



Lasers in Manufacturing Conference 2021

Solvent evaporation and annealing of solution-processed organic materials by laser irradiation on flexible substrates

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Abstract

The market for flexible, printed and organic electronics is rapidly growing. The production is often based on wet-chemical processes and the residual solvent needs to be removed. Conventional methods for solvent evaporation or annealing of functional layers in roll-to-roll processing are circulating-air- or infrared-dryers. These methods require a relatively large drying section and entail a long exposure time at elevated temperatures for the flexible substrates. By utilizing a diodelaser as heating source the installation space and especially the exposure time at elevated temperatures could be minimized.

A LIMO line laser system (450 W, 980 nm) was used to investigate the substitution of conventional drying/ annealing methods on a lab scale (laser line FWHM: 12,22x0,06 mm²) for organic photovoltaic cells resulting in comparable power conversion efficiencies to conventional methods at processing speeds of 1m/min. These results are expected to be transferred from the lab scale to a R2R-system.

Keywords: laser drying; laser annealing; organic electronics; transparent materials; roll-to-roll processing

1. Introduction

The market for flexible, printed and organic electronics as well as their possible applications is rapidly growing. The production is often based on wet-chemical processes and the residual solvent needs to be removed from the functional layer material. Conventional methods for material drying or solvent evaporation

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in roll-to-roll (R2R-) processing are circulating-air-dryers or infrared-dryers. These methods require a relatively large drying section and entail a long exposure time at elevated temperatures for the flexible substrates, which exhibit relatively poor thermal and mechanical properties. By utilizing a diode-laser as heating source installation space and especially the exposure time at elevated temperatures could be minimized. Additionally, to the necessary solvent evaporation certain materials might need a heat treatment to achieve a specific molecular structure or crystallization, such as the photoactive layer in organic photovoltaic (OPV) cells studied in this work.

Within the project "PhotonFlex" a diode line laser module was used to investigate the substitution of conventional drying and annealing methods on a lab scale (laser linewidth SA: 12mm), where commonly a hotplate is used for solvent evaporation and annealing.

The general structure of the used layer stack consists of substrate/ transparent electrode/ electron transport layer (ETL)/ photoactive layer (PAL)/ hole transport layer (HTL)/ top electrode. All applied layers have resulting dry thicknesses in the sub- μ m range. ETL, PAL and HTL were processed from solution and processing windows for each individual layer, as well as for the complete stack, were determined. Depending on the PAL-material combination an additional step, so called solvent annealing (SA), is necessary to achieve the desired crystallisation. This determines the absorption behaviour of the PAL and therefore the efficiency of the OPV-cell.

2. Materials and methods

2.1. Fabrication of OPV-Cells

OPV-Cells were produced on commercial PET-ITO-substrates by spin coating of the ETL (zinc oxide), PAL (P3HT:PCBM) and HTL (PEDOT:PSS) in ambient atmosphere. The top electrode (silver) was applied by sputtering. Three different heat treatments were carried out for each spin coated layer and an additional heat treatment was carried out for the PAL:

- Conventional:
 - Heating on a hotplate for 10 minutes at 120°C (PAL: 2min at 140°C).
- Laser:
 - Transport to laser system and irradiation at processing speed of 1m/min (see section 2.2).
- No annealing:
 - Samples underwent same steps as laser-treated samples to exclude any influence of the time period between the application of the next layer.
- Laser & solvent annealing (only PAL):
 Samples were exposed to a chlorobenzene atmosphere for 10 seconds prior to laser annealing.

2.2. Laser annealing

A LIMO line laser system (continuous wave, 450W, 980nm central wavelength, FWHM 12,22x0,06mm²) was used to perform laser annealing. All samples were laser annealed on a motorized stage at a processing speed of 1m/min. To achieve a good PCE of the resulting cell a crystallization of the PAL is necessary. This is a diffusion-driven process and hence a function of time and temperature. Due to the PET-substrate and the organic materials of the PAL, temperature is the limiting factor and power thresholds (see table 1) were

determined to prevent material failure. Values given in table 1 are about 10% smaller than the value when damage was observed the first time.

Table 1. Power- thresholds for the different materials of the layer stack at processing speed of 1m/min

Material	Power threshold [W]	
PET-ITO	115	
PET-ITO/ETL	75	
PET-ITO/ETL/PAL	65	
PET-ITO/ETL/PAL/HTL	30	

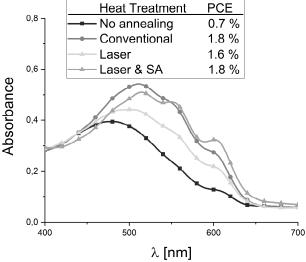
By choosing a working distance 5mm off-focus the line width of the fast axis expands from 0.06mm to almost 1mm, resulting in a lower intensity but enabling a higher total energy input without damaging the sample.

2.3. Characterization

Absorbance measurements of the PAL were carried out on a UV3600+ UV-VIS/NIR spectrophotometer by Shimadzu. As the other layers showed no difference in absorption behavior with or without annealing the quality of the different drying and annealing methods was evaluated by comparing the PCE of the resulting photovoltaic cell. PCE was determined with a Wavelabs Sinus 70 sun simulator and a Keithley 2400 source measurement unit to measure I-V curves.

3. Results and discussion

Fehler! Verweisquelle konnte nicht gefunden werden. shows the absorbance spectra of the PAL after the different heat treatments. While laser annealing initializes the crystallization of the photoactive material (blueshift and increase of the main absorbance peak at 500nm) it gets evident that it is not as effective as the



conventional method on its own.

Fig. 1: Absorbance spectra of PAL with different heat treatments and the respective PCE's. (SA: Solvent annealing)

The additional step of solvent annealing prior to the laser treatment leads to a comparable absorption behavior of the resulting layer with an even more distinct peak at 600nm.

The solvent atmosphere facilitates crystallization of the material as the molecules stay longer in a "mobile phase" [Li et al., 2007]. But solvent annealing does not remove residual solvents, hence an additional drying method is still necessary.

While the absorbance spectra give a direct comparison of the annealing quality of the different heat treatment methods, the drying is qualified indirectly by comparing the PCE's of the whole layer stack for the different heat treatments. The laser heat treatment doubles the efficiency of an untreated sample, the additional solvent annealing or conventional heat treatment leads to even better performances which are comparable (see Table 2).

Table 2. Performance characteristics of the produced solar cells with different heat treatment methods. (Voc: Open circuit voltage; Isc: Short circuit current; FF: Fill Factor; PCE: Power conversion efficiency)

Heat treatment	V _{OC} [V]	I _{SC} [mA]	FF [-]	PCE [%]
No annealing	0.59	0.17	0.35	0.7
Conventional	0.51	0.42	0.44	1.8
Laser	0.57	0.32	0.45	1.5
Laser & solvent annealing	0.54	0.42	0.43	1.8

4. Conclusion

Based on the results the laser treatment of OPV's can be regarded as an equivalent drying method to conventional heating methods. To achieve a good annealing (crystallization) of the PAL the step of solvent annealing must be applied. Regarding cells on a lab scale this is an additional step, but for the R2R-process this can be realized with a relatively small section, where the evaporating solvent is gathered in a chamber to create the necessary atmosphere.

Compared to a conventional drying section the length of the "laser & solvent annealing"- section could be reduced by a factor of five with the additional benefit of shorter exposure times at elevated temperatures. Future works will investigate the transfer from these results on a lab-scale to an industrial R2R-process.

Acknowledgements

This work was supported by "Europäischer Fonds für regionale Entwicklung (EFRE)".

References

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