadow mask with 6 mm x 6 mm openings defining the individual cells of the tandem device. Before each PECVD step and before sputtering ITO, the wafers were dipped in a hydrogen fluoride (HF) solution in order to remove silicon oxide (SiO₂). After ITO sputtering a 1000 nm thick silver layer was deposited on the textured side of the wafer as a rear contact. Finally, the wafers were cut by a laser in 2.5 cm x 2.5 cm large substrates each containing four ITO pads.

4.1.2 | Perovskite top cell fabrication

Perovskite top solar cells were fabricated in the regular n-i-p architecture using a low-temperature process. For the ETL, first a 20 nm thick compact TiO₂ layer was deposited by electron beam evaporation with a rate of 1 nm s⁻¹ in a Pfeiffer PLS 570 tool with a voltage electron gun (Telemark model 267). In the next step, a mesoporous TiO₂ scaffold was deposited by spin coating 150 µL of a commercial paste from Greatcell Solar (18NR-T) mixed with ethanol (99.5%, Carl Roth) and terpineol (65% α, 10% β, 20% γ, Sigma-Aldrich) in a mass ratio of 1:2:4 at 2500 rpm for 10 s and at 7000 rpm for 40 s and dried at 120°C for 10 min. This procedure was repeated a second time. The samples were then kept under UV irradiation for 200 min in a UV/Ozone Cleaner Plus from Bioforce Nanosciences. The thickness of the compact layer and the UV curing time have been optimized in previous work.²⁴,⁵⁵ Afterwards, the substrates were transferred into a nitrogen filled glovebox. According to Peng et al. 70 µL of a solution containing a mixture of 1 mg PCBM (99%, Solenne) and 3 mg PMMA (Fluka) diluted in 1 mL chlorobenzene (Carl Roth) was spin coated at 5000 rpm for 30 s.⁵³ Subsequently, the samples were annealed at 100°C for 10 min. We used a mixed cation mixed halide perovskite absorber proposed by Bush et al.²² The FAD0.75Cs0.25PbI₂Br₂ precursor solution (1 M) contained 0.361 g formamidinium iodide (FAI, Greatcell Solar), 0.182 g caesium iodide (CsI, 99.999%, Sigma-Aldrich), 0.308 g lead bromide (PbBr₂, 99.999%, Sigma-Aldrich) and 0.904 g lead iodide (PbI₂, 99.99%, TCI) dissolved in 0.56 mL dimethyl sulfoxide (DMSO, ≥ 99.9%, Sigma-Aldrich) and 2.24 mL dimethyl formamide (DMF, 99.8%, Sigma-Aldrich) (1:4). The solution was stirred at 60°C overnight and spin coated (150 µL per substrate) first at 1000 rpm for 10 s, then at 5000 rpm for 20 s. 5 s prior to the end of the process, 200 µL of toluene (≥ 99.5%, Carl Roth) was dropped on the sample as antisolvent. Finally, the perovskite was annealed at 100°C for 1 h. Spiro-OMeTAD was used as HTL. The precursor solution was prepared 3 h before using it and contained 56 mg Spiro-OMeTAD (Solarpur) in 650 µL chlorobenzene (Carl Roth). 14 µL of a solution containing 50 mg bis(trifluoromethane)sulphonamide lithium salt (Sigma-Aldrich) in 80 µL acetonitrile (Merck) and 20 µL 4-tert-butylpyridine (96%, Sigma-Aldrich) were added. On each substrate, 70 µL were spin coated at 3000 rpm during 30 s. Before starting the rotation, the solution was kept on the substrate for 30 s. Afterwards, the samples were kept in the nitrogen filled glovebox overnight. The ITO front contact (105 nm thick) was DC sputtered in the Oxford Instruments cluster tool (In₂O₃/SnO₂ = 90/10 wt%, target size 507 cm²), directly on top of the Spiro-OMeTAD without using any buffer layer. Chamber pressure was 0.3 Pa. Contrary to ITO deposited on the silicon bottom solar cells, temperature was 50°C and the first ~30 nm were deposited with a low sputter power (40 W) before increasing to the normal power (200 W). Only argon but no oxygen gas was used. Again, a shadow mask with 6 mm x 6 mm large openings was used aligning the front contact to the recombination layer between the two sub-cells. Subsequently, 150 nm thick gold electrodes were thermally evaporated. Finally, 90 nm of MgF₂ were thermally evaporated as antireflection coating.

4.1.3 | Perovskite single junction solar cell fabrication

Perovskite single junction solar cells shown in Figure 2 were fabricated on commercial ITO coated glasses (AMG, 7 Ω sq⁻¹, 25 × 25 mm²). The substrates were cleaned in acetone (2x), isopropanol (2x) and deionized water 5 min each and exposed to UV irradiation for 15 min. Afterwards, 30 nm of compact TiO₂ was evaporated, followed by mesoporous TiO₂ and PCBM/PMMA as described for the tandem solar cells. For the perovskite three different compositions were tested. The amount of precursor materials diluted in 0.36 mL DMSO and 1.44 mL DMF (1:4) are listed in Table 1 for each composition.

After Spiro-OMeTAD spin coating, the solar cells were finished by evaporation of 80 nm thick gold contacts.

