TOP ELECTRODE INVESTIGATION OF OPV MODULES BASED ON P3HT:PC[60]BM FABRICATED VIA ROLL-TO-ROLL PROCESS

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Abstratc. *Solar photovoltaic (PV) cells allow the direct conversion of sunlight into electricity without* CO_2 *emission. Finding a way to cheaply utilize the vast amount of solar energy is one of the biggest challenges for this technology. The organic photovoltaic cells (OPV) are based on solution-processed photoactive polymers and can be fabricated via roll-to-roll (R2R) processes, which allow high production throughput with low costs. CSEM Brasil is building the foundations of future high-tech industries in Brazil and one of our key technology development areas is OPV modules production using R2R coating. In this work, polymer solar cells based on P3HT: PC[60]BM were prepared by R2R coating (electron transport, active and hole transport layers – ETL, AL and HTL) and by screen printing (top silver electrode). In order to save material and give more transparency of the OPV module were compared and evaluated the performance of two different suppliers of Ag paste (A and B) in three different top contact configurations, solid, grid and honeycomb. Additionally, were compared two different screen suppliers (I and II) for screen printing process and the Ag paste drying time studied. The comparisons were made with modules with an active area of 21.6 cm2 (6 stripes serially connected). Photovoltaic performance was evaluated in terms of Ag paste and screens suppliers, Ag pattern and drying time. Finally, modules were encapsulated in a R2R laminator using a flexible barrier film and evaluated in terms of lifetime.*

Keywords: *OPV, screen printing, Ag paste.*

1. INTRODUCTION

The global energy consumption is increasing steadily while natural energy sources are running out. However, renewable energy sources still have a small hole in the energy mix, which is apparently related with their high costs, as mentioned by Hösel (2013). Solar electricity is one of many renewable energy sources that contribute to the world's demand. Photovoltaic cells generate useful electric energy from sun light through multiple steps of energy conversion processes (Kim, 2009) and they are the only devices that allow the direct conversion of sunlight into electricity without CO_2 emission.

Organic solar cells (OPV) are an attractive 3rd generation solar technology that can be produced cheaply and very fast from solution with coating processes (Hösel, 2013). They stand on conjugated polymers and small molecules and are open a door for low-cost and high throughput production of renewable energy products, as they can be coated on flexible substrates via roll-to-roll process. Low weight, flexibility, shape freedom and semitransparency of final products are the main advantages.

Solution-processed OPV devices can have a broad range of polymer:acceptor material systems and device structures. In this work the system polymer:fullerene materials based on the bulk heterojunction (BHJ) concept was studied. The most common system of poly(3-hexylthiophene) (P3HT) as an electron donor and a fullerene, C_{60} derivative as acceptor, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was used, as shown in Fig. 1.

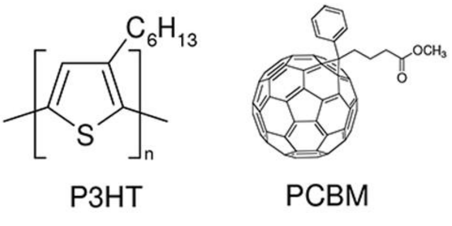


Figure 1 - Donor P3HT and acceptor PC[60]BM.

The working principle of a bulk heterojunction OPV device can be described in four basis steps: exciton generation, exciton diffusion, exciton dissociation and charge carrier transport (Deibel and Dyakonov, 2010), as shown in Fig. 2a. Photon is mainly absorbed in the donor material upon illumination of the active layer and promotes the electron to the lowest unoccupied molecular orbital (LUMO). The same time, a positive charge carrier (hole) remains in the highest occupied molecular orbital (HOMO). The charge carriers are attracted to each other and bound by Coulomb forces forming an electron–hole pair, the exciton. The exciton dissociates into a free electron and hole at the interface of donor and acceptor material. Free charge carriers are separated by an internal electric field due to the different work functions of the electrodes. The charges are transported through the donor and acceptor material and collected at the cathode (electrons) and anode (holes). (Hösel, 2013). Donor and acceptor are usually mixed together in solution prior to deposition and this is the reason of being called bulk heterojunction cells (Fig. 2b). According to Swart *et. al*. (2015), bulk heterojunction significantly improved organic solar cells (OSC) power conversion efficiencies by increasing the excitons access to the donor/acceptor interfaces.

