INFLUENCE OF CONCENTRATION OF PHOSPHORUS DOPANT LIQUID AND PULSE DISTANCE ON PARAMETERS OF LCP SELECTIVE EMITTERS FOR SILICON SOLAR CELLS

Sybille Hopman, Andreas Fell, Matthias Mesec, Sven Kluska, Christoph Fleischmann, Filip Granek, S. W. Glunz
Fraunhofer ISE, Heidenhofstr. 2, D-79110 Freiburg, Germany
Tel: ++49-761-4588-5737, Fax: ++49-761-4588-9250, email: sybille.hopman@ise.fraunhofer.de

ABSTRACT: In this paper newest results concerning n-type Laser Chemical Processing (LCP) doping for varying laser and liquid parameters will be presented with regard to sheet resistance, contact resistance and cell efficiency. In the first part of the paper the influence of dopant concentration reduction is investigated by using a TLM structure. Additionally the pulse energies are varied for different pulse distances to find optimum doping parameters. It is demonstrated that the dopant concentration of the dopant source can be strongly reduced and that for all tested pulse energies an optimal pulse distance exists. To verify if these results are suitable for solar cell production selected laser parameters were tested on a 30×60 mm² screen-printed solar cell structure. An efficiency improvement of 0.4 %abs is achieved for cells with LCP selective emitter in comparison to reference cells without selective emitter under the metal fingers.
Keywords: Laser Chemical Processing, laser processing, selective emitter, diffusion, doping, screen printing.

1 INTRODUCTION

Within our group intensive investigations on laser doping with Laser Chemical Processing (LCP) have been done [1, 2]. This method combines a laser with a liquid doping source which acts as a liquid laser guide. At the PVSEC in Hamburg 2009 [3] a first laser parameter study was presented with the result that better solar cell performances were achieved with low laser fluences.

In this paper the investigation of the most important parameters for the LCP doping process being phosphorus acid concentration, pulse energy and pulse overlap are discussed. These parameters have a major impact on the process costs and processing time of the LCP selective emitter formation. Therefore especially for an industrial realization of this process it is of particular importance to (a) understand the impact of the above mentioned parameters on the quality of the achieved doping and (b) optimize these factors with respect to process quality, costs and processing time.

Process parameter optimization using solar cell structures is time and resources consuming. Therefore a faster method has to be found to get a faster response of trends. A simple TLM structure where contact and sheet resistances of the individual LCP doped lines can be measured on the same sample was proposed by Rodofili et al. [4]. This structure was used to determine if concentration of the dopant source (here phosphoric acid H_3PO_4) can be reduced significantly and if also high process speeds are realistic with the LCP doping.

In parallel also screen-printed solar cells with selected laser parameters are processed and compared to references without a LCP emitter. This was done to find out if the TLM results are suitable for solar cell application and to show the efficiency improvement by using a selective emitter.

2 PARAMETER VARIATION ON TLM SAMPLES

2.1 Sample preparation with evaporated TiPdAg contacts

4 inch FZ(B) wafers with 0.5 Ω cm base resistivity and a dry thermal oxide on the front side with a thickness of 105 nm are used for the variations of the phosphoric acid concentration and pulse energy / distance. Phosphoric acid concentration was varied from low to high concentration: The highest concentration 4 was diluted at different ratios. Concentration 1 and 2 are low concentrated and concentration 3 has a medium concentration. In all studied LCP parameters a laser with a wavelength of 532 nm was applied. The applied pulse energy, repetition rate and pulse distance was the same for all concentrations. Several LCP laser grooves were processed on the wafer parallel to each other without having contact. Between the doped laser grooves a small stripe with an oxide layer is left. Perpendicular to the laser groove structure TiPdAg metal fingers were evaporated after a photolithography masking step. After a tempering step at 300 °C for 15 min the metal fingers were thickened by light induced plating [5] and the TLM structures were cut out with a chip saw. By performing TLM measurements on this structure it is possible to obtain the sheet resistance R_{sh} and the specific contact resistance ρ_c of the LCP grooves.

