DROP-IT

DELIVERABLE 3.3

Inkjet-printed B-LFP solar modules with an active area over 25 cm^2

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4		

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Table of Content

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1 Introduction

Task 3.3 (M18-36). Upscaling of inkjet-printed solar cells based on LFPs. The chosen material combinations (B-/GLFPs) developed in Tasks 2.4, 3.1 – 3.2 will be evaluated on mini-module (> 25 cm^2) configurations. The printing of such devices will be carried out on by means of industrial printheads, and the relevant printing parameters will be optimized to reach the highest performance. Various pre- and post-processing methods (such as surface activation with UV-O_3 or plasma treatments, IR and photonic curing of the deposited materials) will be evaluated to facilitate quick and large-scale deposition methods. Involved partners: SAULE (leader, fabrication, PV module characterization), SRI (evaluation of pre-/post-processing methods).

2 Description of work & main achievments

2.1 Module fabrication

Perovskite solar modules are manufactured by series interconnection of individual solar cells into a single substrate. Applicable substrates can be rigid or flexible – in the framework of DROP-IT project ITO-coated flexible PET substrate have been used as a starting point for the lead-free perovskite solar module fabrication. The first step in the module fabrication is the P1 process, which is the laser etching of the bottom conductive transparent layer (ITO) to provides electrical insulation between the individual solar cells. After the ablation process, the basis for every cell in the module is created. Subsequently the P1 processed substrate is thoroughly cleaned with deionized water and isopropanol to make sure that no residues of dust or particles remain. After the cleaning step, the substrate sheets were annealed for 15 minutes in an oven at 105 °C.

The hole transport layer (HTL) was prepared in the following way: 400 µl of aqueous PEDOT:PSS dispersion (Clevios P VP AI 4083) was mixed with 100 µl of ethanol and 110 µl of 25% ammonia solution. The prepared solution was placed in the fridge and stirred overnight. Deposition of the HTL was done with a blade-coater (height of the blade was 200 µm and speed was 2.5 mm/s). After deposition, the sheets were annealed at 105 °C for 40 minutes.

Deposition of the perovskite active layer was also conducted with the blade-coater under inert conditions, because inkjet-printed large area layers did not lead to working cells or modules. We used two different formulations and the thickness of perovskite layer was varied. Layers were annealed at 100 °C for 30 minutes under inert conditions inside a nitrogen filled glovebox with well controlled humidity and oxygen levels. After annealing, the sheets were transferred into the organic evaporator to deposit 30 nm of C60 electron transport layer (ETL) and 6 nm of BCP.

Before the metal evaporation step, the layer stacks were P2 laser processed. The main problem encountered at this stage was the unavoidable exposure of the functional layers to the atmosphere because the laser system is not situated under inert gas. The P2 line is the most important step, because it allows to do connection between the bottom electrode in one cell to the top electrode of the adjacent cell. We did investigation of different laser powers and different speeds of the laser beam. If the P2 process is not well optimized, the laser may destroy the bottom electrode or the etching of the HTM layer may be incomplete, leading to improper interconnection between cells and improper current flow. After the P2 etching, the layers were transferred into a metal evaporator to

deposit 100 nm of silver to form the backside electrode. A specially designed mask was used to separate the electrodes. In this way we could avoid another air exposure of the solar module by circumventing the P3 laser processing step. The finished flexible lead-free perovskite solar module is shown in figure 1 and a scheme of the module is depicted in figure 2.

Figure 1. 8-cell interconnected flexible large are lead-free perovskite ($Dip_2FA_9Sn_{10}I_{31}$) solar module.

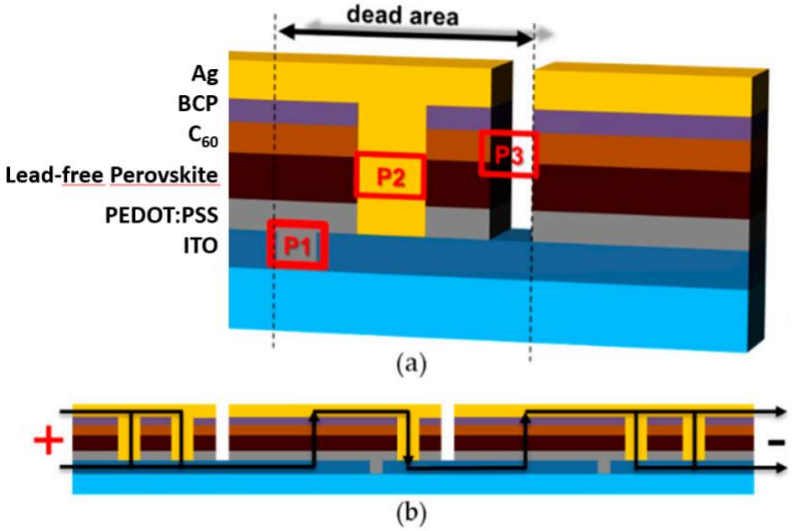

Figure 2. a) A scheme of the module. (b) Charge flow in the series of cells. (Adapted from *Micromachines* 2020, *11*(12), 1127; https://doi.org/10.3390/mi11121127).

