Laser-induced control of the extent of PbI_2 formation for improved interconnection of perovskite solar cells

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Abstract. Upscaling of the currently still small perovskite solar cell sizes requires monolithic series interconnection of the individual cells and thus a laser patterning of the respective solar cell layers. The underlying ablation mechanisms are investigated and optimal laser parameters and process windows are identified. The use of ns laser pulses generates a larger amount of PbI_2 in the processed area than ps laser pulses. The resulting PbI_2 proved to be disadvantageous for the electrical behavior in the P2 patterning of the absorber layer, but is advantageous for P3 patterning of the back contact. By selecting the proper laser pulse duration, the amount of PbI_2 is controlled and electrical losses are minimized. Applying this knowledge led to mini-module efficiencies of over 19%.

1 Introduction

Novel perovskite solar cells are already achieving efficiencies that are competitive with established technologies such as crystalline Si solar cells. To enable industrial manufacturing, the still small sizes on laboratory scale must be increased to industrially relevant module sizes. For this purpose, a series interconnection of perovskite solar cells must be established to minimize electrical losses. This can be done monolithically by alternating solar cell deposition and the three patterning steps (i.e., P1, P2, P3 for the front contact, absorber and back contact layer, respectively). Preferably lasers are used, due to their precision, reproducibility and low tool wear [1]. Suitable and reliable laser parameters must therefore be specified in order to ensure an interconnection without electrical losses and thus to achieve high module efficiencies. Presently, there are challenges in generating low-resistance P2 patterning lines in the perovskite absorber layer and in providing adequate electrical separation without flaking of the back contact for P3 patterning [2-4].

In this contribution, the formation of PbI_2 during the patterning process itself is investigated, since it was found that PbI_2 impedes low-ohmic series resistances [5], while it could be beneficial for the passivation of defects [6, 7]. This can be helpful to optimize the P3 patterning. To be able to control the PbI_2 formation and to use it in mini-module fabrication, the P2 and P3 patterning and the ablation behavior are systematically investigated with ps and an ns laser pulses.

2 Experimental

The perovskite solar cell samples consist of a layer stack as follows: glass substrate, 140 nm ITO transparent front contact layer, 23 nm SnO_2 electron transport layer, 650 nm triple-cation perovskite absorber layer ($Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})$), 180 nm spiro-OMeTAD hole transport layer, 100 nm Au back contact layer [8, 9].

The samples were patterned using a ns laser source (pulse duration $\tau = 20$ ns, wavelength $\lambda = 532$ nm, maximum pulse energy $E_{p,max} = 31$ µJ, pulse repetition rate PRR = 20 kHz) and a ps laser source ($\tau = 10$ ps, $\lambda = 532$ nm, $E_{p,max} = 65$ µJ, PRR = 50 kHz). To determine the optimal laser parameters for the P2 and P3 patterning, parallel lines with systematically varied laser fluences were prepared. The pulse-to-pulse overlap was about 98% for P2 and about 10% for P3 patterning.

Current density-voltage (j-V) measurements were done to demonstrate the electrical functionality of the P2 and P3 scribe lines and to identify the best working parameters. The scribed lines and their vicinities were examined by scanning electron microscopy (SEM) and by spectrally filtered photoluminescence (PL) imaging with a Becker & Hickl DPS-120 FLIM setup.

3 Results and Discussion

P2 patterning. The electrical functionality of the laser scribed P2 lines was verified by j-V measurements and quantitative analysis of the fill factor of three-segmented 2.2 cm² mini-modules patterned with systematically varied fluences (see Fig. 1). The statistical analysis shows, that the perovskite absorber layers can be patterned (i.e. P2 step) using both laser pulse durations, but the usage of ps laser pulses enables higher fill factors of about 10%.