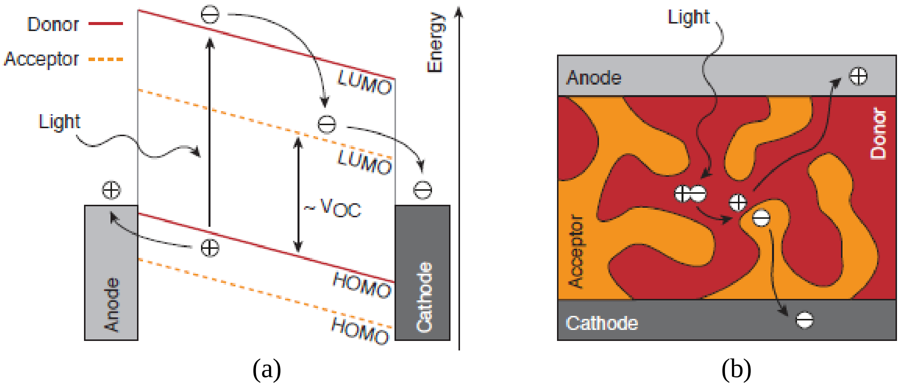


Figure 2 - (a) Schematic band diagram of the photocurrent generation in a BHJ solar cell and (b) Intermixed BHJ structure with charge carrier transportation paths. (Hösel, 2013).

R2R process allows large-scale manufacturing of organic solar cells. However, not every method is suitable for the OPV layers. Thus, a combination of process has to be found for efficiency stack preparation. The slot-die coating is a non-contact large-area processing method for the deposition of homogeneous wet films with high cross-directional uniformity (Fig. 3a). A broad range of formulation viscosities might be used on slot-die coating and the film thickness can be controlled by the flow rate. Slot-die coating is communally used in OPV layers deposition.

Printing technologies, which are typically a contact-based ink deposition, are widely used in the "printed electronics" industry. The printing methods allow the formation of different patterns and a wide range of thickness, depending of the process setup. In OPV these techniques are very useful for top electrodes deposition, which usually is silver. For R&D projects the flatbed screen printing (Fig. 3b), which was used in this work, is very suitable. For production lines the rotary screen printing is the most appropriate technique.

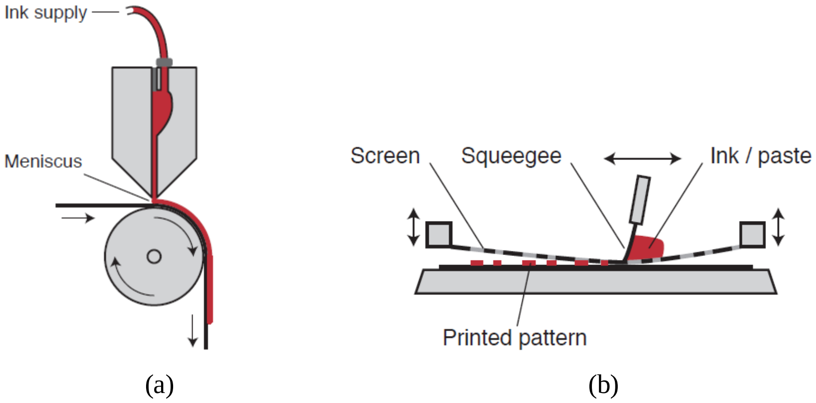


Figure 3 - (a) Slot-die coating and (b) Flatbed screen printing methods. (Hösel, 2013).

In this work a standard amine based polymer was used as electron transport layer (ETL), the P3HT:PC[60]BM blend as active layer (AL) and the conducting polymer polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) as hole transport layer (HTL). An inverted OPV structure was prepared via slot-die coating with layers deposited in a PET substrate coated with indium tin oxide/metal/indium tin oxide (IMI). The six strips coated via R2R were serially connected by a silver top electrode deposited by flatbed screen printing process. 21.6 cm^2 active area modules (3x10 cm samples) were prepared.

2. MATERIALS AND METHOD

Electron transport, active and hole transport layers were slot-die coated in a R2R machine using an IMI-coated PET substrate. P3HT:PC[60]BM polymer blend 1:0.8 was used as AL and PEDOT: PSS 450 nm-thick as HTL. An inverted structure was prepared (Fig. 4) and modules with and active area of 21.6 cm^2 (6 cells serially connected) finished by flatbed screen printing process using Ag paste.

