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Femtosecond laser ablation of ITO/ZnO for thin film solar cells

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Abstract

Femtosecond laser ablation of an Indium tin oxide/Zinc oxide (ITO/ZnO-Nanoparticles) multilayer coated on polyethylene terephthalate (PET) substrate has been investigated. Single pulse ablation thresholds were determined for front side and back side irradiation. The ablation behavior of ITO/ZnO on PET is studied and laser scribing using single-pass and multi-pass patterning is performed and analyzed regarding the usability to serial connect organic solar cells.

Selection and/or peer-review under responsibility of the German Scientific Laser Society (WLT e.V.)

Keywords: laser ablation, ablation threshold, P1 patterning, scribing, femtosecond laser, inverted organic solar cell, ITO/ZnO

1. Motivation / State of the Art

The roll-to-roll production of flexible organic solar cells offers the potential of low cost production, because of the facility to use simple printing techniques like Knife-over edge coating or slot-die coating. An organic solar cell consist of a photo active polymer blend layer (P3HT:PCBM) between two electrode layers (ITO and Al). Figure 1(a) shows the solar cell geometry of the conventional organic solar cell. Regarding roll-to-roll processing, the conventional organic solar cell offers a disadvantage concerning the deposition of the aluminum layer. The deposition of the aluminum demands a vaccum deposition technique. This condition makes it difficult to fulfill the requirements on low cost roll-to-roll production of the organic solar cell using the conventional geometry. A complete solution based organic solar cell production is possible by using the inverted solar cell geometry, shown in figure 1 (b). By considering the

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production of a large scale organic solar cell on roll-to roll production, it is necessary to serially connect the large solar cell to reduce resistive losses [1].

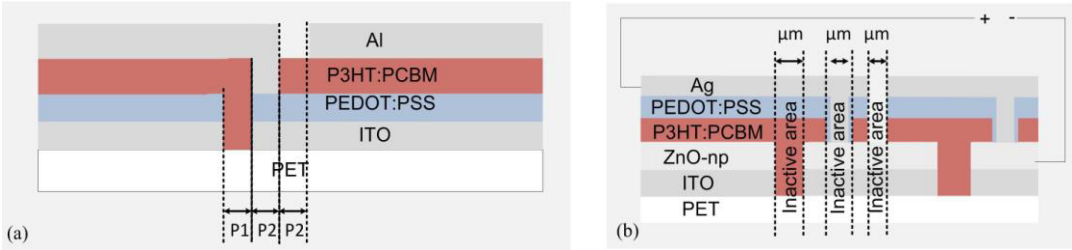

Figure. 1 (a) Conventional organic solar cell; (b) Inverted organic solar cell

The common way to serial connect a large scale organic solar cell considers etching processes [2], macroscopic structuring processes by using mechanical printing technologies and in some cases vacuum deposition techniques using masks. The disadvantage of these techniques is the loss of the active area within the solar cell. To overcome this drawback, research is undertaken to use lasers for serial connection. The structuring steps which are necessary to serial connect the cells with lasers application are commonly described as patterning steps P1, P2 and P3 and refer to the selective laser scribing of the conventional solar cell (Figure 1(a)). The patterning steps P1, P2 and P3 of the inverted solar cell differ from the patterning steps of the conventional cell. For P1 processing it is necessary to apply a laser scribing process by simultaneous ablation of the ITO/ZnO multilayer. Laser scribing processes currently focus on the P1 process regarding the ablation of ITO on PET or glass [3, 4, 5, 6] and in some cases the PEDOT:PSS layer is included [7, 8]. Very good results were found for selective laser scribing of ITO on glass by front side [3] ablation and scribing of ITO on PET by back side [9] ablation. Fewer publications investigate the structuring steps P2 and P3. The applied laser sources for the structuring processes P1, P2 and P3 differ and besides nanosecond lasers, also picosecond and femtosecond laser are used. Within this publication the ablation behaviour of ITO/ZnO on PET for P1 structuring of the inverted solar cell is studied.