3 Results

3.1 Thickness dependence

The perovskite layer was prepared with different blade speeds. Blade speeds of 0.5, 1.0, 1.5, 3.0, 3.5 and 4.0 mm/s have been investigated. The optimized P2 process parameters were used for all modules: laser operating current – 20.0 A (output power – 1.356 W), speed of the laser beam – 600 mm/s. Perovskite chemical formula: $Dip_2FA_9Sn_{10}I_{31}$. We used this composition because of its increased stability and well-optimised deposition process.

Before the deposition process 15 µl of BAAc was added into 600 µl B-LFP precursor solution. Results from current density vs voltage measurements are displayed in figure 3. Module made with 3.0 mm/s speed has parameters out of the trend, but in J_{sc} and V_{oc} graphs we observed that higher speed of the blade lead to a better solar module performance. The best results were obtained for a deposition speed of 3.5 mm/s.

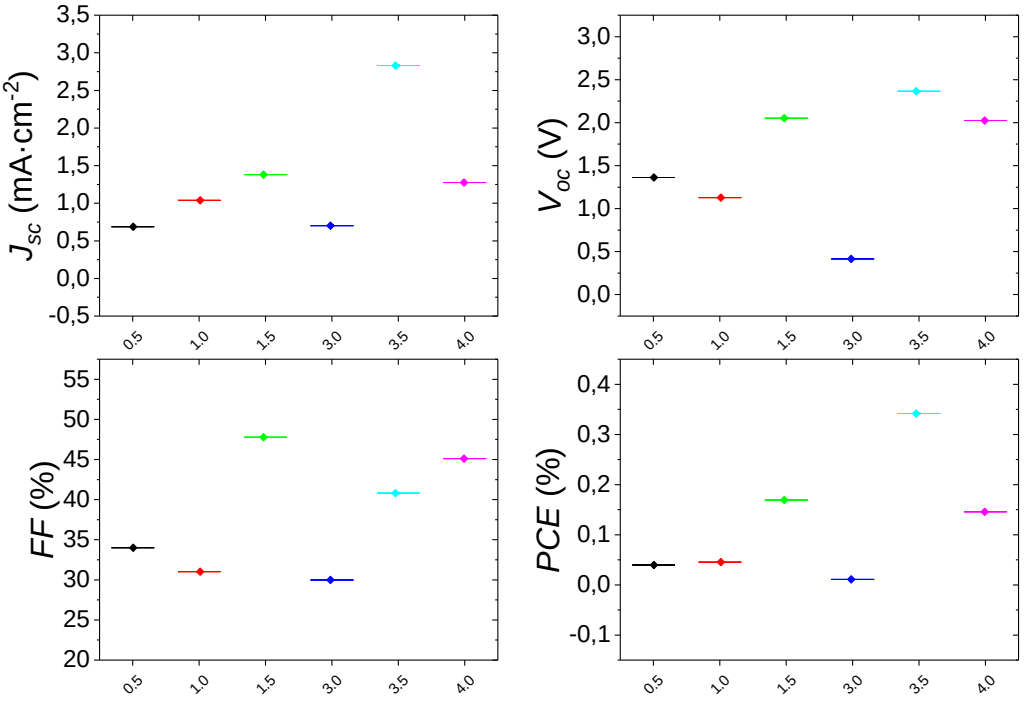

Figure 3. Parameters from J-V curves for different speeds of the blade (in mm/s).

3.2 P2 process optimization for $(BA_{0.5}PEA_{0.5})_2FA_3Sn_4I_{13}$

The blade speed was kept constant for all modules (3.5 mm/s) for the optimization of the P2 processing parameters. We were changing 2 parameters in P2 process: speed of the beam and laser power. Perovskite chemical composition was $(BA_{0.5}PEA_{0.5})_2FA_3Sn_4I_{13}$ – note that the perovskite formulation was different than in the previous experiment. Results for different speeds (in mm/s) are shown in figure 4. Current of the laser was 18.0 A (output power – 0.481 W). We obtained very low efficiency values here, most likely because the processing parameters were not even close to properly adjusted for this type of perovskite. For this type of perovskite we still need to optimize deposition process by blade-coating and then find appropriate parameters for P2 ablation.

