

## CHARACTERIZATION OF DOPING VIA LASER CHEMICAL PROCESSING (LCP)

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**ABSTRACT:** Laser Chemical Processing (LCP) is a laser-assisted technique that allows for various applications within solar cell fabrication. With appropriate chemicals as dopant media, the LCP process can be used for local doping of silicon wafers. With n-type LCP selective emitters efficiencies exceeding 20% have been achieved. However for further optimization and understanding of the process, a detailed characterization has to be performed. But appropriate methods for such a characterization are not available, yet. This paper presents a test structure that allows to measure the average sheet resistance of single LCP grooves and the specific contact resistance of contacts to LCP grooves. It is used here to study the impact of laser pulse energy on sheet and contact resistance. With phosphoric acid (85 wt%) as dopant a minimum sheet resistance of  $13 \Omega/\square$  and a minimum specific contact resistance of  $2 \times 10^{-5} \Omega\text{cm}^2$  for evaporated contacts have been achieved in the low pulse energy range between 20  $\mu\text{J}$  and 30  $\mu\text{J}$ . The proposed test structure can be used for future characterization of the LCP process focusing on new doping chemicals and for studying the influence of other process parameters.

**Keywords:** c-Si, selective emitter, laser processing, doping, laser chemical processing

## 1 INTRODUCTION

In recent years laser processes have drawn the attention of photovoltaic research, as fast and cost-effective production techniques in solar cell fabrication. Their applications include microstructuring (e.g. edge isolation, opening of passivation layers, buried-contacts solar cells [1]), wafering and doping. Laser doping is commonly investigated as a mean to produce selective emitters and local back surface fields (LBSF), local heavily doped layers underneath the contacts that enhance the performance of the solar cell by lowering the surface recombination and the contact resistance. With Laser-Fired Contacts (LFC), for example, local contacts are formed and at the same time local doping takes place by the diffusion of aluminium into the silicon [2]. Other laser doping processes use a dopant-containing layer on the silicon surface (e.g. [3]). The silicon and the layer are melted by laser irradiation and the dopant diffuses into the liquid silicon.

Laser Chemical Processing (LCP) [4] is a laser technique that allows for several applications in solar cell fabrication including microstructuring, wafering and doping. It was proposed by Willeke and Kray in 2001 [5] and is based on the liquid jet guided laser system LaserMicroJet®, patented and commercialized by the company Synova®. The principle is to couple a laser beam into a laminar liquid jet in which it is guided onto the silicon wafer by total internal reflection at the jet surface. LCP extends the system by the use of different chemicals instead of water as liquid jet. Here the laser beam can thermally treat the material or it can trigger photochemical or thermochemical reactions.

The advantage of LCP over other laser processes is that it is very flexible since the possibility of choosing different chemicals gives rise to a large amount of potential applications. For example: by adding potassium hydroxide to the liquid jet the laser-induced damage can be reduced by etching [4]. For deep cutting [6], appropriate chemicals and solvents can enhance the ablation by means of chemical reactions and by convenient physical properties for the expulsion of the silicon melt.

## 2 LASER-ASSISTED DOPING WITH LCP

This paper deals with the doping applications of LCP. Doping is possible with a liquid jet containing the dopant compound. Here the silicon is melted by laser irradiation and the molecules in the liquid dissociate and diffuse into the silicon melt. Up till now, for n-type doping, phosphoric acid has been used and efficiencies of higher than 20% have been achieved with n-type LCP selective emitters [7]. First encouraging results exist for p-type doping with aluminium [8] and boron.

The lifetime of the silicon melt caused by a single laser pulse is mainly affected by the laser pulse duration and the pulse energy and proved to be a crucial parameter for LCP doping. It not only constitutes the time in which the diffusion can take place but also determines whether the silicon melt can be expelled by the liquid jet. For cutting applications the expulsion by the liquid jet is favourable, but for doping it is detrimental. Consequently LCP doping requires its own laser characteristics. So far the best doping results have been achieved with pulse durations in the nanosecond range.

Although parameters have been found that give good results, there are still many influences that have to be characterized for further optimization and understanding of the process. Such influencing parameters are, e.g. the laser pulse energy, the pulse duration, the wavelength, the pulse overlap, the pressure of the liquid jet, and the concentration of the chemicals in the liquid jet. In addition, different chemicals need to be tested especially for the p-type doping. The standard characterization tool that has been used so far is the production of solar cells. However, this method is expensive and time-consuming and the results are often difficult to interpret since many process steps are involved and it is in practical cases impossible to quantitatively attribute a certain effect to the change in one parameter.

For this reason, an alternative characterization method is presented in this paper that allows for measuring the sheet resistance of doped LCP lines and the specific contact resistance of contacts to such lines.

The presented method is based on the transfer length method and has been used here to characterize the impact of pulse energy variation on n-type doping with phosphoric acid as dopant medium.

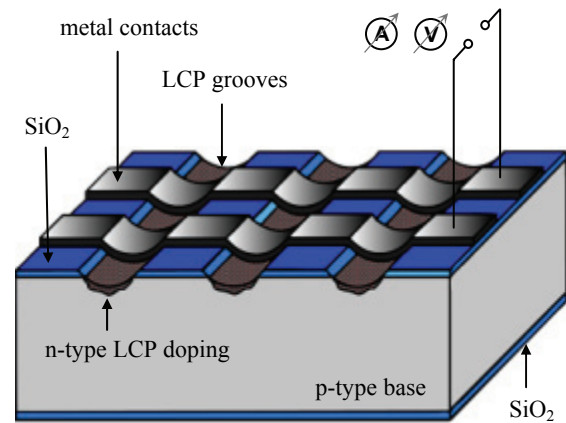
### 3 TEST STRUCTURE

The transfer length method (TLM) [9] is based on the transmission line model, which was independently proposed by Berger [10] as well as by Murrmann and Widmann [11]. The TLM allows for a complete characterization of a contact structure consisting of an emitter with contacts spaced at definite distances. It provides the sheet resistance of the emitter between the contacts, the sheet resistance of the emitter below the contacts and the specific contact resistance of the contacts.