2. Experimental

For laser processing, a commercially available ITO on PET foil with a sheet resistance of 50Ω/sq was purchased. The ZnO layer was spin coated on top of the ITO layer starting with a rotational speed of 150rpm for 15s followed by an additional rotation step at 1000rpm for 30s. After coating an annealing step at 80°C for 15 minutes was carried out.

The thickness of each single layer lies at 175µm for PET, 100 nm for ITO and 40 nm for the ZnO layer. The thickness of the spin coated ZnO layer varies within a standard deviation of about ±10nm. The multilayer sample PET/ITO/ZnO was stored for several days at surrounding atmosphere and applied to the laser without any further treatment. The total size of the multilayer counts 25x25 mm.

For laser processing the experimental setup consists of a commercially available Yb-doped fiber laser, Tangerine-fs (Amplitude system). Wavelength is 1030 nm, the pulse duration is set to 400fs and the repetition rate was chosen to be 200 kHz. The Gaussian beam diameter is 7mm after beam expansion and offers an M^2 quality of 1.3. To move the beam on the sample a galvanometric scanner (SCANcube©7) equipped with an f-Theta objective lens and a focal distance of 63mm was used. The sample was positioned on a sample holder, which was equipped with a groove to minimize the influence of back reflection.

For analysis purposes a microscope (Nikon eclipse LV100) a profilometer (AmBios, XP-2) and a scanning electron microscope (LEO 1530, Zeiss) was used.

3. Results and Discussion

3.1 Single-pulse experiments

Single pulse ablation was realized by setting the scanning speed up to 3m/s and the repetition rate to 200 kHz. Back side and front side ablation of ITO/ZnO and ITO on PET was performed. Lowest ablation thresholds were found for front side ablation (figure 2). The ablation threshold fluence of ITO was found to be 0,45 J/cm² and underlies slightly the calculated ablation threshold reported for a picosecond laser source according to [9]. The calculated ablation threshold fluence for front side ablation of ITO/ZnO reveals no relevant difference compared to the front side threshold fluence of ITO using a fs-laser. For back side ablation of ITO and ITO/ZnO higher fluences need to be applied. Higher ablation thresholds for back side ablation of ITO on glass and on PET could also be reported by [3, 9] and [10] using a ps-Laser source. For Glass/ITO and according to [10] the differing ablation threshold fluences for front side and back side ablation are attributed to the relation between the film thickness of the ablated material and the optical penetration depth using ultrashort laser pulses. The back side ablation threshold of ITO within this study is 0,56 J/cm² and the ablation threshold of the multilayer ITO/ZnO is 0,67 J/cm².

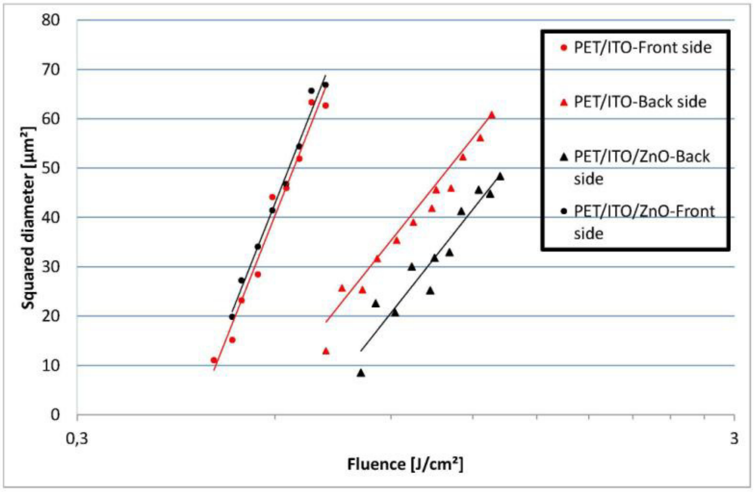

Figure 2: Ablation thresholds of PET/ITO and PET/ITO/ZnO

Regarding the ablation mechanisms of ITO and ITO/ZnO on PET there was no difference between front side and back side irradiation obvious. Figure 3 shows the SEM pictures for the single spot ablation of ITO/ZnO for different fluences applied. At fluences slightly under the ablation threshold of ITO it is possible to ablate the ZnO layer without damaging the underlying ITO layer. Similar to the observation of [11] for ITO the fractured topology of the ZnO crater reveals the photomechanical character on the ablation. This is obvious by observing that incomplete ablation at certain ZnO crater edges results partially in lifted-off ZnO flakes.