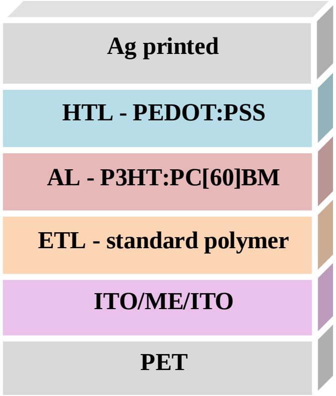
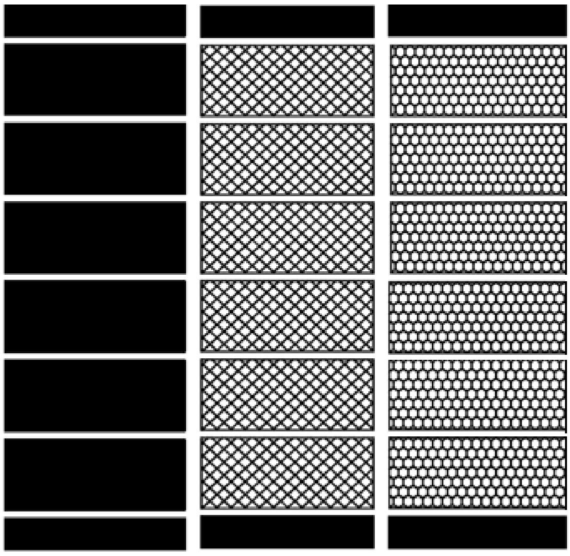


Figure 4 - Module architecture used in this work.

Polyester screens from two different suppliers (I and II) were tested in order to evaluate Ag printed lines quality. Samples were checked under the optical microscope and lines width and height measured using a profilometer Bruker, DektakXT Stylus.

Three different top contact configurations tested: solid, grid and honeycomb (Fig. 5). Additionally, two different Ag paste suppliers (A and B) were evaluated. Paste B is 20.0 % less expensive than A and seems to be less hazardous due to the change of the solvent inside. After screen printing all samples were dried at the same temperature inside ovens and the drying time was studied. 5, 10 and 15 minutes tested.

All modules were measured at room temperature in ambient air but under nitrogen-flow. A solar simulator model WXS-156S-10, AM 1.5G with illumination of 100 mW/cm² was used to measure current density-voltage (J-V) curves.



(a) (b) (c)

Figure 5 - Modules with (a) solid, (b) grid and (c) honeycomb top contact configuration.

The encapsulation used a multilayer of PET barrier films with a water vapor transmission rate in the order of 10^{-3} g/cm^{2}day, glued together thanks to use of an UV-curable adhesive with barrier properties. Photovoltaic performance compared before and after encapsulation.

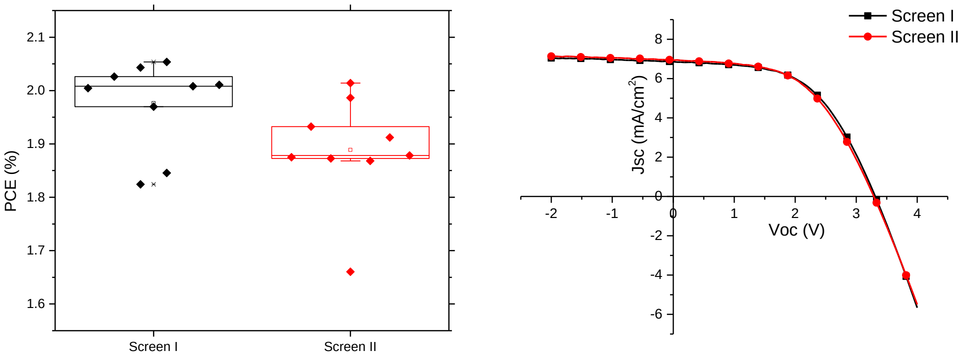
For lifetime investigation encapsulated modules were evaluated in an outdoor test in an open circuit (ISOS-O-1) and in a dump heat test (ISOS-D-3) inside a climate chamber at 65 °C and 85 % of relative humidity