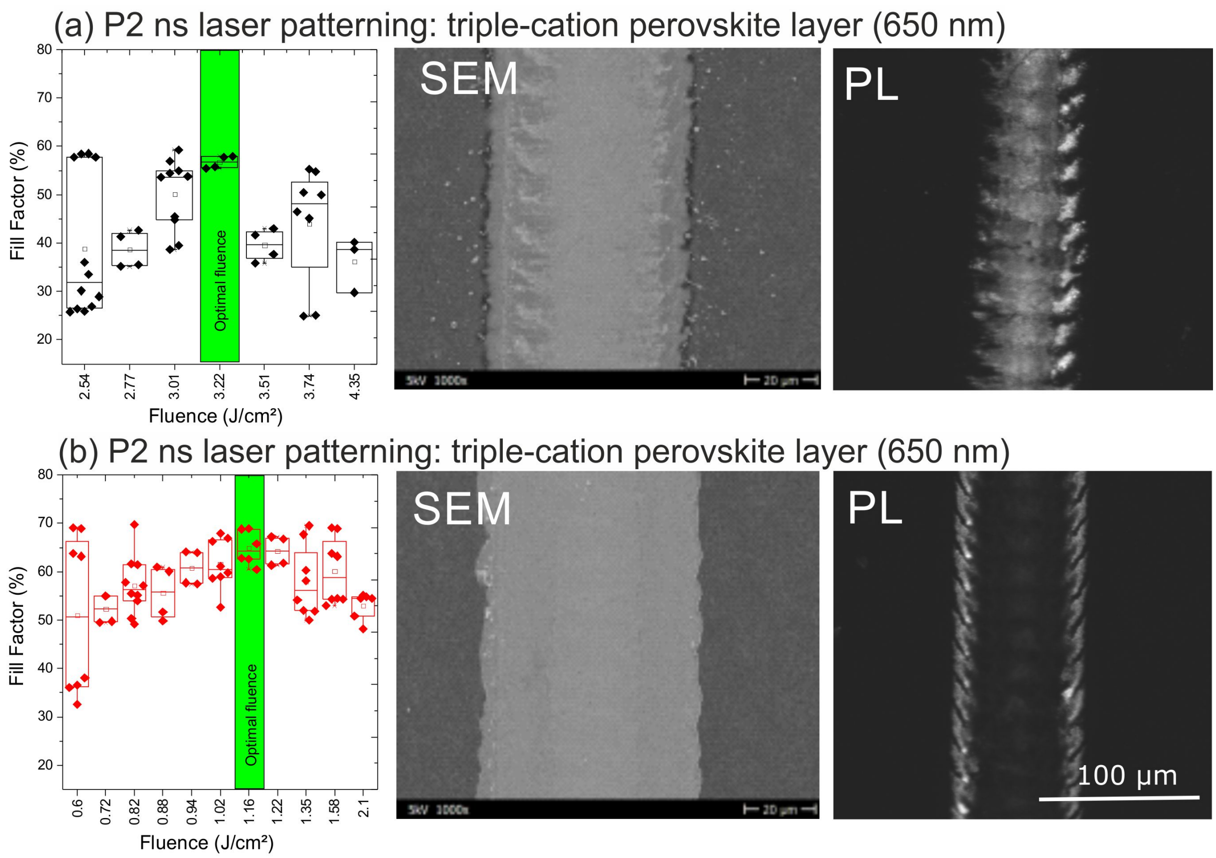

Figure 1: Fill factor as a function of the applied laser fluence for P2 patterning using (a) ns and (b) ps laser pulses. The marked ranges indicate the respective optimal fluences. The SEM and PL images show the area of the P2 scribe lines patterned with optimal laser fluences.

The origin of this better j-V performance is revealed by comparing the morphologies shown in the SEM images. When patterning with ns laser pulses the scribe lines show residual material at the scribe line bottom that can be assigned to PbI_2 [5] and splashes and bubbles at the edges. In contrast, the appearance of the ps laser scribe line, is free of these features and shows a lower amount of PbI_2 at the laser scribe line bottom. Thus, a predominantly thermally driven material ablation process is thus concluded for ns laser patterning, while in the case of ps laser pulses a mechanically, stress-assisted material ablation occurs [9].

The local distribution of the remaining PbI_2 can be seen in the PL images taken with a band-pass filter that transmits the emission of PbI_2. When patterning with ns laser pulses, there is a broad and intense signal from PbI_2 at the scribe line bottom, while the line patterned by ps laser pulses shows a moderate PL signal at the edges, but only very low PL intensity from the scribe line bottom. Apparently, P2 ps laser patterning suppresses PbI_2 formation more effectively, which leads to higher fill factors.

P3 patterning. The investigation of the material removal during P3 patterning by means of ns and ps laser pulses was carried out analogously to the investigation of the P2 patterning. The quality of the P3 patterning has a decisive influence on the efficiency, since this is affected by possible leakage currents (low parallel resistance) as well as by laser-induced damage to the ITO (high series resistance). Figure 2 shows the power conversion efficiencies that were determined from j-V measurements of all prepared 3-segmented mini-modules, patterned by ns and ps laser pulses. It turns out that there are suitable process windows for both pulse durations, though higher efficiencies are achieved when ns laser pulses are used instead of ps laser pulses.

