PerTPV – Perovskite thin film photovoltaics

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Deliverable 3.5

1 cm^2 Efficient 4T tandem solar cell, having V_{oc}, FF, J_{sc} above 2.25 V, 0.83 and 13.4 mA/cm^2, respectively leading to efficiency > 25%

WP3

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1. Introduction

All-perovskite 4-terminal (4T) and 2-terminals (2T) tandems with efficiency of 25% on 0.059 cm^2 and 24.8% on 0.049 cm^2 (22% on 1.05 cm^2), respectively, were recently demonstrated in the literature.[1,2] Considerable improvements have been done on the mixed Pb-Sn based perovskite cell to tackle the fabrication challenges related to the Sn^{2+} oxidation to Sn^{4+}. However, most of the efficient (>17%) low-bandgap perovskite solar cells reported in the literature contain large amount of methylammonium (MA), despite the well-known stability issues. Only a very recent publication by the NREL group reported 17.5% efficiency on 1 cm^2 for a MA-free Pb-Sn perovskite on 1 cm^2 area.[3]

For our PERTPV tandems we focus on robust low bandgap perovskites containing no MA. UOXF works on solution-processed $Cs_{0.17}FA_{0.83}Pb_{0.50}Sn_{0.50}I_3$ stoichiometry, CSEM has recently started to work on solution-processed $Cs_{0.25}FA_{0.75}Pb_{0.50}Sn_{0.50}I_3$ and UVEG has proved that the evaporation of a MA-free low bandgap perovskite is possible.[4] However, the thermal evaporation method suffers of low reproducibility related to the evaporation of the FAI component and in addition unknown challenges with vapour deposited Sn containing perovskites. Hence, for the remainder of the project, the Pb:Sn perovskites are being developed via solution coating. Solution processing of the Pb:Sn perovskites is also not without its challenges, and some reproducibility issues for the tin-containing perovskite have also been encountered by UOXF, and are somewhat retarding rapid advancement of the overall efficiency of the tandem cells.

4T tandems are made by mechanically stacking two complete cells and measuring independently the wide bandgap cell and the low bandgap cell with the light filtered through the wide bandgap cell. The main advantages of the 4T tandems is that the current produced in the two cells does not have to be matched and the two cells are fabricated independently. The main disadvantage of the 4T is that two measurements are needed and optical losses through the three transparent conductive electrodes can be important, especially in the case no optical coupling medium is used. An ordinary optical coupler is polydimethylsiloxane (PDMS).

While it is interesting to assess 4T tandems performance, without the current-matching and fabrication constraints of a monolithic device, the goal of PERTPV is the fabrication of efficient and stable 2T cells and mini-modules. We are following two approaches for the 2T tandems. On one side we are pursuing a full solution process approach and focusing on achieving a dense and pinhole-free recombination layer that can also serve as a barrier to solvents used to process the second perovskite cell. On the other side, we are developing a process in which the solution-processed low-bandgap perovskite is deposited first and the wide-bandgap perovskite is evaporated on top. Indeed, there are less constraints in the evaporation of a pure lead perovskite compared to a mixed Pb-Sn perovskite. This deliverable presents the experiments done on 4T tandems, while most of the project partners' efforts are dedicated to the fabrication of 2T tandem, which is likely to make up the majority of the final deliverable for the tandem solar cell devices.

2. 4T Tandem demonstrators

2.1 UOXF-CSEM Tandems

The low bandgap (1.24 eV) solar cell developed at UOXF consists of ITO/PEDOT:PSS/ $Cs_{0.17}FA_{0.83}Pb_{0.50}Sn_{0.50}I_3$ /PCBM/BCP/Ag.

For the 4T tandem a semi-transparent wide bandgap solar cell was stacked on top of the masked low bandgap. As there is no current matching limitation in the 4T tandem, CSEM developed semi-transparent cells with three different bandgaps. The semi-transparent cells architecture for all is ITO/NiO/poly-TPD/perovskite/LiF/C60/SnO_2/ITO and the perovskites compositions are $Cs_{0.15}FA_{0.8}MA_{0.05}Pb(I_{0.95}Br_{0.05})_3$ (1.55 eV bandgap), $Cs_{0.17}FA_{0.83}Pb(I_{0.83}Br_{0.17})_3$ (1.62 eV bandgap) and $DMA_{0.15}Cs_{0.35}FA_{0.50}Pb(I_{0.80}Br_{0.20})_3$ (1.72 eV bandgap).