3. RESULTS AND DISCUSSION

3.1 Performance analysis

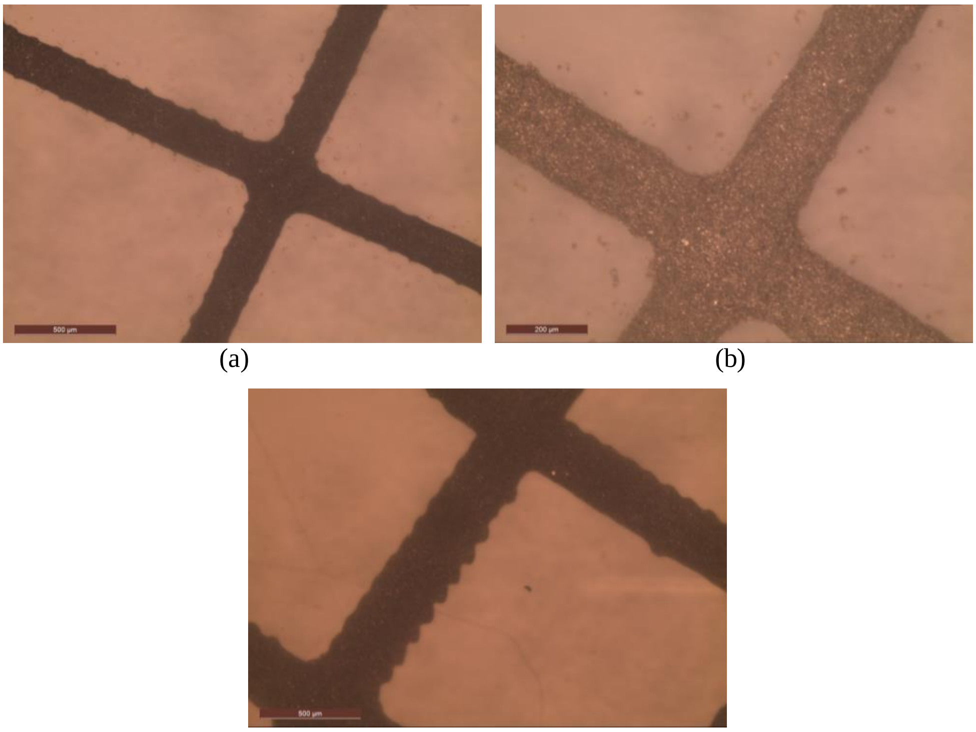
Samples printed with screen II showed slightly lower performance than samples prepared with screen I (Fig. 6a). However, the best modules (efficiency around of 2.0 %) for both conditions showed comparable results (Fig. 6a). The best Ag line definition achieved when screen II was used (Fig. 7a). However, some spots close to the printed lines were observed under the microscope (Fig. 7b). These spots might affect module performance by increasing the series resistance (Rs). They could be connected to the quality of the screen manufacturing process. Printed lines definition might be improved using metal mesh screens and in that case the performance may increase due to a better electronic collection. However, metal mesh screens are more expensive than polymer screens, which make them more suitable for production lines.

Line width values achieved for both screens above the reference value (between 150 and 170 µm). However, in terms of height the screen II provided values as expected and the screen I values below the reference (between 10 and 15 µm). Profilometer results are summarized in Tab. 1.



(a) (b)

Figure 6 - (a) Power conversion efficiency (PCE) graphs for samples printed with screens I and II and (b) the best modules I-V curves.



(a) (b)

(c)

Figure 7 - Optical microscope images of Ag printed lines using (a) Screen II (5x magnification) , (b) Screen II (10x magnification) , (c) Screen I (5x magnification).

Table 1 - Profilometer results for Ag printed lines using screens I and II.

Supplier	**Line width (μm)**	**Line height (μm)**
I	230.3 ± 25.36	8.46 ± 0.21
II	268.9 ± 31.20	13.7 ± 0.28

Solid samples have a big silver area on top of HTL, facilitating the charges collection. However, the mirror effect, which improves modules performance by reflection of the light, is very small for theses samples in comparison to the ones with evaporated silver. Photovoltaic performance of grid and solid samples prepared with Ag paste A and B are presented in Fig. 8. As expected, solid samples showed short circuit current density (Jsc) higher than grid samples.

When paste B was used the Rs was slightly increased and fill factor (FF) decreased. Rs values indicated that the solvent inside paste B is different from the solvent in paste A, which might have an effect on silver particles distribution. Another possible justification for this variation is the quantity and the quality of the silver particle involved in terms of dimension and shape. The solvent change might be an advantage in terms of chemical risk (unpleasant smelling). However, the highest Rs values may indicate that this paste needs longer time and/or higher temperature during drying process.

Overall, grid and solid samples printed with paste B showed similar performance (mean around of 2.10 %). Solid samples printed with paste A had performance slightly higher than grid samples. No differences between grid and solid samples printed with pastes A and B found.

Modules transparency improved by use of the grid pattern, which is an advantage in terms of OPV applications.