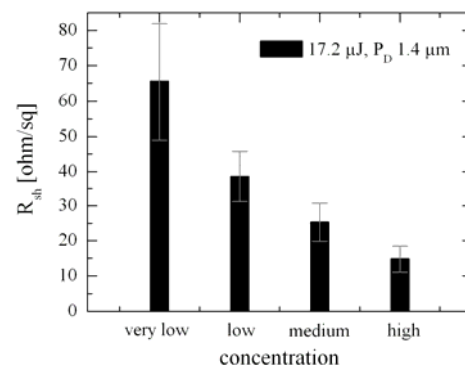### 2.2 Impact of the phosphoric acid concentration

Figure 1: Sheet resistance R_{sh} plotted versus concentration of phosphoric acid (H_3PO_4) applied as a liquid medium in the LCP doping process.

Figure 1 shows that the sheet resistance decreases rapidly with the increase of concentration of phosphoric acid from low to medium concentrated. Concentration 3 still achieves low sheet resistances which satisfy the

requirements for a good contact resistance between metal and highly doped selective emitter. The lowest contact resistance was achieved with the highest concentration 4 reaching 15 Ω/sq.

2.3 Impact of the pulse energy and pulse distance

The sheet resistance results for increasing pulse distances and different pulse energies are plotted in figure 2. Three main effects can be seen in this diagram: 1) For all of the applied pulse energies an optimal pulse distance exists with a minimum sheet resistance. 2) With increasing pulse energy the minimum of the curves shifts towards higher pulse distances and the sheet resistance saturates to a certain value between $25 - 28$ Ω/sq. The practical importance of this observation is that it should be possible to achieve good LCP doping properties even at very high pulse distance, which could result in a significant increase of the processing speed. 3) Starting from the minimum of the curves R_{sh} increases with decreasing pulse distance.

The shift of the minimum can be explained by an increasing of pulse diameter with rising pulse energy. Therefore to achieve a sufficient overlap for low pulse energy also a lower pulse distance is necessary in comparison to higher pulse energies.

The rising sheet resistance with decreasing pulse distance can be explained by an inhomogeneous doping quality within single laser pulse craters due to evaporation and melt removal by the liquid jet which becomes dominant at higher pulse energies. The quality of doping seems to be changing across the groove. Whereas for small pulse distances only the rime zone of single laser pulses contribute to the contact formation, for high pulse distances also the inner part of the single laser pulses make contact to the metal. It is assumed that the rim zones have a higher R_{sh} than the inner zone because of melt removal by the liquid jet momentum and melt expulsion by the recoil pressure of the evaporation which affects the doping quality negatively [6]. Thus for low pulse distances where the rime zone dominates the laser line, R_{sh} is higher.
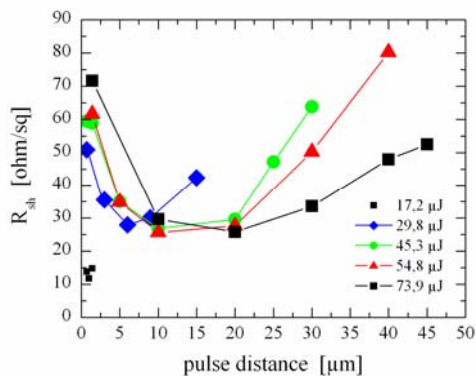

Figure 2: Sheet resistance results of pulse energy variation plotted against pulse distance. Phosphoric acid with a high concentration was applied in this variation.

However it has to be mentioned that the sheet resistance values are calculated using the measured average line width. Varies the laser line as it is the case

for high pulse distances the calculated sheet resistance is higher than the actual average sheet resistance of the line because the narrow parts of the line contribute more to the total resistance than the wider parts. Therefore the calculated value can be regarded as an upper limit for the actual average sheet resistance. The difference between the actual average sheet resistance and the calculated sheet resistance does not affect the conclusions in this paper.

In table 1 the contact resistances are listed for all pulse energies in each case for the minimum sheet resistance.

Table 1: Obtained specific contact resistances and minimum sheet resistances for different pulse energies.