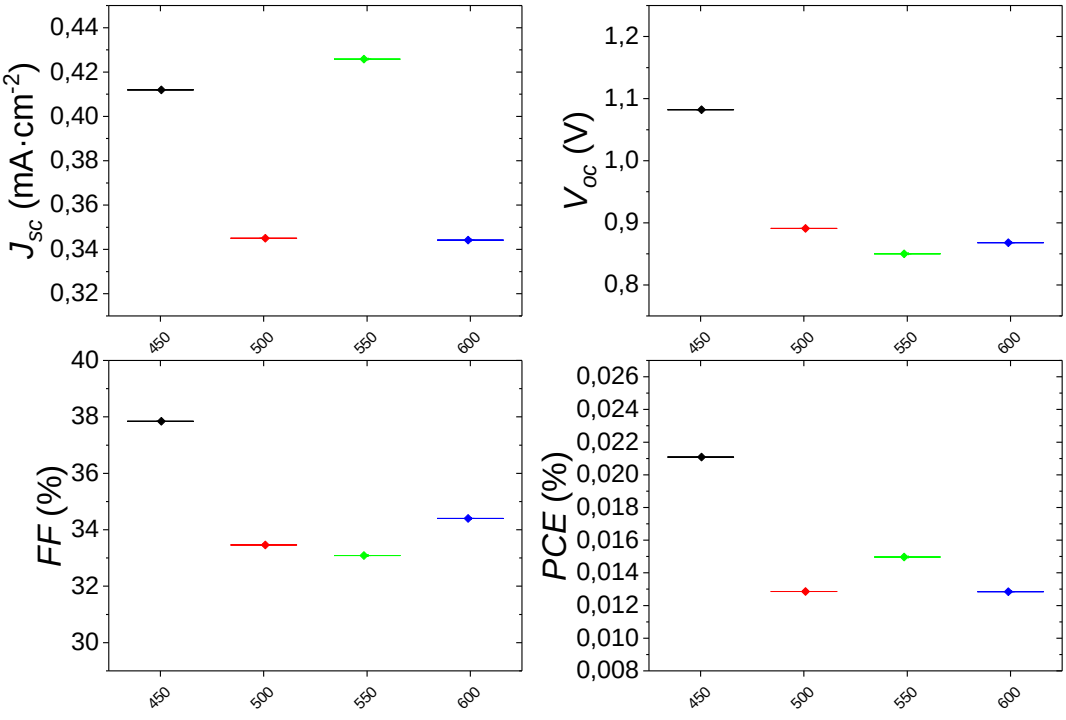

Figure 4. Parameters from J-V curves of **$(BA_{0.5}PEA_{0.5})_2FA_3Sn_4I_{13}$** solar cell modules for different speeds of the laser beam (in mm/s).

In the next experiment we fixed the speed at 600 mm/s and were changing the current of the laser. Results for different laser currents are shown in figure 5. For the lowest current we obtained the best result, indicating that the perovskite layer did not need much power to ablate efficiently. On the other hand, during the previous experiment the power was probably too low to make good interconnection between ITO and silver – that's most likely why for the lowest speed the best result was obtained.

Lower speed means more energy is delivered to the layer, comparable to higher power of the laser. In all following experiments the laser speed was fixed to 600 mm/s.