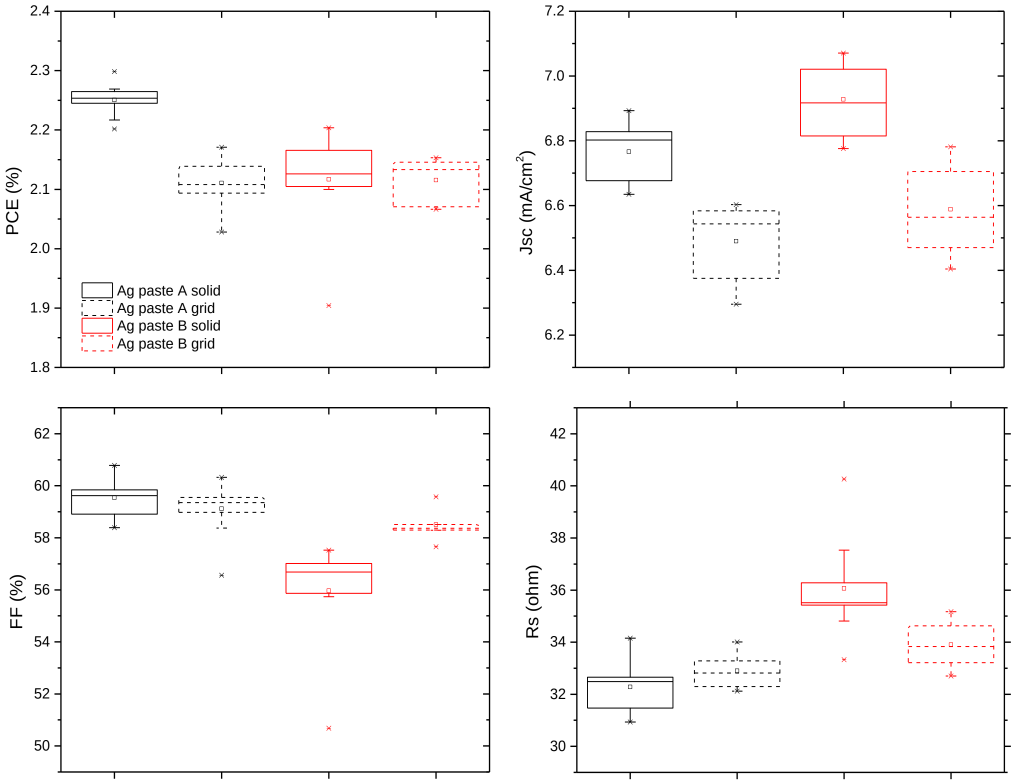


Figure 8 - Photovoltaic performance of grid and solid samples prepared with Ag paste A and B

As the Rs values indicated that paste B might require longer drying time during the process, grid and solid samples printed with this paste were evaluated in three different drying conditions: 5, 10 and 15 minutes. The drying temperature was maintained for all tested conditions and the photovoltaic performance analyzed (Fig. 9). The best results for grid samples were found for 5 minutes drying. However, small differences were observed among the three conditions. No difference between 5 and 10 minutes drying for solid samples, but a small drop of performance observed when 15 minutes drying time was used. Drop of FF observed for samples dried for 15 minutes for both top contact configurations. Results indicated that longer drying didn’t help performance and should be avoided for both kinds of samples.

In order to improve OPV modules transparency, grid and honeycomb samples were prepared and compared in terms of photovoltaic performance (Fig. 10). Theoretically, honeycomb is the geometry figure that allows a large covered area with silver with a less amount of material. However, samples analyzed demonstrated that the amount of silver used for grid and honeycomb samples is the same. Thus, there isn’t advantage in terms of the usage of silver.

Additionally, printed lines definition using polyester screens is a challenge and in the case of honeycomb pattern is hard to keep the proper image, which makes the process more critical. In that case, the use of metal mesh screens might improve the quality of the process. In terms of performance, grid and honeycomb samples showed very similar results. Honeycomb samples showed Jsc values slightly higher than grid samples, but on the other hand had low FF values.