Pulse energy [µJ]	R_{sh} [Ω/sq]	ρ_c [$\times 10^{-5}\Omega cm^2$]
17.2	11.8	1.5 ± 0.5
29.8	28.0	8.2 ± 2.3
45.3	26.9	5.8 ± 2.1
54.8	25.7	5.0 ± 1.4
73.9	25.8	5.2 ± 1.7

The formation of a homogeneous and not interrupted selective emitter for low pulse energy (17.2 µJ) and low pulse distances (1.4 µm) is demonstrated in figure 3. This picture was received by a 3-dimensional secondary ion mass spectroscopy (SIMS) where a 150×150 µm² area was measured by scanning the LCP sample with an ion beam. Afterwards a line profile along the cutting direction was evaluated. In comparison to the commonly known SIMS the detection limit of the 3-D SIMS at higher concentration of phosphorus. Therefore phosphorus is only detected down to a concentration level of 10^{18}-10^{19} cm⁻³. A highly doped region with concentration of 10^{20} cm⁻³ and above extends 300 nm into the silicon. This region is distributed homogeneously along the whole cutting length which is due to multiple melting and solidification because of the low pulse distance. The 120 µm line profile was molten more than 80 times. Thus a lot of phosphorus atoms are diffused into the silicon which homogenizes the doping profile.
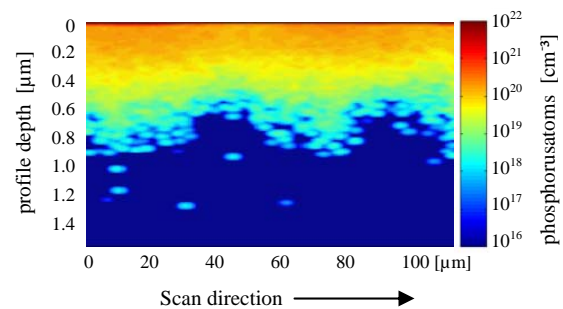

Figure 3: Line profile of a 3-dimensional secondary ion mass spectroscopy (SIMS) measurement for a selective highly doped laser groove with low pulse energy (17.2 µJ) and low pulse distance (1.4 µm). Note that in the graph only a 2-dimensional selection of the 3-dimensional measurement is presented.

3 LCP PARAMETER VARIATION ON SCREEN-PRINTED SOLAR CELLS

From the good sheet resistance results of the applied laser pulse energies shown in the first part, one cannot conclude that these parameters are all applicable for selective emitter formation on solar cells. It is e.g. possible that the pulse energies which still deliver low contact and sheet resistances induce crystal damage into the silicon, which is not considered in this method. To get a complete picture of the doping process it is necessary to investigate defined parameters also on solar cell structures. This will be discussed in the following section.

3.1 Sample preparation for screen-printed solar cells

125×125 mm² monocrystalline silicon wafers with 1-3 Ω cm base resistivities and a random pyramids texture on the front side are used for the variations of the pulse energy and pulse distance. After the 80 Ω/sq diffusion the LCP selective emitter was processed. To see the contact formation improvement also a 55 Ω/sq reference was processed. The phosphoric acid which was used was high concentrated. Comparable to the experiments in the first part a laser with a wavelength of 532 nm was applied. On each wafer four fields with phosphorus doped laser fingers were processed with constant pulse energy and varying pulse distances. The distance of the fingers is 1.8 mm and the same for all fields. One laser processed finger consists of 5 single laser lines with 40 µm distance so that a final laser finger width of 200 µm was obtained. This made sure that the 100 µm screen-printed metal fingers hit the laser grid. In addition to the laser processed fingers also two busbars with a width of 1.5 mm were generated. The busbars were processed for all wafers with the same laser parameters. Then a 70 nm thick SiN$_x$ layer was deposited by PECVD on the front side. Before firing the contacts the front and rear side was screen-printed. It has to be mentioned that no additional firing variation was performed. Afterwards the four fields were cut with a picosecond laser from the rear side to avoid laser damage in the emitter on the front side. The four fields were than further cut out to get two solar cells with one busbar placed in the middle of the cells and with a dimension of 30×60 mm². The references for this experiment were placed on wafers processed with low pulse energies. In this case one of the four fields was not processed with LCP to ensure that the references were also exposed to phosphoric acid and DI-water rinsing comparable to the LCP samples. Because of technical limitations the busbars had to be processed with LCP also on the references. Therefore the difference between reference and LCP solar cells is caused by the different fingers (with and without LCP selective emitter). The solar cells were electrical characterized by measuring the IV-curves. In total 192 cells were processed in this experiment to achieve at least 4 cells per laser parameter. Because of lack of time only one cell per parameter was measured. The final results with statistic will be published elsewhere.