The tandem results for these three stacks are shown in Figure 1-3. As the aperture area for the bottom cell was defined by inserting a mask in between the two cells (0.2 cm^2), there was an air gap in the stack, which lowered the current produced in the bottom cell. To have a good optical coupling between the two cells, a layer of PDMS as thick as the mask should be inserted in the aperture area of the mask.

The most efficient tandem (17.5%) was obtained by using a 1.55 eV top cell, which was also the most efficient wide bandgap cell. In fact, by increasing the bandgap of the top cell from 1.55 to 1.72 eV, the current in the bottom cell only increased from 5.1 mA to 6.5 mA and the efficiency from 2.03% to 2.25%, while in the top cell the efficiency decreased from 15.52% for the 1.55 eV to 13.04% for the 1.72 eV. When these experiments were carried out, the efficiency of the low bandgap Pb:Sn system was lower than usual and about 13%, as opposed to the record of 18% having ben achieved. Also, the cells presented have quite high hysteresis in the current-voltage characteristics, probably due to the very high scan rate used at that time at UOXF (5 V/s, now reduced to 0.3 V/s).

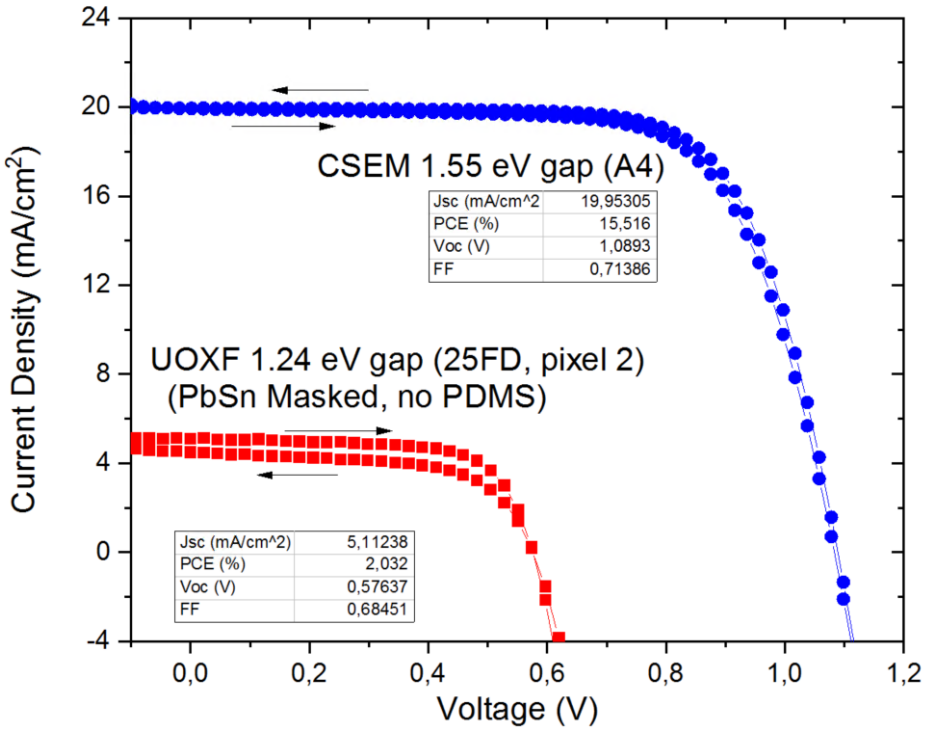

Figure 1. Current-voltage characteristics of a 4T tandem stack consisting of a 1.24 eV perovskite bottom cell masked with a 0.2 cm^2 mask and a 1.55 eV top cell.

