VIPERLAB

D8.6

PERFORMANCE DIFFERENCES OF CELLS AND MODULES FABRICATED UNDER AMBIENT CONDITIONS WITH THOSE UNDER N_2 ATMOSPHERE

DELIVERABLE REPORT

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FULLY CONNECTED VIRTUAL AND PHYSICAL PEROVSKITE PHOTOVOLTAICS LAB VIPERLAB

DELIVERABLE

D8.6 Performance differences of cells and modules fabricated under ambient conditions with those under N_2 atmosphere

Project References

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DISCLAIMER

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TABLE OF CONTENT

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N°101006715

FIGURES

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EXECUTIVE SUMMARY

The impact of the processing atmosphere (nitrogen, dry air, ambient air) on the performance of perovskite solar cells and modules is investigated for three different process methods: spin coating, hybrid process and slot die coating. Here, the hybrid approach refers to a process with two sequential process steps: a first vacuum deposition step to deposit a first perovskite precursor followed by a second, wet chemical process step – here spin coating – to deposit the second perovskite precursor and to form the perovskite layer by a thermal anneal step.

For industrial manufacturing, processing under ambient conditions is preferred as it lowers the capital expenditure and process cost. However, if the process conditions impact the device performance, it may be essential to control the atmosphere for improved performance, reproducibility and yield.

The three selected process methods are relevant for small scale research devices (spin coating), medium sized (wafer-like) sheet-to-sheet devices and compatible with textured substrates like perovskite/cSi hybrid tandems (hybrid process) and large-scale sheet-to-sheet and roll-to-roll processes (slot die coating).

An overview of the various devices, process atmospheres and process methods applied is presented in the table below.

Cells	Modules	Technique	Partner	Data (N_2)	Data (<20% R.H.)	Data (>20% R.H.)
yes	yes	Spin coating + gas quenching	UNITOV	✓	✓	-
yes	no	2 step hybrid	EPFL/ CSEM	✓	✓	✓
yes	no	Slot die + gas quenching	SU	-	✓	✓

Table 1: Overview of the involved partners, type of samples, deposition methods and process conditions which are part of deliverable 8.6 to evaluate the impact of process atmosphere of device performance.

Spin coated devices

Cells and mini-modules were processed under a nitrogen or dry air atmosphere. SEM analysis shows, the morphology of the films is similar, both in uniformity and grain size. The analysis also indicated only small differences caused by the drying process. Also, XRD measurements show similar results for layers processed under a dry air or nitrogen atmosphere. From this we conclude that similar perovskite layers (homogeneity, grain size, crystallinity) can be obtained under these conditions.

The photovoltaic performance measured with current-voltage curves and external quantum efficiency spectra reveal a small difference in fill factor and short circuit current density. Samples process under dry air conditions perform slightly better. This is the case for both cells and mini modules. Tentatively, the difference is attributed to different passivation of the perovskite layer when processed under nitrogen or dry air conditions.

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Hybrid processed devices

Contrary to one step spin coated perovskite devices, hybrid process devices show a strong dependence on the process atmosphere when processing and annealing the second perovskite precursor. When the annealing is done in air, the performance increases drastically, even if there is no evidence of bulk differences between the films annealed in different environments.

The impact of the atmosphere is again attributed to passivation effects: under air this process is more efficient compared to annealing under nitrogen. This passivation effect is confirmed by adding a passivating agent in the solution during the second process step of devices processed under nitrogen. This yields well performing devices. This shows that the addition of additives or the different transport layers used can have a huge impact on the selection of the best processing gas for the deposition and crystallization of the perovskite layer.

Slot die coated devices

Flexible perovskite solar cells fabricated by slot die coating and gas quenching have been tested to evaluate how different levels of relative humidity impact the device efficiency. The results indicate that an increase from 20 to 40% of R.H. induces a significant drop in the performance. This result indicates that moisture can strongly affect the performance of perovskite solar cells, especially if above a given threshold that will depend on the formulation used. The different relative humidity also has an impact on the film morphology, as confirmed by SEM and XRD: at higher relative humidity there is a lack of PbI_2 grains that can passivate defects in a perovskite layer.

1. INTRODUCTION

The industrial development of perovskite-based photovoltaics requires the development of facile and robust layer deposition processes. The environmental conditions of the coating/deposition step can play a major role in the quality of the films. A strict control on the key parameters such as water concentration/humidity, temperature, oxygen concertation, residual solvent concentration can increase the reproducibility of the deposition process. On the other hand, the use of demanding process conditions as the deposition in a nitrogen environment complicates and increases the cost of a production facility and of the operating costs. This aspect is particularly relevant for the perovskite layer: during its deposition, the polycrystalline perovskite film crystallizes in situ and the environmental conditions can change the nucleation and growth processes. Furthermore, some components of the perovskite ink and some intermediate phases are sensitive to moisture, so humidity is expected to be a key parameter to be controlled: high humidity are generally harmful to the process, while sometimes a controlled humidity level (either during the deposition or the annealing phase) might be even beneficial. The impact of oxygen is less evident: This is strongly dependent on the ink formulation, the deposition technique, and the crystallization method adopted. For this reason, we focused on studying the effect of the most relevant processing environment (i.e., air vs. nitrogen) on a set of crystallization methods that can be suited for upscaling: the gas quenching method (by either spin coating or slot die coating) [1] and the 2 step hybrid approach[2]. Each of them has specific advantages that will be explained in the following sections. All the tests have