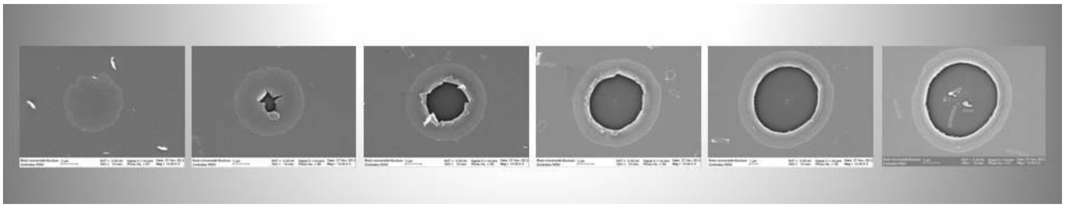

Figure. 3 Single spots at different fluences for PET/ITO/ZnO front side configuration. Applied fluence increases from left to right side within the SEM picture.

Regarding the ablation mechanism of ITO no homogeneous delimitation process could be observed for any fluency applied. The ablation mechanism seems to start with a initially cracking of the ITO followed by delimitation. The delimitation process increases with increasing fluency until the ITO seems to be molten at the edges. Besides molten edges at high fluences there is further a slightly lift-off of the ITO from PET substrate, as outer ring, visible.

Microscopic pictures in figure 4 show that the back side ablation results of ITO within the PET/ITO or PET/ITO/ZnO configuration were similar to the front side ablation results.

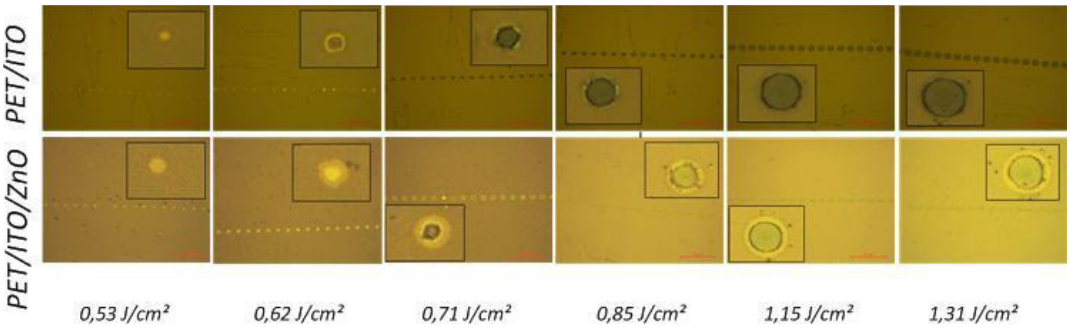

Figure 4: Single spots over fluences for PET/ITO and PET/ITO/ZnO back side configuration.

Compared to [9] where a clean ablation of ITO from PET could be observed by back side ablation with fluencies close to the ablation threshold, no homogeneous ablation of ITO was observed in this study. ITO gets cracked, creates sharp rims at the edges and the ITO gets totally ablated already at low fluencies. Regarding to [10] ablation quality is very sensitive to focus position. Much difference was observed by focus and defocus ablation. So far, an optimization of ablation process could not be found within this study by defocusing. Also the described dependence in [10] regarding the ablation mechanism on the material thickness and the thermal penetration dept was not observed.