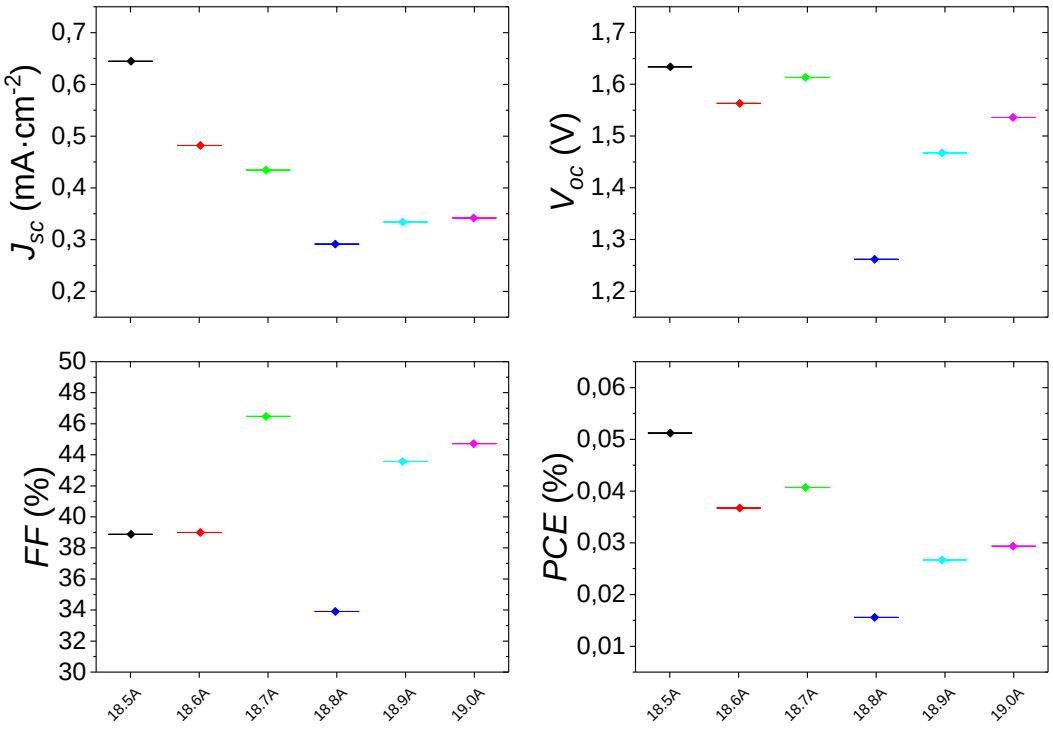

Figure 5. Parameters from J-V curves of **$(BA_{0.5}PEA_{0.5})_2FA_3Sn_4I_{13}$** solar cell modules for different laser operating current.

3.3 P2 process optimization for $Dip_2FA_9Sn_{10}I_{31}$

Due to poor results in previous experiment we changed perovskite composition to a "well-optimised" $Dip_2FA_9Sn_{10}I_{31}$. The speed of the blade during the perovskite deposition was 3.5 mm/s. Speed of the laser was set at 600 mm/s and at these settings we tested different laser powers – operating current from 17.8 A to 18.9 A (output power from 0.396 W to 0.835 W) – results are on figure 6. We can see a correlation between V_{oc} and FF: best FF values (up to 58 %) are measured for the highest V_{OC} values (up to near 2 V), but the main factor that has the greatest impact on the resulting PCE was the J_{sc}. Higher J_{sc} and PCE are observed by increasing the laser power, but the absolute J_{sc} values are most likely the result of exposing samples to air during the P2 process. Furthermore, the J-V measurements were performed in ambient atmosphere, which is also likely to affect the LFP solar module's performance before, as well as after the initial J-V characterization.

However, considering the level of difficulty encountered in the multi-step fabrication of large area tin based lead-free perovskite solar modules, the **obtained functional perovskite solar modules with**

PCEs of up to 1%, using an industrially applicable and scalable method can be considered as a remarkable milestone. In fact, till date no reports on flexible tin-based perovskite solar modules on polymer substrates were published, which makes the results obtained in the framework of DROP-IT **the highest module efficiency for tin-based perovskites on a flexible polymer substrate**.

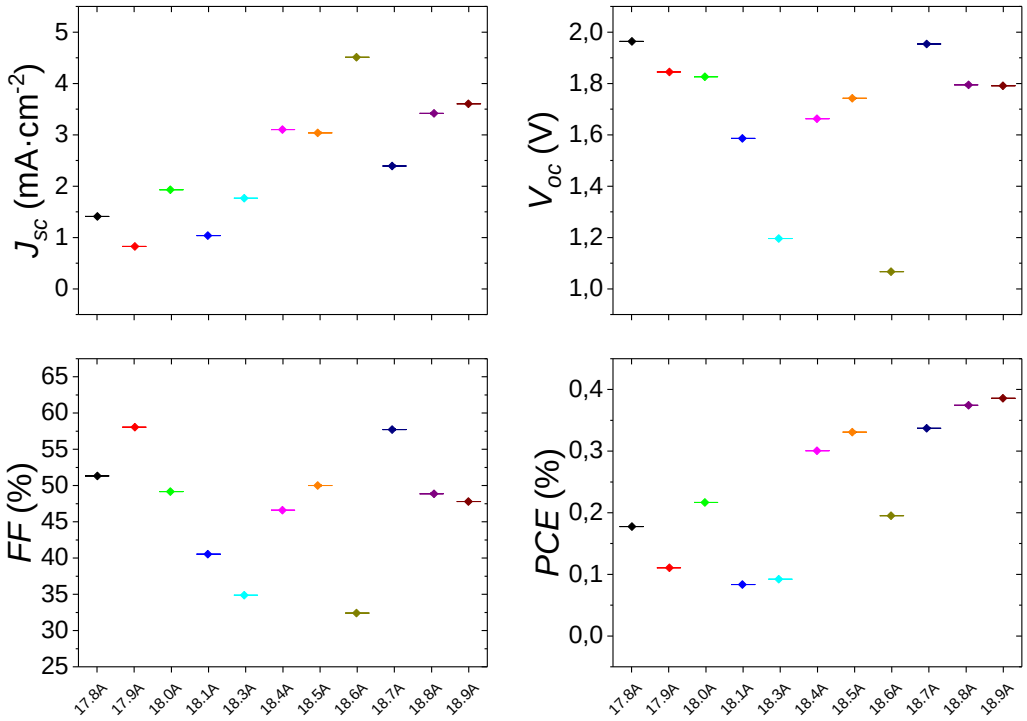

Figure 6. Parameters from J-V curves of **$Dip_2FA_9Sn_{10}I_{31}$** solar cell modules for different laser operating current.