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been performed on a p-i-n stack to have a common architecture: given the very large variety of transport layers available for perovskite solar cells, we did not investigate the impact on the environment of such layers. As proof-of-concept, we show that even small changes in the transport layers can drastically change the effect of the processing environment (for the 2-step hybrid approach). For this reason, we highlight how the feasibility of coating in air should be checked according to all the materials used for a perovskite cell. On the other hand, if the processing conditions are fixed beforehand, the layers and their deposition can be tailored to be compatible with such boundary conditions,[3] for example, by employing additives makes the deposition resilient to high humidity.[3]

2. EFFECT OF PROCESSING ENVIRONMENT ON DIFFERENT CRYSTALLIZATION METHODS

2.1 Gas quenching method (UNITOV)

In this section, we investigate the impact of processing environment on a perovskite film deposited using the gas quenching method. We used a wide band-gap formulation (1.73 eV) that is optimal for perovskite-Si tandem, either two terminal or four terminal ones. The $Cs_{0.3}DMA_{0.1}FA_{0.6}PbI_{2.1}Br_{0.9}$ perovskite was deposited by spin coating in a flow box conditioned with either nitrogen or dry air (20% RH), and the same gas was used also for the gas quenching phase: In this crystallization method the crystallization is controlled by using a pressurized gas flow on the samples during the ink drying phase. The fast drying given by the gas flow induces a supersaturation of the ink that causes a dense nucleation of the perovskite grains. The crystallization is finalized during thermal annealing. The architecture used is described in Figure 2. The effect of the processing environment has been tested in cells and modules to understand if it has an impact on devices with larger active areas.

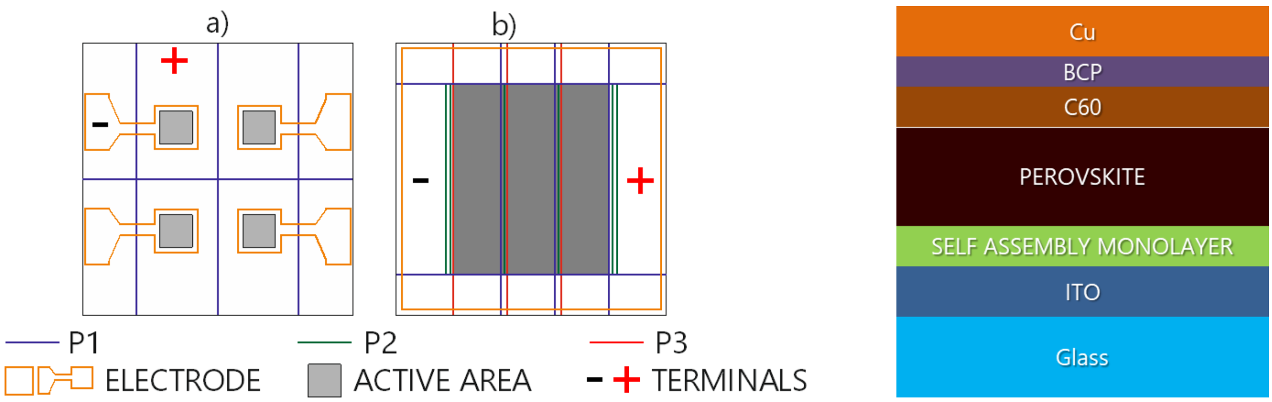

Figure 2: Left, a) cell layout and b) module layout used for the comparison of processing a gas-quenched perovskite film in air and nitrogen. Right, stack used for the comparison.

At first, we evaluated the films deposited in air and nitrogen by morphology and crystallinity by SEM and XRD. From the SEM (see Figure 3) the morphology of the film appears similar, with almost no apparent change in the grain size. Both layers are also uniform, with no obvious pinholes. The low magnification images show how there is a texturing in the nitrogen processed samples that results

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in areas with different concentrations of PbI_2 crystals: these are the brighter ones, as evidenced in the backscattered electron images (not shown). This is evidence of a slightly different drying behavior that might be reflected in the device performance.