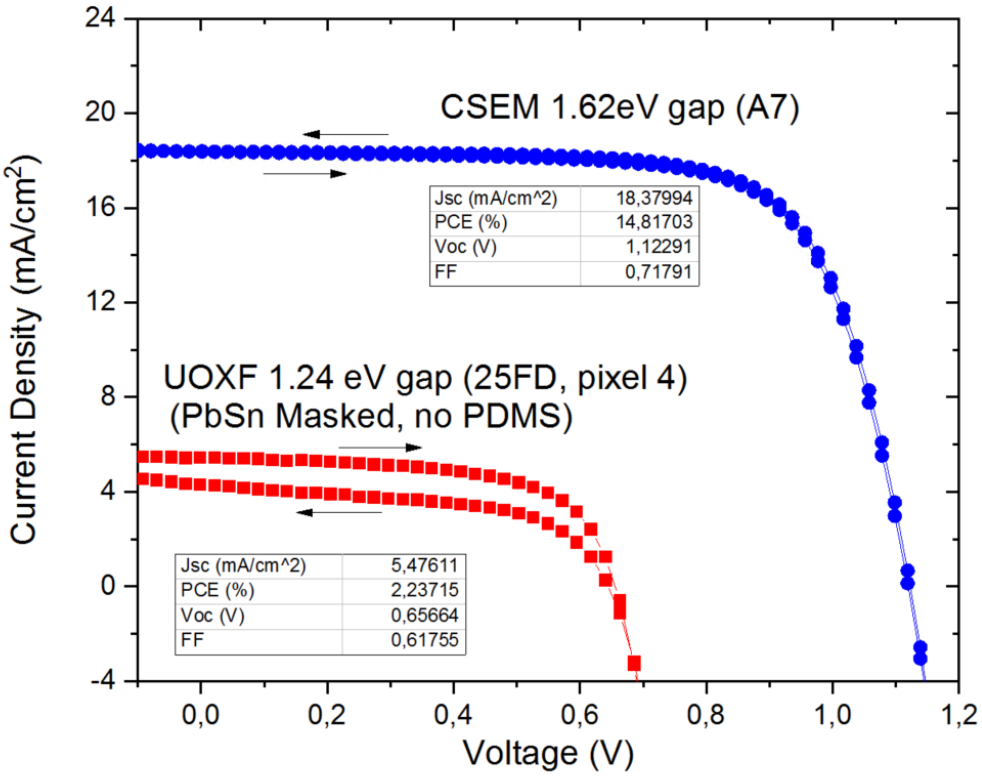

Figure 2. Current-voltage characteristics of a 4T tandem stack consisting of a 1.24 eV perovskite bottom cell masked with a 0.2 cm^2 mask and a 1.62 eV top cell.