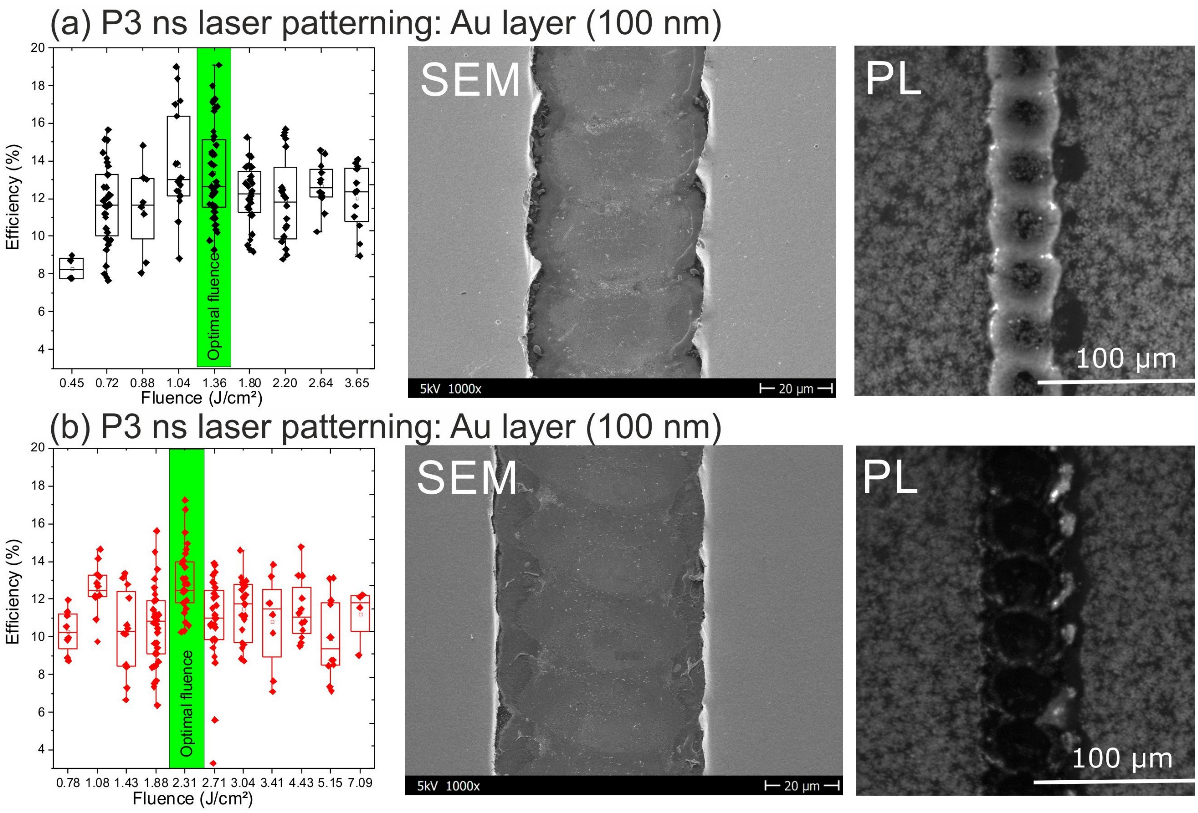

Figure 2: Efficiency as a function of the applied laser fluence for P3 patterning using (a) ns and (b) ps laser pulses. The marked ranges indicate the respective optimal fluences. The SEM and PL images show the area of the P3 scribe lines patterned with optimal laser fluences.

Also in the P3 step, the scribe lines patterned by ns laser pulses show signs of re-solidification and splashes, which are not observed when patterning with ps laser pulses (cf. SEM images). The comparison of both spectrally filtered PL images shows a strong difference between the ns and the ps laser scribed lines. In the case of ns laser pulses an intense PL signal (corresponding to the emission from PbI_2) is observed within the scribed line, in contrast to the image of the scribe line patterned by ps laser pulses, in which there is almost no PL emission of PbI_2.

From this it is concluded that the use of ns laser pulses for P3 patterning generates significantly more PbI_2 within the laser scribe line than it is the case with ps laser pulses. This higher amount of PbI_2 obvisously has a positive effect on the electrical properties of the interconnected cells, which is reflected in higher efficiencies. The reason could be the passivation of defects, an observation that is not made when patterning with ps laser pulses.

4 Summary and conclusion

P2 and P3 laser patterning for monolithic series interconnection of perovskite solar cells was systematically investigated. Suitable laser parameters (fluences) and process windows for processing with both ns and ps laser pulses were identified. When using ns laser pulses a larger amount of PbI_2 is generated in the processed area than when using ps laser pulses, due to the larger thermal impact. The resulting PbI_2 proved to be detrimental for the result of the P2 patterning, but advantageous for P3 patterning. Thus, for optimized mini-module fabrication, the P2 step was carried out with ps laser pulses, while the P3 step was carried out with ns laser pulses. Based on these findings, small mini-modules consisting of three interconnected sub-cells were patterned as follows: ns laser pulses for P2 patterning and ps laser pulses for P3 patterning, each with optimal fluence (cf. marked areas in Figs. 1 and 2). Efficiencies of over 19% and fill factors of 77% were achieved [10].

5 References

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