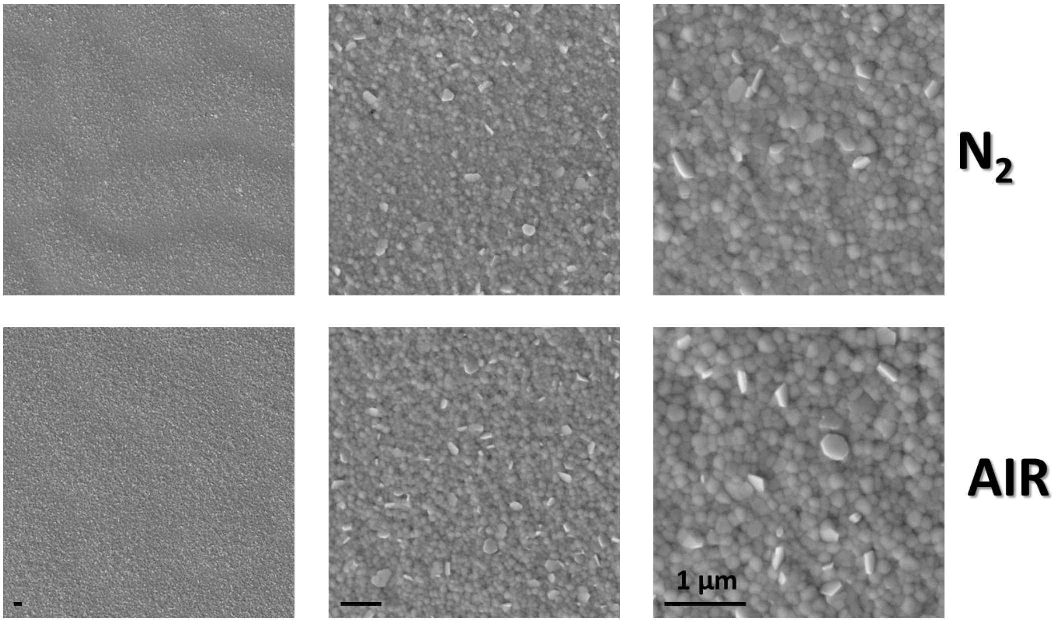

Figure 3: top row, SEM images of perovskite films prepared in N_2; bottom row, SEM images of perovskite films prepared in air.

The crystallinity and crystal phases have been analyzed by X-ray diffraction (XRD). The diffraction patterns of the two types of films are reported in Figure 4. The patterns show a very similar crystal composition of both films, showing that the impact of the processing environment is limited.

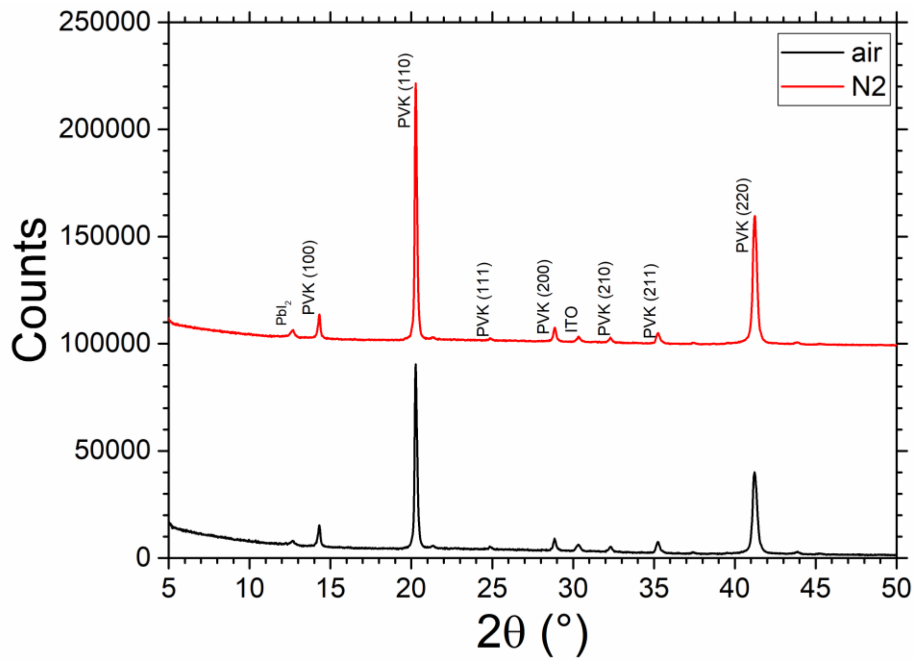

Figure 4: XRD patterns of the perovskite film deposited in air and nitrogen.

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The layer was later tested on the device architecture described in Figure 2 and the results are shown in Figure 5.