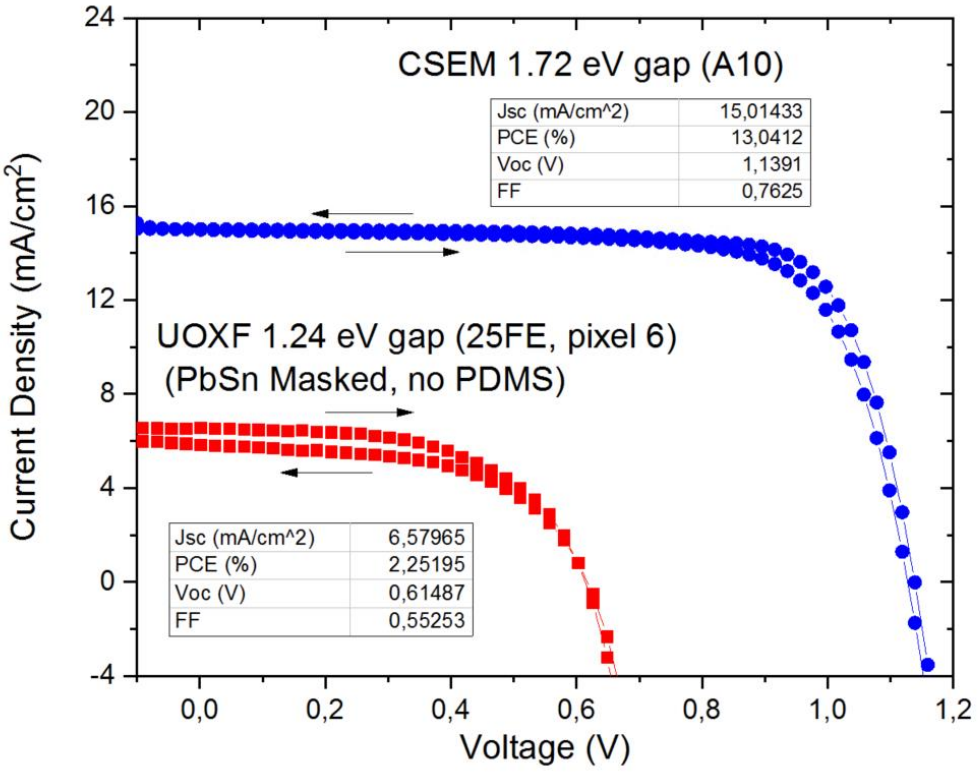

Figure 3. Current-voltage characteristics of a 4T tandem stack consisting of a 1.24 eV perovskite bottom cell masked with a 0.2 cm^2 mask and a 1.72 eV top cell.

From these results we see that improvements are needed on both subcells in order to bring the 2T tandems Voc above 2V and the FF beyond 80%. At present the major limitations come from the Pb-Sn based perovskite, particularly in terms of Voc and FF. In the Pb-based perovskite we observe that while good FF is achieved with the 1.72 eV, the higher the bandgap the higher the Voc deficit, defined as the difference between bandgap value and measured Voc (Voc loss of 580 mV, 490 mV and 460 mV with bandgaps of 1.72 eV, 1.62 eV and 1.55 eV, respectively). This phenomenon has been partly attributed to photo-induced halide segregation. However this is unlikely to be the case here because all the perovskites contain ≤ 20% Br. Instead, the charge extracting materials have been kept the same for all the Pb-based perovskites, thus interfacial recombination is probably to blame and HTMs (and ETMs) with a lower VB (and higher CB) may be better suited for perovskite with bandgaps >1.7 eV. Specifically addressing this challenge is part of ongoing efforts in WP1 and 2.

2.2 CSEM Tandems

In the frame of this deliverable CSEM has recently started to develop low bandgap perovskites based on a mixed Sn-Pb system. The perovskite stoichiometry contains more Cs than UOXF Pb-Sn perovskite, which slightly increases the bandgap to 1.25 eV. The solar cell stack is ITO/PEDOT:PSS/$Cs_{0.25}FA_{0.75}Pb_{0.50}Sn_{0.50}I_3$/C60/$SnO_2$/Ag. Thanks to the good thermal stability of $Cs_{0.25}FA_{0.75}Pb_{0.50}Sn_{0.50}I_3$, the perovskite is stable during the one-hour long ALD SnO_2 process under vacuum at 100°C and moreover it was found that the cells with SnO_2 have longer shelf life compared to those with BCP, likely due to SnO_2 being a more compact and thicker barrier against iodide and silver diffusion. The efficiency of this tandem is 17.7% on 1 cm^2 and improvements are expected by increasing the current in the bottom cell. In fact, the Pb-Sn perovskite thickness has not been optimised as of yet and it is actually thinner than the wide bandgap perovskite, therefore the J_{sc} is lower compared to UOXF cells. The lower observed hysteresis for the low bandgap cell may be due to a lower scan rate (0.1 V/s) than that used at UOXF.