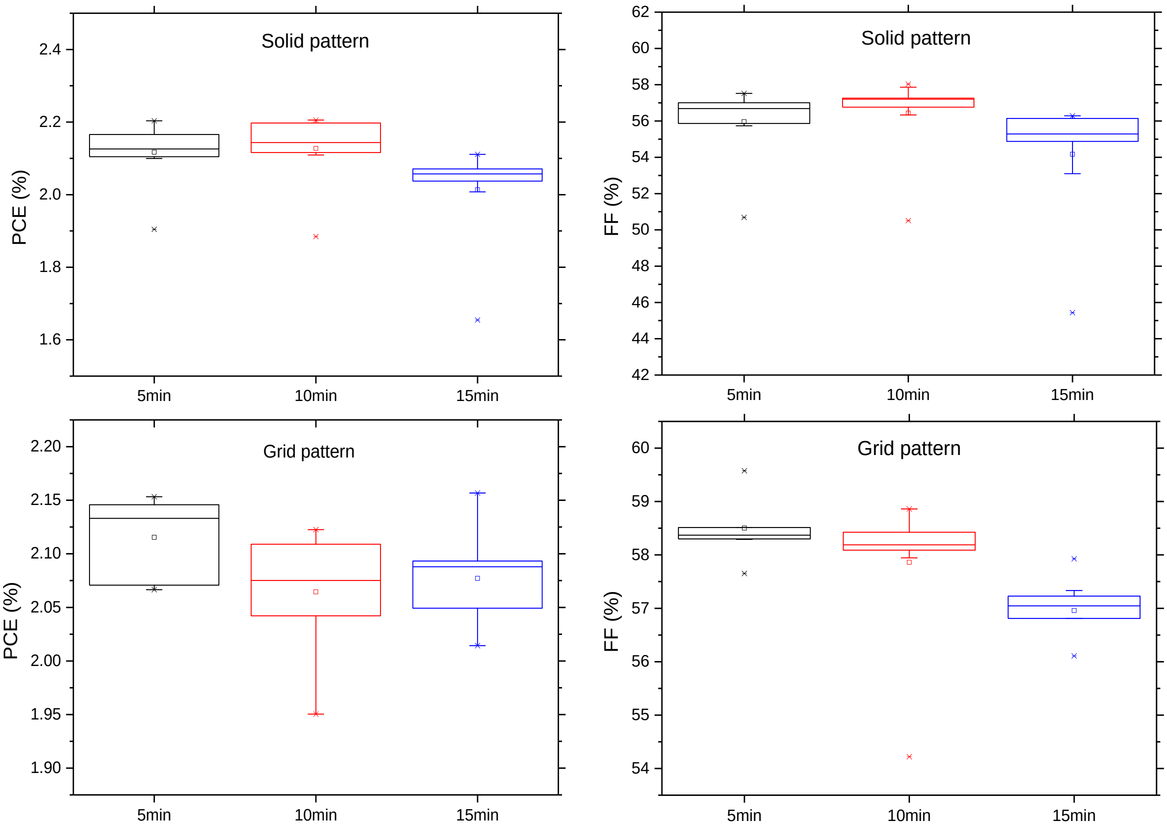


Figure 9 - Photovoltaic performance of grid and solid samples dried for 5, 10 and 15 minutes.