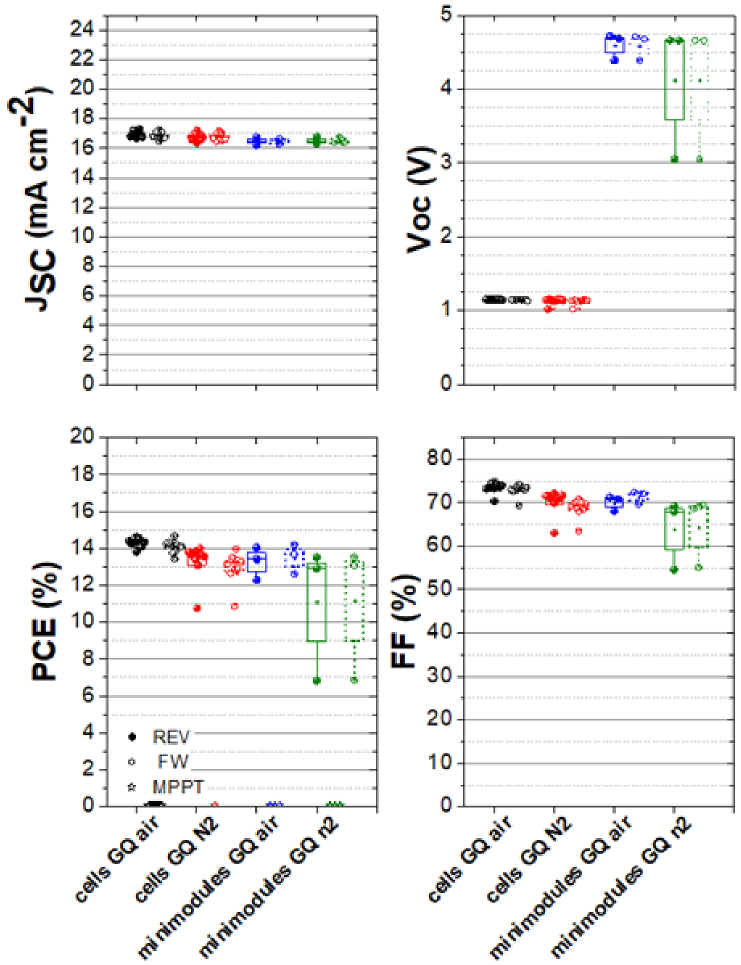

Figure 5: PV parameterizers for cells and minimodules processed by gas quenching in air and nitrogen

The results indicate that it is possible to achieve very similar results with both dry air or nitrogen as a processing gas. In particular, the cells processed in dry air exhibit an improved fill factor that is reflected in a minor improvement in efficiency. This is also due to a small change in the Jsc, as also confirmed by IPCE (see Figure 6). The results achieved on cells and minimodules are well aligned and confirm that the impact of the processing environment is the same for both types of devices.

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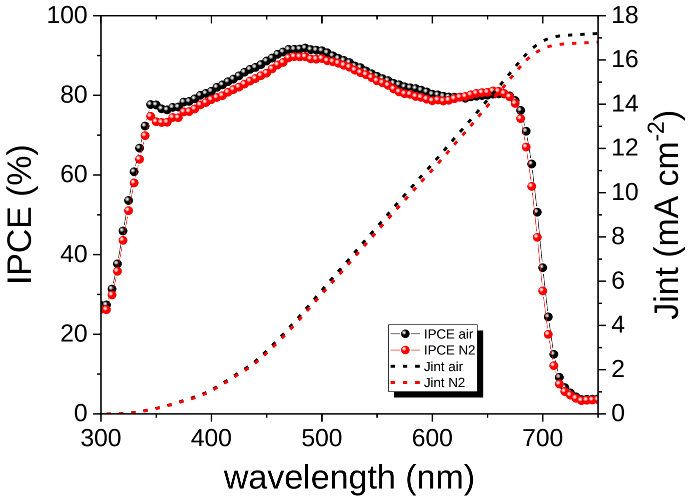

Figure 6: IPCE of cells processed by gas quenching in air and nitrogen.

To understand the feasibility of using air with higher efficient structure has been tested to provide passivation of the perovskite structure: a thin layer of PEACl has been deposited over the perovskite before the deposition of the ETL (still in air).[4] The results are shown in Figure 7;

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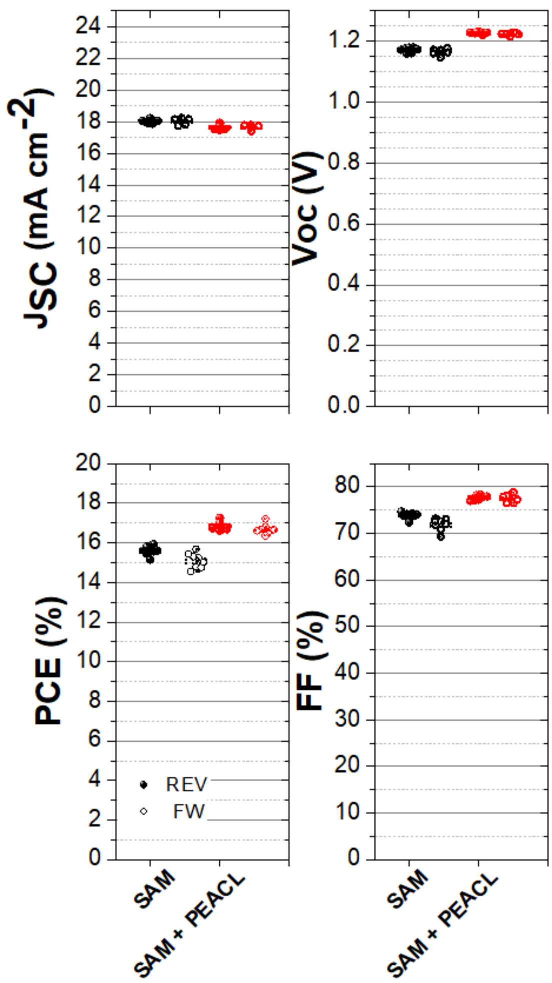