3.2 Single-pass scribing experiment

Figure 5 and 6 show the line scribing results for front and back side ablation of PET/ITO and PET/ITO/ZnO. Shown are patterns for different fluencies applied at two different overlapping rates of 30% and 70%. The overlapping rates were chosen here based on single pulse results.

Since there was no clear delamination process observed for single pulse ablation it is reasonable to estimate, that clean line scribing is not reached by using low overlapping rates. For all fluences and overlapping rates applied for single-pass scribing the PET substrate gets damaged, less at fluences close to the threshold fluence. Further, sharp flakes are created in all cases at the edge of the scribed lines. At high overlapping rates the flakes get pushed to the outer side of lines. At low overlap rates the lines look clearer and the flakes stay mostly within the scribed lines. The same scribing behavior regarding PET damage and flake behavior could be observed by [9].

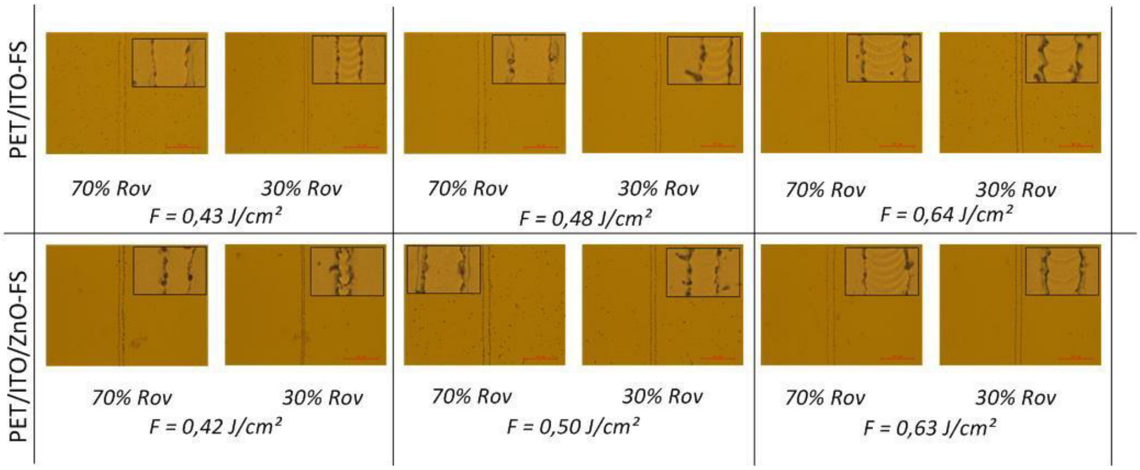

Figure 5: Single-pass scribed lines for PET/ITO and PET/ITO/ZnO front side

For the application of laser scribing process within roll-to-roll production of organic solar cells sharp flakes could lead to a rip-off of the next layer which is applied to the solar cell. Further high flakes could lead to short cuts within the cell. A little damage of PET could probably be tolerated if oxygen diffusion is still avoided and the transparency of the PET does not change. Even regarding the encapsulation process of organic solar cells, it is possible to process a back and front side encapsulation without using the PET substrate itself as oxygen/humidity barrier.