3.3.1 Results after 2 weeks storage in glovebox

We stored modules from previous experiment in the glovebox for 2 weeks and remeasured once again reaching a champion module with 0.87 % of efficiency. Initial and “2-weeks” results are on figure 7. There is a huge increasement in J_{sc}, especially for the right half of the graph (18.4A – 18.9A). In one sheet we can fit six patterns of modules - this means that we do deposition of PEDOT:PPS and perovskite at the same time for six modules. Despite the fact that all parameters were the same, there is noticeable difference between those two sets of modules. Probably the first set was longer time in ambient atmosphere during P2 process.

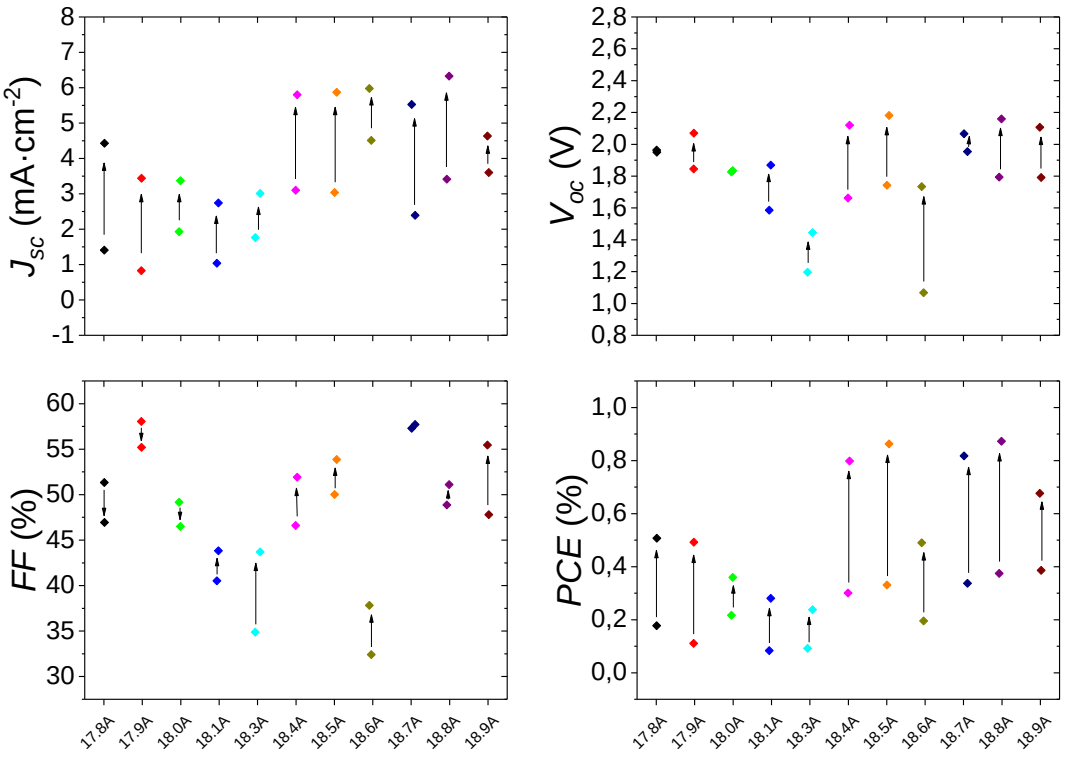

Figure 7. Parameters from J-V curves of **$Dip_2FA_9Sn_{10}I_{31}$** solar cell modules for different laser operating current after 2 weeks storage in nitrogen atmosphere.

3.3.2 Results after 6 weeks storage in glovebox and 1 day under the lamp

After 4 weeks we placed the 4 best modules under LED lamp illumination inside the glovebox and we noticed further enhancement in PV parameters, resulting in a champion module PCE of 1%. This means that we doubled the efficiency of initial results due to a net increase in J_{sc} up to values close to 7 mA/cm^2, as well as V_{oc} from 1.8 V to 2.4 V. The change of PV parameters is shown in figure 8 and the J-V curve for the champion module is displayed in figure 9.