3.2 Experimental results

The results of the IV measurements are shown in figure 4. A low pulse energy (20.7 µJ) and a high pulse energy (31.4 µJ) were chosen for this experiment and with regard to an industrial application of the LCP process only high pulse distances (15-30 µm) were used.

For the low pulse energy all measured cells with varying pulse distances achieve efficiencies higher than the reference value or at least the same. This is a convincing result showing the potential of the selective
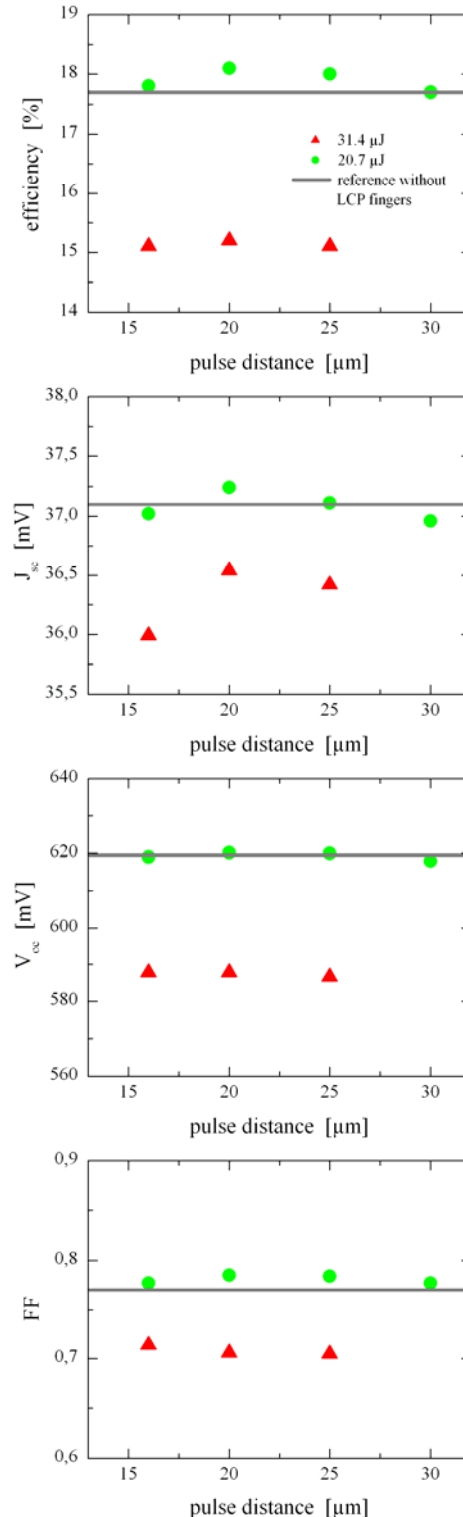

Figure 4: Results of screen-printed solar cells (efficiency, V_{oc}, J_{sc} and FF) for high and low pulse energies plotted against pulse distance.

emitter process since it is the first time that this efficiency improvement can be shown for the LCP n-type doping. Expect for the best LCP solar cell having an efficiency of 18.1 % all the other cells have lower J_{sc} than the reference. The reason for this is that the LCP cells have LCP finger widths twice the metalized finger widths. This area next to the metalized fingers in fact is passivated but do not have a perfect texturization any more because of the laser treatment. The difference becomes even bigger with higher pulse energy. This is due to additional induced laser damage which also reduces J_{sc} by recombination.

V_{oc} is nearly not affected by the low pulse energy but with higher energy all V_{oc} values are reduced about 30 mV. This is also caused by laser induced damage which cannot be compensated by the highly doped emitter. The damage increases the recombination current density J_{02} in the space charge region which reduces V_{oc}. This also influences the efficiencies of the solar cells. All cells processed with high pulse energies do not achieve reference values. They lose more than 2 %abs in efficiency.