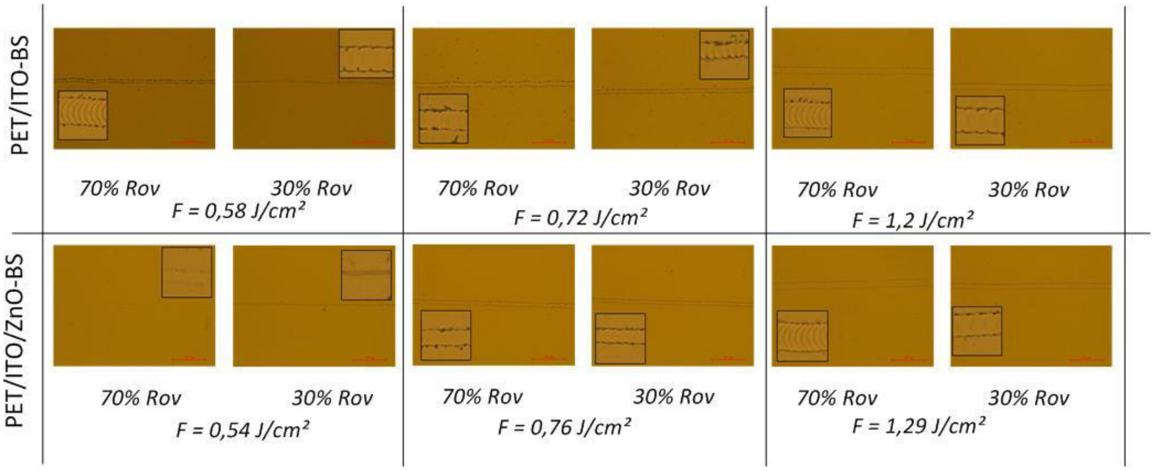

Figure 6: Single-pass scribed lines for PET/ITO and PET/ITO/ZnO back side

3.3 Multi-pass scribing experiments

Based on the results of single-spot and single-pass scribing multi-pass scribing was investigated. Multi-pass scribing offers the opportunity to optimize the requirements on line scribing for serial connection of solar cells by the absence of a clean ablation process. Figure 7 shows microscopic pictures of the multi-pass scribing results for front-side irradiation of ITO/ZnO on PET substrate for an overlap rate of 30%. The quantity of lines scribed increases from (a) to (d) within figure 7.

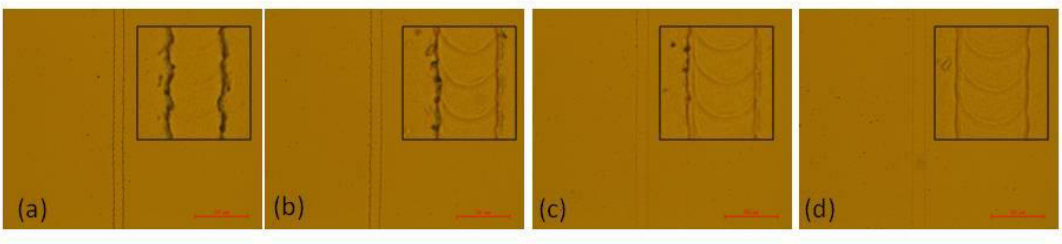

Figure 7: Multi-pass scribed lines of ITO/ZNO front side at a fluence of 0,71 J/cm², 30% Rov : (a) Single-pass, (b) 2-times scribed lines, (c) 5-times scribed lines, (d) 10-times scribed lines

Compared to single-pass ablation (figure 7 (a)) multi-pass ablation (figure 7 (b,c,d)) shows an improvement regarding the requirements of undesirably sharp, high flacks created at the edges of the scribed lines. The applied fluence was chosen relatively high at 0,71J/cm² and resulted in damage of the PET substrate.