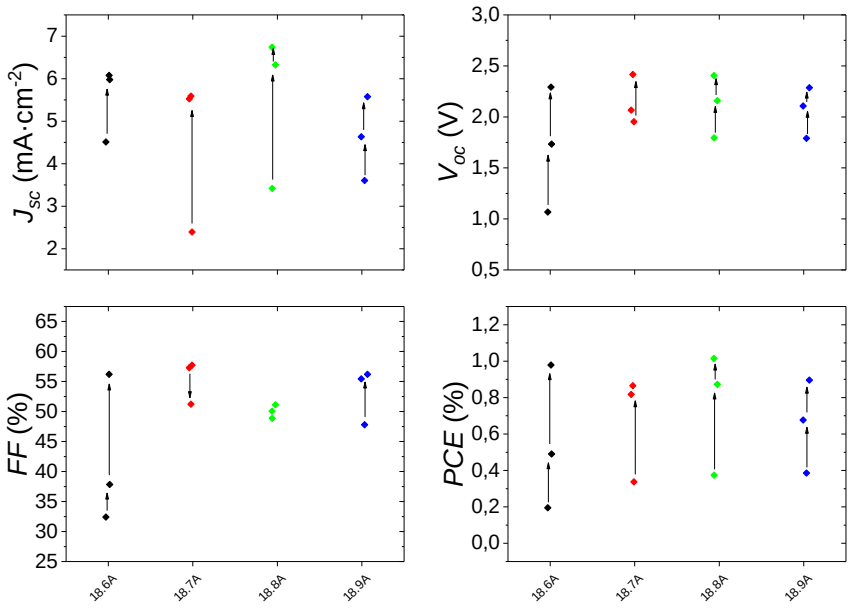

Figure 8. Parameters from J-V curves of **$Dip_2FA_9Sn_{10}I_{31}$** solar cell modules for different laser operating current after 6 weeks storage in nitrogen atmosphere and 1 day under LED lamp.

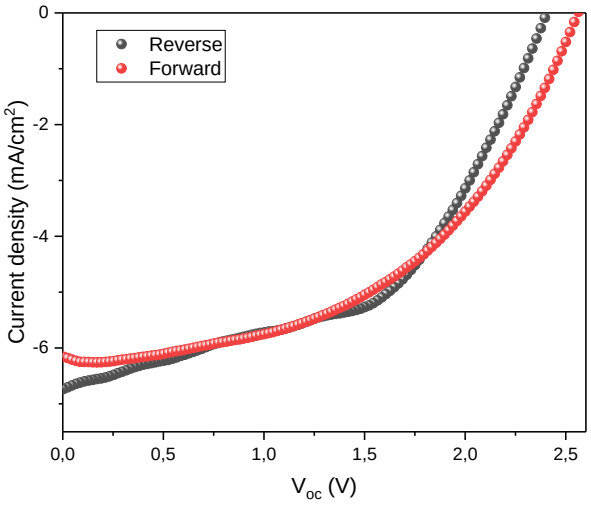

Figure 9. J-V curve for the best working module (18.8A).

3.3.3 P2 ablation images

To check if P2 is done correctly, we measured the resulting ablation pattern under optical microscope. We checked champion device (18.8A) and module with the lowest used laser power (17.8A). In figure 10 silver contacts are visible from both sides of the modules. In the champion device we can see that in P2 holes we have good planar silver layer that can connect to the bottom electrode. In another device it looks like in holes there are residues of other layers (perovskite or ETM) and the silver is mixed with this and does not provide good connection with the bottom electrode. In that case current of the laser was too low. To check this, we took photos also from the PET side of modules (figure 11). In the case of high laser power, we can see that there is no perovskite or other layers in holes and we have proper connection between silver and ITO layer. In the picture for the 17.8 A condition we can still see perovskite grains in P2 pattern, so this confirms that laser did not sufficiently remove the other layers. Still the perovskite layer suffered from many pinholes made probably in during the laser etching process (ambient atmosphere) and this is probably the main reason for the low efficiency measured in the as-prepared modules.