Figure 7: PV parameters of cells processed with gas quenching in air, with and without PEACL as passivation layer.

2.2 Hybrid 2 step method (EPFL/CSEM)[9]

The crystallization method described in this section is based on a hybrid approach based on two sequential steps: first, a layer of PbI_2+CsBr is deposited by PVD (thermal evaporation), and later this layer is converted to perovskite by spin coating a solution of cations followed by an annealing step. This approach is useful to allow controlled and conformal growth of the film, without the need to deposit the organic cations by PVD (a challenging task). It is also interesting since it provides a very different type of crystallization process, where the humidity plays a very different role. When the layers are deposited on inorganic hole transport layer as NiO_x (see Figure 8), the presence of water and oxygen is needed to achieve an efficient device. When the annealing is carried out in nitrogen, the J_{sc} of the cells is limited to less than 2 $mA{\cdot}cm^{-2}$. When the annealing is done in air, the performance increases drastically, even if there is no evidence of bulk differences between the films annealed in different environments (Figure 9).

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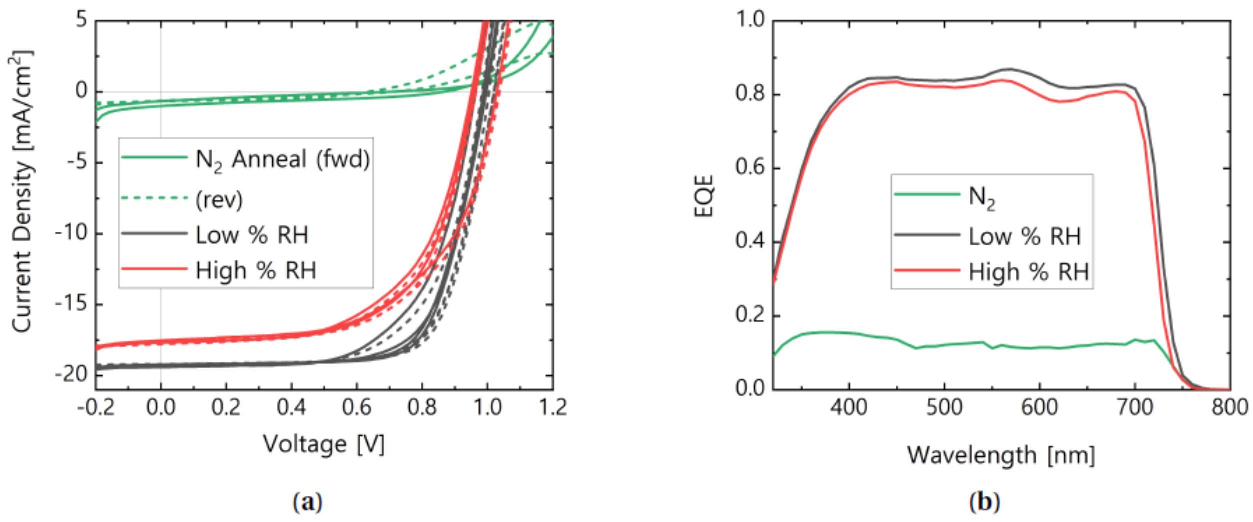

Figure 8: JV curves of perovskite solar cells processed in different environments by a hybrid 2 step method. The architecture used is glass/ITO/NiO_X /perovskite/LiF/C_{60}/Ag. Adapted and reproduced from [5]

It is believed that the effect is due to the presence of oxygen and heat during the annealing process, which induces defect passivation in the perovskite layer. Indeed, there are no major differences in the morphology of the film as shown by AFM or cross-sectional SEM, as well as a lack of differences in XRD. This data confirms that the conversion is rather similar in all the different annealing environments tested here.