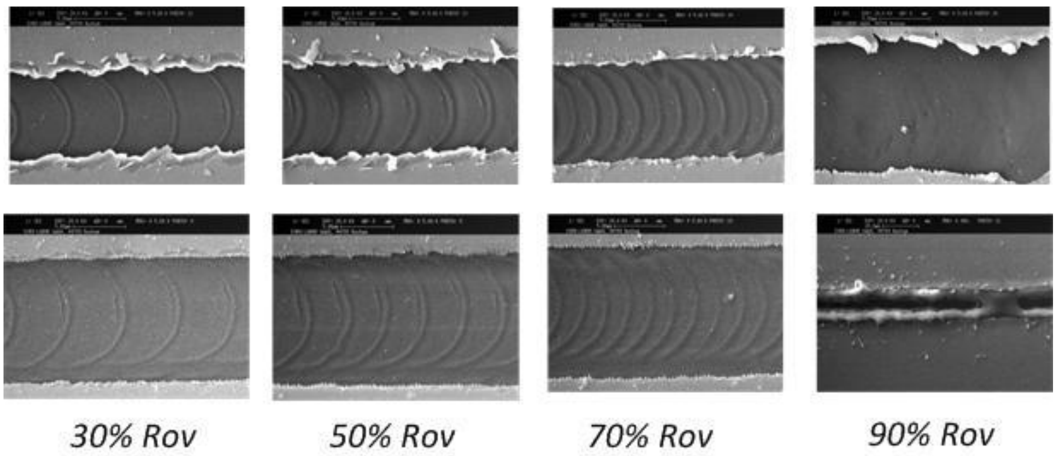

Figure 8: Multi-pass scribed lines of ITO/ZNO fornt side at a fluence of 0,71 J/cm² and different overlapping rates : Single-pass scribed lines (top) , (b) 10-times scribed lines (bottom).

The observations of the microscopic pictures could be confirmed by SEM (Figure 8) and profilometer (figure 9) measurements. SEM show that for high fluencies, high overlap rates and multi-pass ablation, the PET substrat gets totally damaged with no possibility of reaching clean, smooth rims at the edges of the ablated line. For low overlap rates a damage of the PET is also observed but with improved edge quality. According to profilometer measurements, the rim quality at the edges shows a bulge formation with a maximum height

of 80 nm. Since the overlying photoactive layer has a thickness of around 150nm it should be still possible to generate working organic solar cells.
It should be mentioned at this point that the ablation results could differ depending on the pre-treatment of the used sample. The results for plain PET/ITO or PET/ITO/ZNO samples which means the absence of an tempering process could differ from heat treated samples. Regarding undertaken studies for serial connection of organic solar cells with laser application the processing steps for an organic solar cell should always be taken into concern.

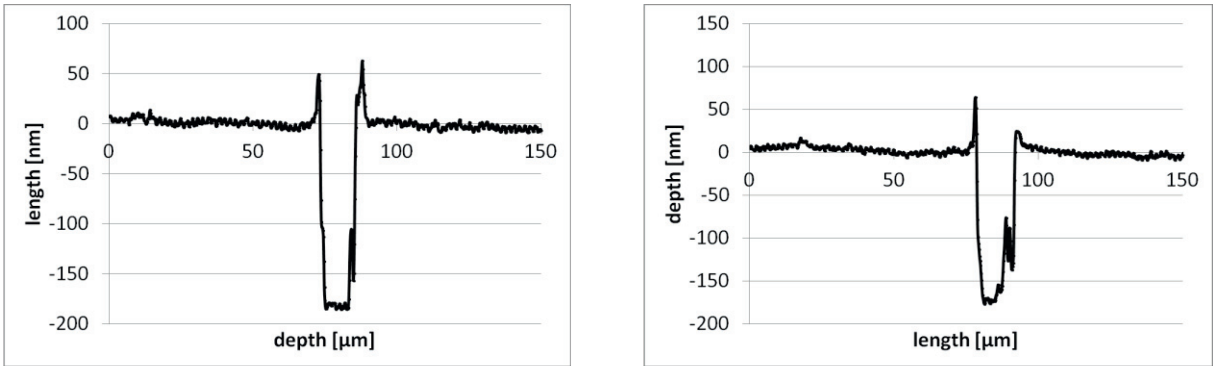

Figure 9: Profilometer measurements of multi-pass scribed lines of ITO/ZNO fornt side at a fluence of 0,71 J/cm² : 10-times scribed lines with 30% Rov (left), 10-times scribed lines with 70% Rov (righ)

4. Conclusion

Investigations have been performed to study the possibility to structuring a multilayer of ITO/ZnO on PET using femtosecond laser source. It has been shown that at given system parameters of 1030nm Wavelength, 400fs pulse duration and a repetition rate of 200 kHz no clean delamination of ITO/ZnO was possible. Based on this results and further investigation of single-pass ablation multi-pass ablation was performed and showed the potential to optimize line scribing for serial connection of organic solar cells by the absence of perfect process conditions.

5. Acknowledgments

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