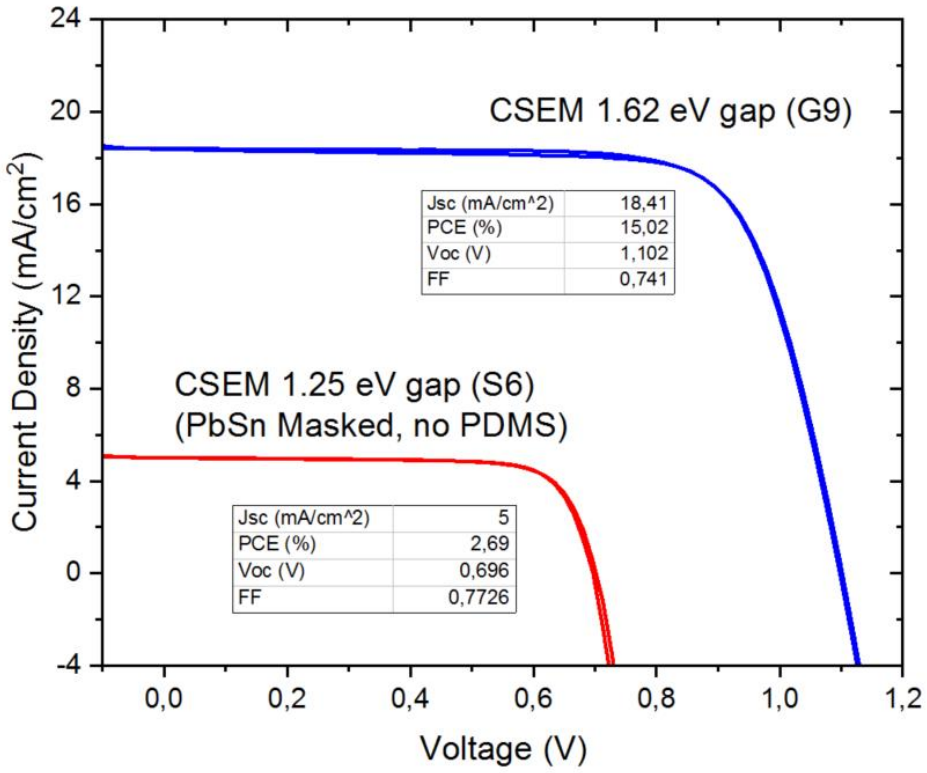

Figure 4. Current-voltage characteristics of a 4T tandem stack consisting of a 1.25 eV perovskite bottom cell masked with a 1 cm^2 mask and a 1.62 eV top cell.

3. Conclusions and outlooks

The 4T tandems presented in this deliverable achieved 17.7%, which remains a significant way off our target of 25%. The main limitations are the Voc and the FF of the subcells, particularly for the low bandgap cell. Indeed, we have encountered several problems in the fabrication of the low bandgap perovskite, both by solution processes and by evaporation. However, earlier this year CSEM has started to work on the mixed Pb-Sn based perovskite and achieved encouraging results. We expect that by strengthening the collaboration between UOXF and CSEM on the Pb-Sn perovskite good progresses will be possible in the coming months. Environmental conditions during the fabrication of the low bandgap perovskite play a crucial role on crystallisation of the low-bandgap cell and are also hard to control. UOXF have set upo a dedicated glove box for Pb-Sn perovskite processing, which is expected to greatly improve the reproducibility and increase the overall efficiency. A thick Pb-Sn perovskite layer is also required to provide a high current when the light is filtered through the wide bandgap cell, therefore photo-generated charge extraction over long distances is essential, i.e. bulk recombination in the perovskite layer should be minimal. In the case of the Pb-Sn perovskite there is still much to explore in terms of defect passivation agents compared to the Pb-based perovskites.

In parallel to the work on the low bandgap absorber, the recombination junction has to be optimised for full solution processed 2T tandems, in order to be as dense and thin as possible. Indeed, compact and pinhole-free recombination junctions serve as physical barriers to the strongly coordinating solvents (DMF and DMSO) used to process the second perovskite layer. Because ITO has a lower refractive index than perovskites, it is also important to limit its thickness as much as possible, in order to reduce internal reflective losses as well as transmission losses. Moreover, sheet resistance decreases with increasing ITO thickness, thus increasing the risk of connecting defect-related current shunts in the cell or module and lowering the efficiency. A recent study showed that ALD SnO_2 does not nucleate easily on a fullerene layer because of its lack of hydroxyl groups, resulting in pinholes in the ALD layer. [5] However, a very thin layer of hydroxylated polyethylenimide (PEIE) on the fullerene can help increasing the density of the ALD SnO_2. Previous experiments on the 2T tandems between CSEM and UOXF have indicated that the ALD layer was not compact enough to avoid Pb-Sn perovskite discolouration during the spin-coating of the wide bandgap perovskite, while this did not seem to be the case for the reversed stack (Pb-Sn on top of Pb perovskite). It is possible that the PEDOT:PSS employed in the Pb-Sn cell offers a further barrier to the DMF-DMSO mix, or that the pure Pb perovskite is intrinsically more resistant to strongly coordinating solvents than the Pb-Sn perovskite. For the full solution processed 2T tandems we will therefore pursue the approach of depositing the wide bandgap perovskite first, followed by the low bandgap perovskite. Based on optical modelling, the thickness of our 1.72 eV perovskite is optimised for current matching in the 2T tandems with 1.24 eV perovskite and will be tested next in tandem devices.

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