Furthermore, it is also worth noting that the impact of the processing environment might change significantly if one modifies the cation solution or the hole transport layer. The addition of ethanethiol in the cation solution can significantly improve the performance of the cells annealed in nitrogen: being a Lewis base, it can passivate undercoordinated Pb^{2+} defects, removing the need for oxygen during the annealing phase. As shown in Figure 10, the JV curves confirm that, by using this additive, the cells annealed in nitrogen have performance like that of the one annealed in air. The need for the passivation achieved by oxygen can also be different if the perovskite is deposited on different transport layers. As shown in Figure 10 the impact of nitrogen annealing is less evident when the perovskite is deposited on a self-assembly monolayer (MeO-2PACz), as compared to cells deposited on TaTm or NiO_x.

These results show that, depending on the crystallization method used, it might be necessary to tune the processing environment: the addition of additives or the different transport layers used can have a huge impact on the selection of the best processing gas for the deposition and crystallization of the perovskite layer.

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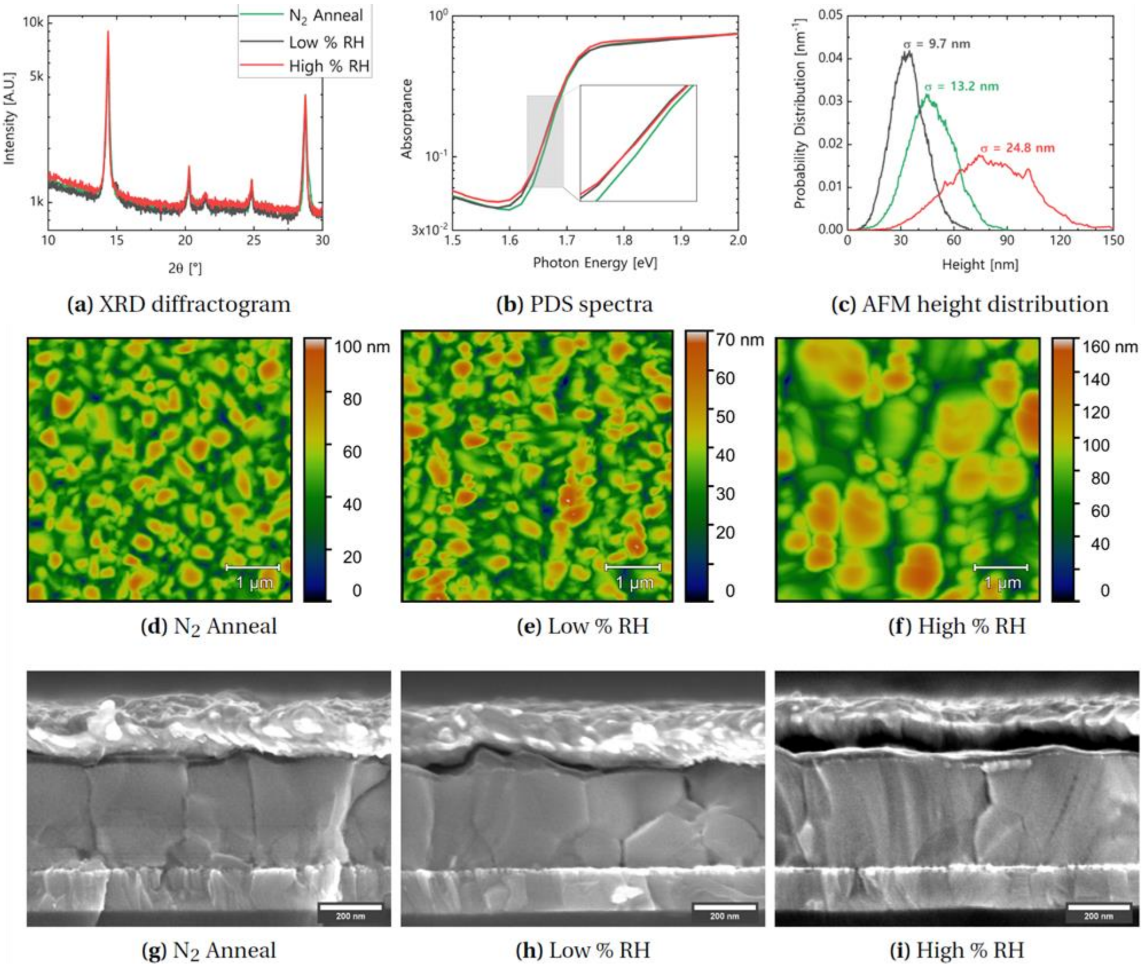

Figure 9: Film characterizations for the perovskite layer obtained with the 2 step hybrid method in different environment: a) XRD pattern, b) photothermal deflection spectroscopy, c) AFM height distribution, d, e, f) AFM height maps, g, h, i) cross-sectional sem. Reproduced from [5].