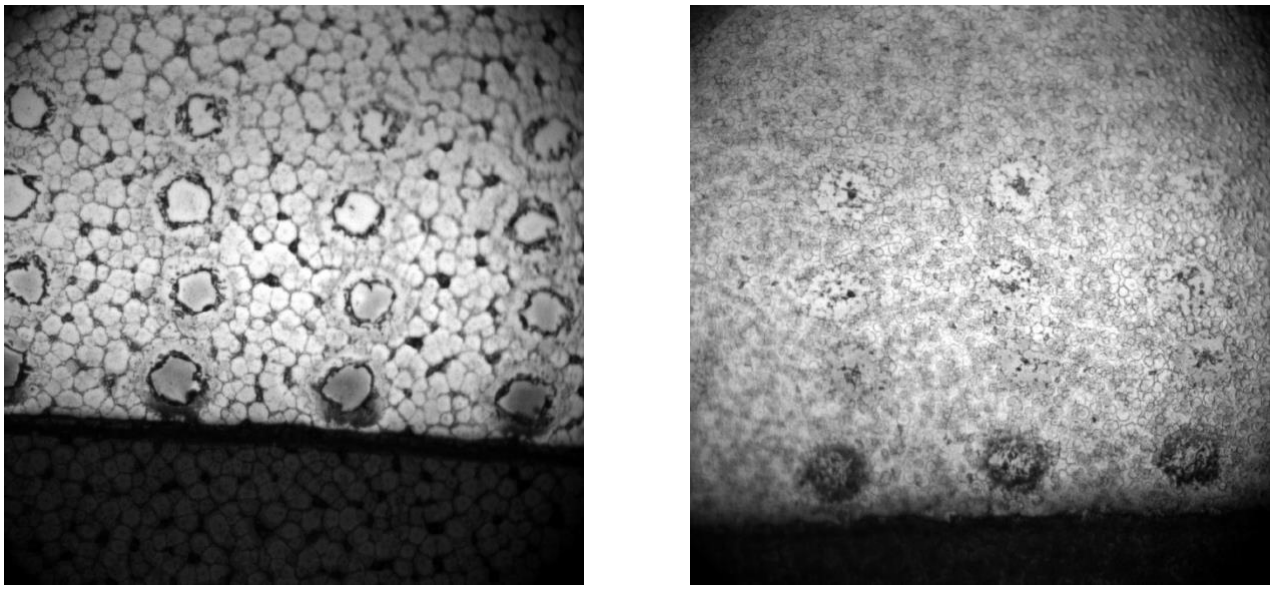

Figure 10. P2 pattern done with high power – 18.8A (left picture) and low power – 17.8A (right picture). Pictures were taken from the silver side.

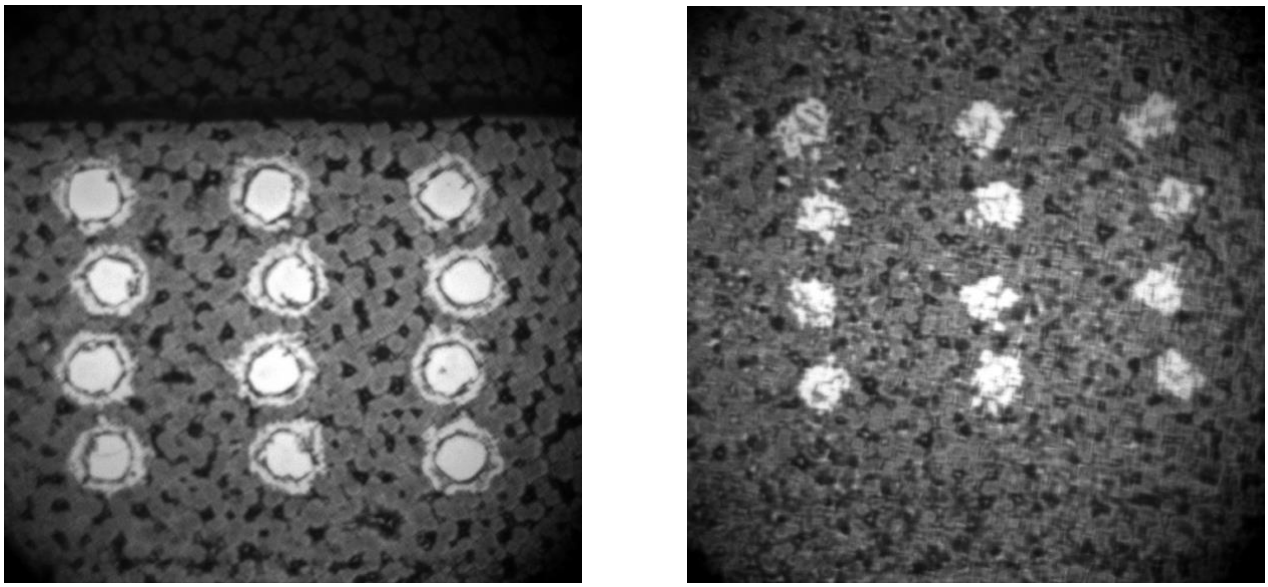

Figure 11. P2 pattern done with high power – 18.8A (left picture) and low power – 17.8A (right picture). Pictures were taken from the PET side.

3.3.4 SEM cross-section images

We made cross-section SEM images of the champion module in the region with and without silver (figure 12). These measurements indicate that thickness of ITO is ≈ 100 nm, the PEDOT:PSS – about 40 nm, the perovskite ≈ 120 nm, C60 - BCP about 40 nm and silver with 100 nm. In the case where there is no silver layer (right picture in figure 12) only degradation of perovskite layer is well visible, because the thickness is reduced down to 40-50 nm or even the perovskite disappears in some places. The degradation of the perovskite can be also observed on SEM images registered in a top view of the module in the area without silver (figure 13).