Normally the series resistance R_s is improved by an application of the selective emitter structure by reducing the contact resistance which should then be seen in *FF*. This is the case for cells with selective emitter structure and low pulse energy. Better FF results are achieved and the cells are not negatively affected by laser induced damage. In contrast to this the *FF* of the high pulse energy is reduced by higher J_{02} values.

The reference solar cells without LCP selective emitter exhibit *FF* of 77 %. Such a reduced *FF* result is caused by the application of the lowly doped emitter (80 Ω/sq), which results in a higher contact resistance for the screen-printed contacts in comparison to the 55 Ω/sq emitter reaching a *FF* of 78.2 %.

For all diagrams the pulse distances do not play an important role. No significant trend was found.

In table 2 the best LCP screen-printed solar cell result is compared to the reference cells. Nearly the same values for J_{sc} and V_{oc} are obtained for the cells with the 80 Ω/sq emitter. The fill factor and the efficiency exceed the reference values. An efficiency improvement of 0.4 %abs is achieved with the LCP selective emitter because of the better contact formation.

Table 2: Comparison of best LCP screen-printed solar cell with reference cells with two different emitters.

	LCP cell	reference cells	
Emitter	(80 Ω/sq)	(80 Ω/sq)	(55 Ω/sq)
η [%]	18.1	17.7	17.7
V_{oc} [mV]	620.0	619.5	617.5
J_{sc} [mA/cm²]	37.2	37.1	36.6
FF [%]	78.5	77.0	78.2

4 SUMMARY

Important doping parameters like dopant concentration, pulse overlap and pulse energy were investigated in the first section of the paper with TLM structures. Sheet resistance and specific contact resistance

were measured using the same test structure. Concentration variation showed acceptable sheet resistances at medium phosphoric acid concentration which demonstrates that a reduction of phosphoric acid and thus the reduction of the process costs is possible.

The pulse energy and combined pulse distance variations showed three main effects: A minimum of sheet resistance could be found for each pulse energy tested, which moves towards higher pulse distances with increasing pulse energy and the with decreasing pulse distance the sheet resistances increase starting from the curve minimum.

To verify these results and find out which laser parameters are applicable for solar cells with selective emitter selected laser parameters were tested on screen-printed solar cell structures with lowly doped emitter (80 Ω/sq). This showed that for high pulse energies and high pulse distances the laser induced damage dominates the LCP process although good sheet and contact resistances were obtained. As a consequence it is not possible to achieve good solar cell results in this parameter region. In contrast to this an efficiency increase of 0.4 %abs was demonstrated for low pulse energies and high pulse distances. With regard to industrial application this is an important result showing that a fast process is possible.

REFERENCES

[1] D. Kray, A. Fell, S. Hopman et al., "Laser Chemical Processing (LCP) - A versatile tool for microstructuring applications," *Applied Physics A*, vol. 93, pp. 99-103, 2008.

[2] S. Hopman, A. Fell, K. Mayer et al., "Characterization of laser doped silicon wafers with laser chemical processing," presented at Proceedings of the 22nd European Photovoltaic Solar Energy Conference Milan, Italy, 2007.

[3] S. Hopman, A. Fell, K. Mayer et al., "Study on laser parameters for silicon solar cells with LCP selective emitters," presented at Proceedings of the 24th European Photovoltaic Solar Energy Conference, Hamburg, Germany, 2009.

[4] A. Rodofili, S. Hopman, A. Fell et al., "Characterization of doping via laser chemical processing (LCP)," presented at Proceedings of the 24th European Photovoltaic Solar Energy Conference, Hamburg, Germany, 2009.

[5] A. Mette, C. Schetter, D. Wissen et al., "Increasing the efficiency of screen-printed silicon solar cells by light-induced silver plating," presented at Proceedings of the 4th World Conference on

Photovoltaic Energy Conversion, Waikoloa, Hawaii, USA, 2006.

[6] A. Rodofili, S. Hopman, A. Fell et al., "Characterization and analysis of laser-doped lines and single-pulse craters produced by laser chemical processing (LCP)," *Applied Physics A* in preparation.