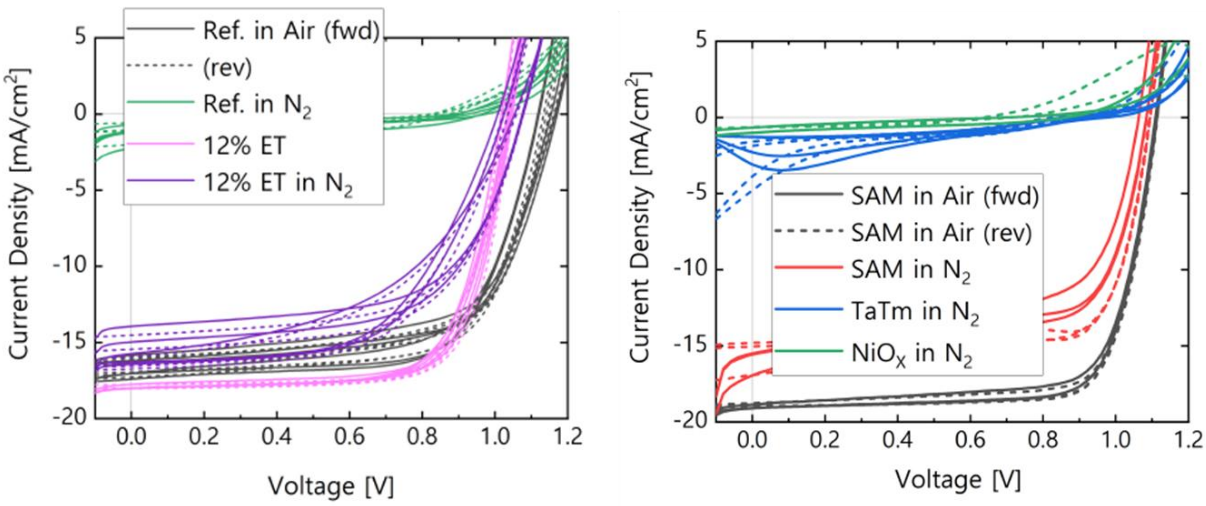

Figure 10. JV curves of solar cells with the perovskite obtained by the 2 step hybrid method. Left, cells with glass/ITO/NiO_X/perovskite/LiF/C_{60}/Ag architecture, using ethanethiol (ET) as additive in the cation solution. Right, cells with different HTLs annealed under different conditions. Adapted and reproduced from [5].

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2.3 Flexible substrates: slot die coating + gas quenching (SU)

To confirm that it is possible to effectively fabricate perovskite solar cells in air, we tested a slot die coating process over flexible substrates. Slot die coating is considered the most suitable technique to achieve large area coating by sheet-to-sheet or roll to roll manufacturing.[6] [7] However, the use of nitrogen as processing gas in a roll-to-roll line can be unpractical, as the whole coating station and dying furnace should be conditioned. It is more convenient to control the relative humidity and perform all the processes in air. [8] In this section we evaluate which is the impact of different levels of relative humidity over the performance of slot die coated perovskite solar cells. All layers up to the perovskite (see Figure 11) are deposited by a slot die coating over a commercial PET/ITO substrate, in a processing environment with 20 or 40% R.H.

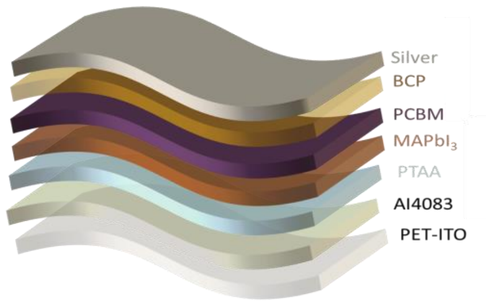

Figure 11: architecture used for the flexible cells coated by slot die coating (up to the perovskite).

The PV parameters (see Figure 12), show a clear impact of the processing environment: the increase of the relative humidity from 20 to 40% have a negative effect on the device performance. J_{SC}, V_{OC} and FF show a significant decrease when the humidity is higher, suggesting this is a parameter that needs to be controlled during the processing of perovskite solar cells. If we consider a production line, fluctuations of R.H. should be avoided to increase the reproducibility and the yield.