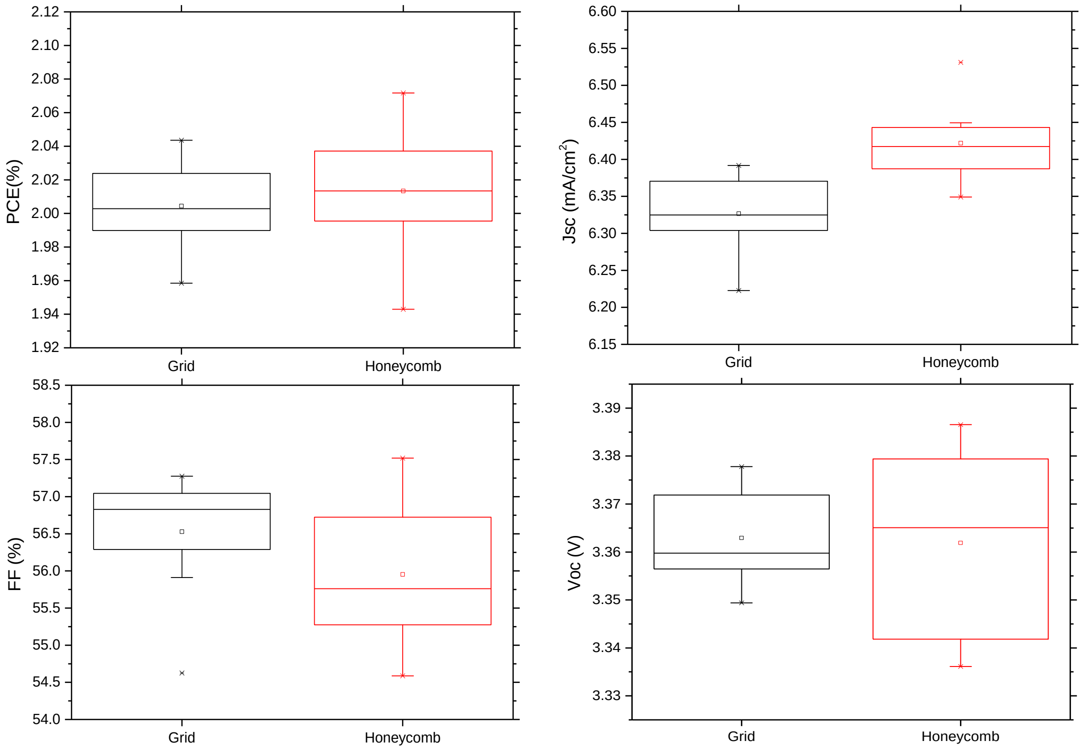
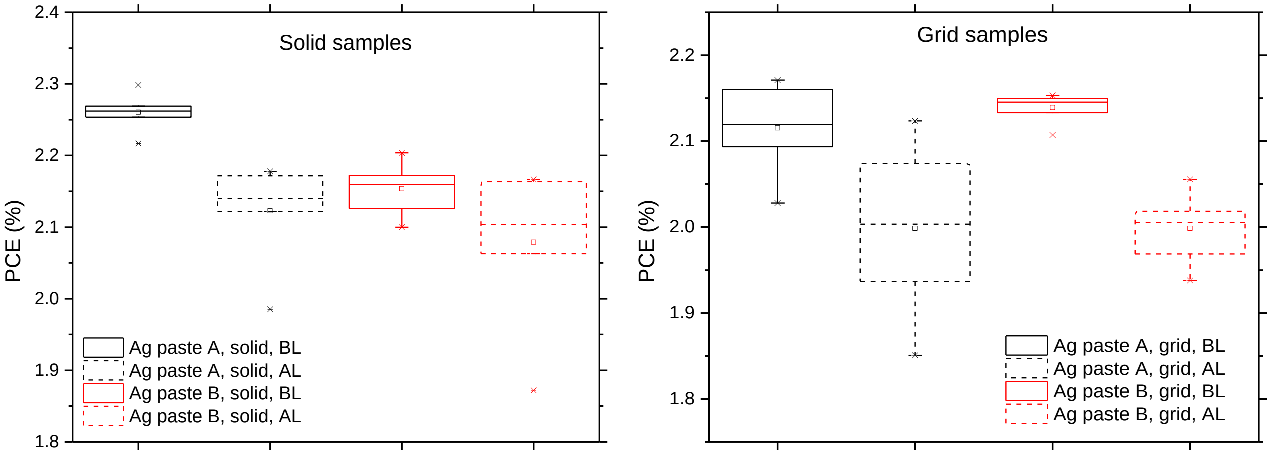


Figure 10 - Photovoltaic performance of grid and honeycomb samples.

3.2 Lifetime study

The best samples were selected for encapsulation in order to have the lifetime studied. All samples were laminated in a R2R machine using a barrier film PET based with a water vapor transmission rate in the order of 10^{-3} g/cm^{2}day. As adhesive an UV-curable epoxy resin with barrier properties was used.

After encapsulation samples were measured in air under a solar simulator without nitrogen. Power conversion efficiency was decreased by 5.0 %, as shown in Fig. 11, which is a standard drop for this kind of samples. The drop of performance is mainly connected to the transmission of the barrier film. Similar results after encapsulation for both silver pastes tested were found.

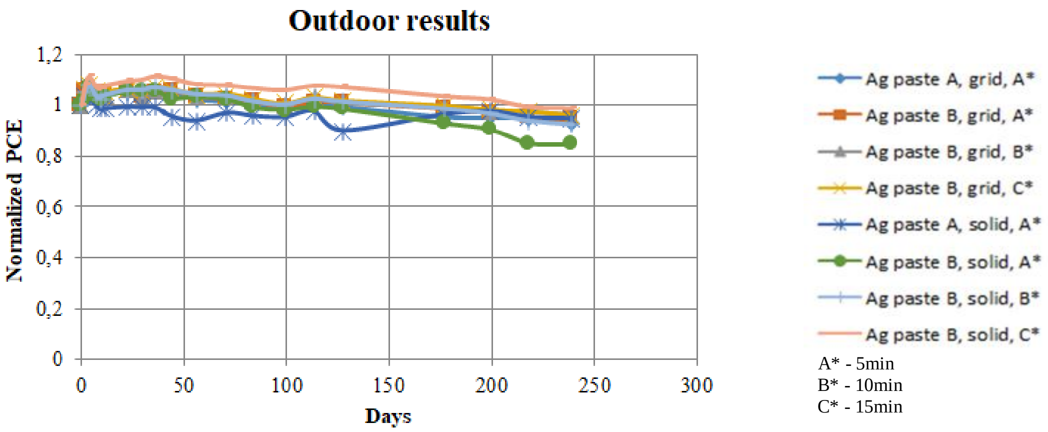


(a) (b)

*BL – before lamination ; AL – after lamination

Figure 11 - PCE results for (a) solid and (grid) samples after encapsulation.