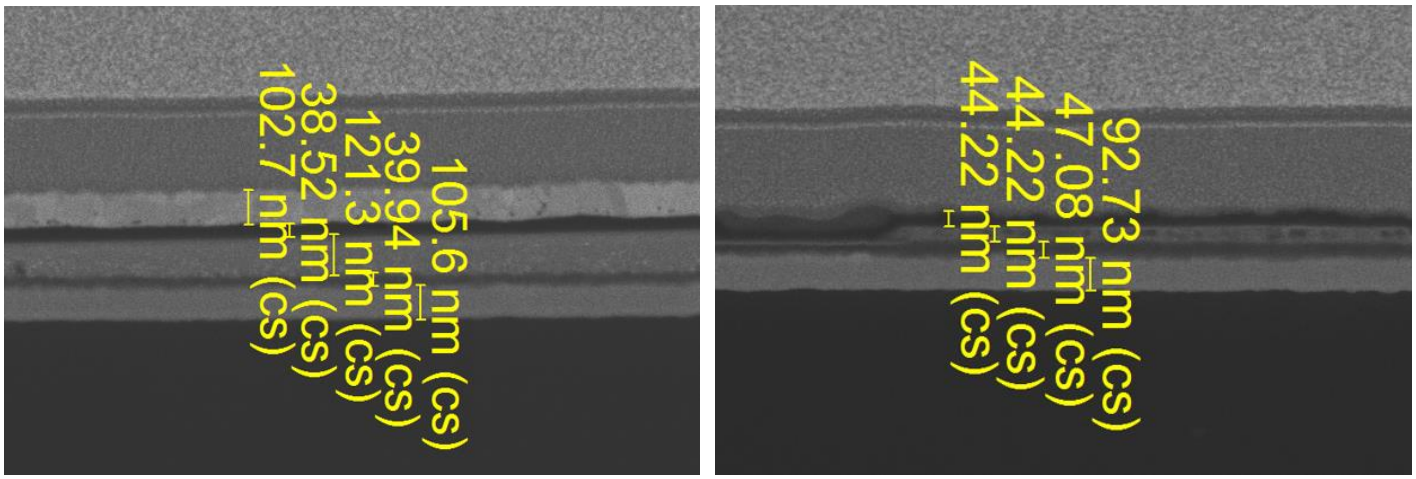

Figure 12. SEM cross-section images in area with silver (left picture) and without silver (right picture).

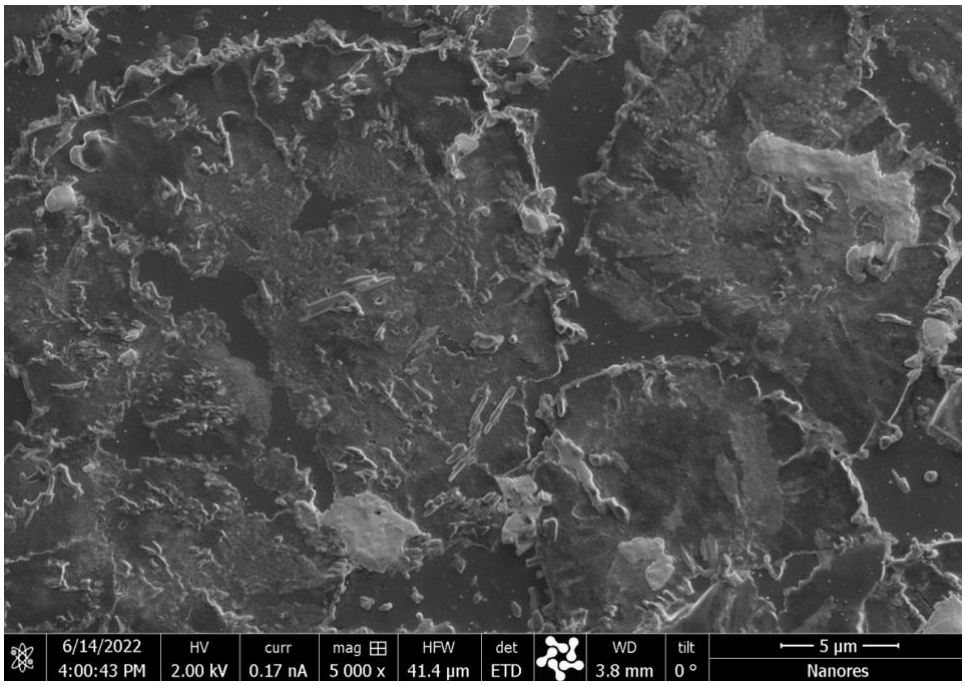

Figure 13. SEM image from top side in area without silver.

4 Deviations from the workplan

Due to the delay in equipment installation in glovebox environment reproducible inkjet-printed devices with good enough quality (pinhole-free) are still under development. The experiments on the module preparation were mostly conducted on blade coated perovskite samples, since the inkjet printed perovskite films did not lead to functional PV modules for the moment.

5 Conclusions & Future directions

We demonstrated module fabrication based on lead-free perovskite and P2 process optimization. We tested different perovskite thickness, compositions, speed of the laser beam and especially laser power in the fabrication of the P2 line, which is one of the most important parts of preparing a working module. For the champion device we obtain 1% of power conversion efficiency, short-circuit current density close to 7 mA/cm^2, open-circuit voltage 2.4 V (for 8-cells module) and fill factor of around 50%. The main problem in fabrication process is possibly due to the oxidation of perovskite during the P2 line ablation.