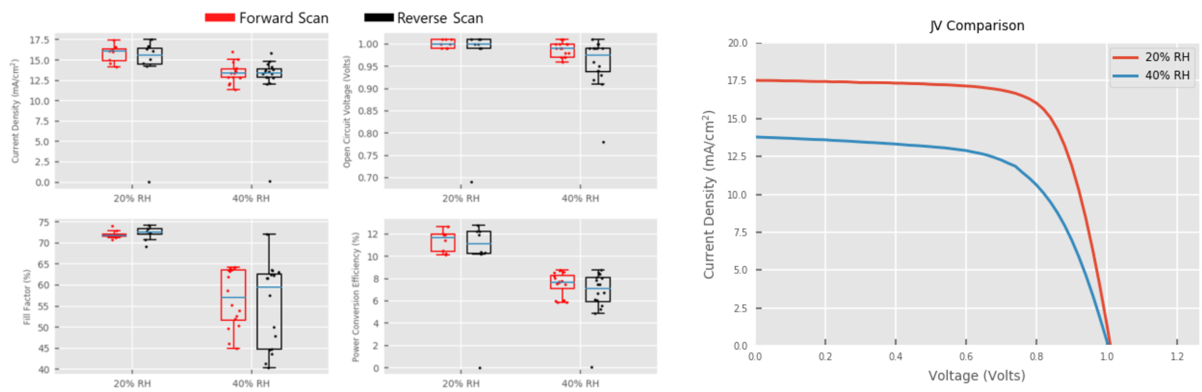

Figure 12: Left, statistical comparison of the performance of the devices fabricated with 20% and 40% R.H. The crystallization was achieved by a gas quenching process. Right, JV curves of representative devices fabricated at 20 and 40% R.H.

The morphological analysis of the perovskite film deposited under 20% and 40% are shown in Figure 13. The SEM reveals minor differences in the morphology: while the grain size do not change significantly, small PbI_2 grains can be observed in the the film processed at 20% R.H. This is also

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evident by the XRD patterns, where a small PbI_2 peak is present at 12.7°. These small grains might passivate defects on the perovskite layer, promoting a higher device efficiency.

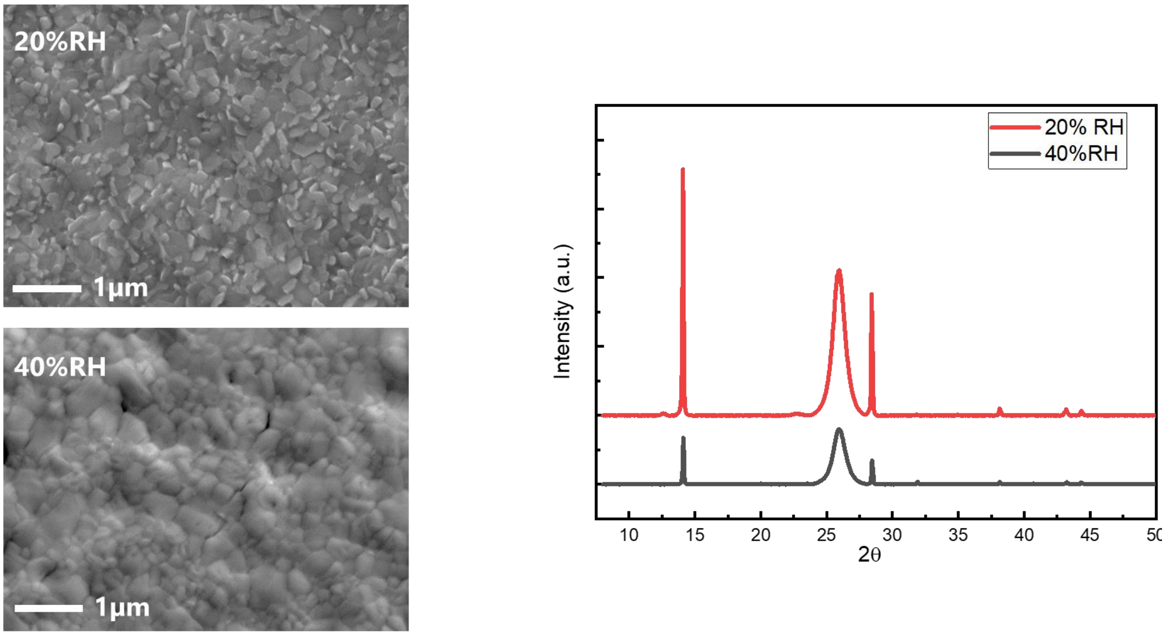

Figure 13: Left, SEM and right, XRD pattern of a perovskite layer coated by slot die coating in air with 20 and 40% R.H.

The results shown in this section demonstrate that is possible to deposit perovskite solar cells by slot die coating in air, but the relative humidity should be controlled.

3. CONCLUSIONS

In this deliverable we tested different processing routes to deposit the perovskite layer in nitrogen or in air with different relative humidity. The results show that according to the perovskite formulation and its crystallization method, the processing environment can have a relevant impact on the device performance. For example, in the 2-step hybrid process, the presence of oxygen is needed to achieve good device performance (> 10x efficiency improvement). Also, the impact of moisture appears negligible if the R.H. is properly controlled below a given threshold. Even if the threshold of R.H. needed to achieve efficient devices might change for different perovskite formulations and crystallization processes, it unlikely that an uncontrolled environment will not harm the reproducibility of the deposition and the device efficiency. For this reason, it will be recommended to have controlled processing environments for large area manufacturing, using dry air with a low relative humidity (i.e., < 20%). On the other hand, the use of pure nitrogen as a processing is not needed and not suggested as it will significantly increase operative costs and might even negatively impact device performance due to the lack of the passivation provided by oxygen.

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