For lifetime investigation encapsulated modules were evaluated under outdoor tests in an open circuit (ISOS-O-1). Results, Fig. 12, demonstrated the stability of the samples that remained above T80 over 200 days. Solid samples printed with paste A had results slightly lower than others. However, overall, all samples showed similar results on outdoor test.



A* - 5min
B* - 10min
C* - 15min

Figure 12 - Normalized PCE results of outdoor tests.

Samples were also tested inside of a climate chamber at 65°C and 85% of relative humidity (ISOS-D-3). Results presented in Fig.13. Solid samples printed with paste B had the performance decreased faster than grid prepared with the same Ag paste. This condition could be justified by the higher amount of the silver and surface involved creating higher probability of local defect on the long term. The best results found for samples printed with paste A using solid and grid top configurations. Overall, samples achieved the T80 after 1000 hours inside the climate chamber. No significant differences found for the different silver drying time tested.

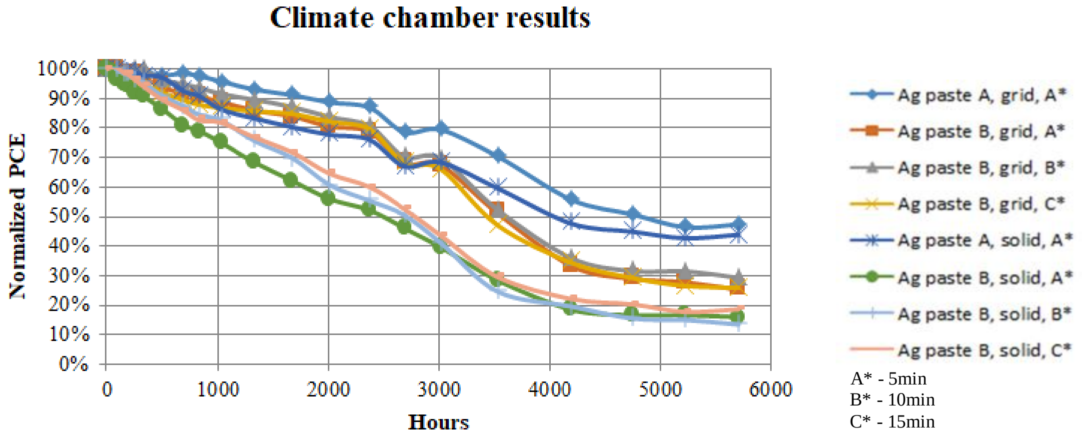


Figure 13 - Normalized PCE results of climate chamber (65°C / 85% relative humidity) tests.

4. CONCLUSIONS

The best line definition found when screen II was used. However, the spots observed close to the printed lines should be an issue, which have to be further investigated. Despite the lines definition, the best results were found when screen I was used. Screen II manufacturer might be a second screen supplier. However, technical aspects regarding the printed lines quality still need to be discussed.

Grid and honeycomb top contacts allow OPV modules transparency improvements with comparable performance with solid samples. However, grid samples seem to be more suitable as silver pattern due to the quality of printed lines and ease of the process. Honeycomb lines printing might require metal mesh screens for better quality.

Specific silver drying time should be selected in order to avoid the drop of the performance. Results indicated that drying times between 5 and 10 minutes provide the best results.

Encapsulation process using flexible barrier film was successfully done. Performance drop was around of 5.0 % after encapsulation, which might be considered standard for this material and this kind of process.

Comparable performance for grid samples printed with pastes A and B. As paste B is less expensive than A and seems to have a different solvent inside, it might be considered as a second Ag supplier. However, LT should be further investigated, since the preliminary results showed lower stability for samples printed with paste B in comparison to paste A.

Acknowledgments

This work was supported by the department of Organic Electronics of CSEM Brasil located in Belo Horizonte, under supervision of Dr. Diego Bagnis. CSEM Brasil is a private and non-profit center for applied research, which has by institutional mission, among others, performs activities of basic and applied research of scientific or technological character, as well as technological development. The authors declare no conflict of interest.

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