4.2 | Characterization

4.2.1 | IV measurement

Current–voltage characteristics of perovskite silicon tandem solar cells were measured using a LED sun simulator (Wavelabs, Sirius-220); the perovskite single junction solar cells presented in Figure 2 were measured with a sun simulator equipped with a xenon short arc lamp and a Keithley 2651A source meter. In both cases light intensity was calibrated to 1 sun under the AM 1.5 g spectrum using a silicon reference cell. All solar cells were first measured in forward scan direction (from ~0.1 V to 1.9 V for tandem solar cells and ~0.1 V to 1.2 V for perovskite single junction solar cells), followed by the reverse scan direction (from 1.9 V to ~0.1 V for tandem solar cells and 1.2 V to ~0.1 V for
perovskite single junction solar cells). The scan speed was 25 mV s⁻¹, the voltage step 10 mV. For stabilized measurements, a fixed voltage (mean value of the maximum power point voltages obtained from forward and reverse scan direction) was set and the current was tracked over time. A shadow mask was used to define an active area of 0.25 cm². All measurements were carried out in ambient air. It has to be noted that all measurements (IV scans and stabilized measurements) have been repeated several times for each solar cell and the data of the measurement resulting in the highest efficiencies are shown in the graphs.

4.2.2 CalLab PV cells measurements

A shadow mask was used during all measurements to define an active area of (0.249 ± 0.013) cm². The spectral response of the perovskite silicon tandem solar cell was measured with a laser-based measurement setup.²³ Two different selective bias-illuminations and required bias-voltages were used, to resolve both sub-cells.²⁴ The bias-settings were adjusted to minimize measurement artefacts.²⁵-²⁷

The current–voltage characteristics of perovskite silicon tandem solar cells were measured using a dual source sun simulator (Wacom, WXS-220SL2). The light intensity was calibrated using filtered reference cells matched to each sub-cell. The spectral response of the sub-cells was used for retrieving the spectral settings of the sun simulator, which is calculated by a generalized mismatch correction [IEC 60904-7; Ed.3 2008] as described by Meusel et al.²⁶ Please note, that for the spectral correction procedure only relative EQE spectra are required.

For an efficiency certification we measured the IV curve in both directions \((V_{OC} \rightarrow I_{SC} \text{ and } I_{SC} \rightarrow V_{OC})\) within approximately one minute per IV curve. Then the cell was set to the determined \(P_{mp}\) and the maximum was followed by variation of the voltage. The current and voltage was logged for 5 min (steady state measurement). At the end we repeated the IV scan in both directions. The IV-measurement and the 5 min \(P_{mp}\)-Log are stated in the certificate.

For the spectrometric characterization the mean value of the IV-scans in both directions was chosen, as the focus was on analyzing the characteristic behavior regarding spectral variations. The metastable behavior changed slightly with the spectral variation, but is of minor importance on the outcome showed here.

A detailed description of the measurement uncertainties can be found in literature.²⁸⁻²⁹

4.2.3 Photoluminescence spectroscopy mapping

Photoluminescence measurements were conducted using a confocal microscope with a moveable XY stage, collecting the entire PL emission spectrum for every point by scanning the sample. The perovskite layer was probed with a frequency-doubled Nd:YAG solid state laser (532 nm, 0.5 µW µm⁻²) focused onto the sample via a lens with NA = 0.26. The emitted PL is collected by the same lens and collimated onto a 1000 µm pinhole, spurious laser light is deflected by a beam-splitter and an additional long pass filter (650 nm). A 600 g mm⁻¹ grating spectrometer is employed and the spectrally resolved signal detected via a silicon line charge coupled device (CCD). The silicon layer is probed using a 905 nm diode laser (0.1 µW µm⁻²), employing the same lens and pinhole size as for the perovskite measurement. Detection is realized via a mirror based grating spectrometer (160 g mm⁻¹) and a InGaAs line CCD. PL measurements were carried out under open circuit conditions. More details about the setup and the multi-wavelength approach can be found in previous publications.³⁷³⁹

4.2.4 Further characterization methods

\(V_{OC}\) values for the silicon bottom solar cells were determined using a Suns\(V_{OC}\) measurement tool from Sinton Instruments.³⁴ The Suns\(V_{OC}\) method allows characterization of solar cell precursors. The solar cell is illuminated by a light flash and the voltage of the cell is recorded during the decay of the light intensity. As only the voltage is measured no front side metallization is needed. From the current of a reference cell measured simultaneously the light intensity – voltage curve can be transferred to a pseudo current – voltage curve without series resistance effects.

Reflectance measurements were carried out using a Lambda 950 spectrophotometer from PerkinElmer equipped with an integrating sphere to be able to detect also diffusely reflected light. Samples were measured in a wavelength range of 250 nm – 1200 nm with a step size of 2 nm.

SEM pictures were taken using a Schottky emission scanning electron microscope (Zeiss, Auriga 60) at 3 kV. In advance samples were broken and a thin platinum layer was sputtered on the cross section to have a good conductivity.

Grazing incidence X-ray diffraction was performed with a X'Pert MRD system (PANalytical) equipped with a copper anode X-ray source (\(Kα_1 = 1.5406\) Å). Scans were recorded within the 2θ range of 5° to 65° with a step size of 0.05° and an integration time of 1 s.

Refractive index \(n\) of ITO was determined by spectral ellipsometry using a J. A. Woollam M-2000 ellipsometer. An oscillator model containing a Gaussian and a Lorentz oscillator was fitted to the measured data using the CompleteEASE software.

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