TLM measurements have already been performed on LCP solar cells, by sawing cells into stripes that corresponded to TLM structures. However, this method has several problems. On LCP solar cells, the shape of the contacts is determined by the LCP lines. But the LCP lines do not have very sharp edges and in some cases they can be slightly undulating. This can lead to considerable errors, since the TLM requires a very sharply defined geometry. Furthermore the TLM gives reliable results for the emitter sheet resistance between the contacts but rather imprecise values for the LCP sheet resistance under the contacts especially if the contact geometry is not clearly defined. Another problem is that the full-area emitter diffusion, which is performed before the LCP step, can influence the sheet and contact resistance. But for the characterization of the LCP process it is desirable to measure the sheet and contact resistance that depends only on LCP doping.

Sheet resistance measurements of LCP grooves have already been performed by Hopman [12] with the four point probe method on doped fields, which consisted of many overlapping LCP grooves. However these results depend on the overlap of the grooves and therefore cannot be carried over to single LCP grooves.

These restrictions have been overcome by using the test structure shown in Figure 1. The main features of this structure are as follows: (i) there is no emitter diffusion except the LCP diffusion, which means that there is no emitter between the LCP lines and (ii) the contacts are arranged perpendicular to the LCP grooves. To produce such a structure a silicon wafer with both sides passivated by thermally grown silicon oxide is used. On one side the oxide layer is opened with LCP lines and the silicon in the lines is doped simultaneously. The metal contacts are formed subsequently perpendicular to the LCP grooves without etching the oxide. Thus a contact is formed only in the LCP lines while the base areas between the LCP lines are electrically isolated from the metal contacts. The base doping is chosen such that there is a pn-junction between the base and the LCP doped layer. This ensures that a current flowing from one contact to the next can flow only through the LCP layer. The LCP lines can then be viewed as connected in parallel. On such a structure TLM measurements can be performed if the sum of the LCP line widths is assumed as the TLM contact width. The measurements yield the LCP emitter sheet resistance and the specific contact resistance of the contacts formed in the LCP grooves.



**Figure 1:** Schematic view of the TLM test structure

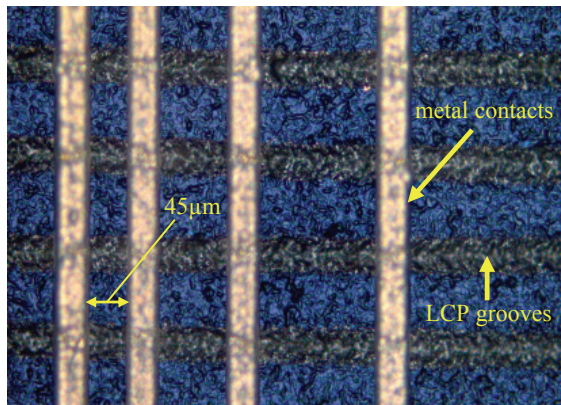
This structure solves the problems mentioned above. Firstly, the LCP doping of separate lines can be studied since the measured values are averaged over many lines that do not overlap. Secondly, there is no emitter other than the LCP emitter. The LCP doping is not influenced by other doping (except base doping in some cases). Thirdly, the shape of the contacts is independent of the shape of the LCP lines. The metallization can, for example, be made photolithographically, which assures straight contacts with sharp edges. Additionally this method facilitates the measurement, because several structures can be produced on one wafer and can be measured without the need to be isolated.

It was not known before if there could be a contact to the base since there was only the LCP emitter. Such a contact would lead to a leakage current through the base. This effect was assumed to occur at the edges of the grooves. To investigate this, two different base materials have been chosen: one heavily doped material exhibiting a low sheet resistance and one lightly doped material with a correspondingly high sheet resistance. A leakage current would result in a lower sheet resistance on the heavily doped material while on the lightly doped material the difference would be less visible.

## 4 EXPERIMENTAL

### 4.1 Sample preparation

As base material, three four inch p-type float zone silicon wafers with a thickness of 250  $\mu\text{m}$  were used. Two wafers (Wafer #1 and #2) had a specific resistance of 0,5  $\Omega\text{cm}$  which corresponds to a sheet resistance of 20  $\Omega/\square$  and their surface was shiny etched, while the third wafer (Wafer #3) had a specific resistance of 10  $\Omega\text{cm}$  which corresponds to a sheet resistance of 400  $\Omega/\square$  and its surface was damage-etched. After a cleaning step the wafers have been thermally oxidized to an oxide thickness of 105 nm. On each wafer fields consisting of parallel LCP grooves with a length of 22,5 mm have been produced with phosphoric acid (85 wt%). A Nd:YVO<sub>4</sub> diode-pumped laser, frequency doubled to 532 nm and with pulse lengths between 10 ns and 15 ns was used. Wafers #1 and #3 contained seven fields but wafer #2 only six. Here the field that was not treated with LCP has been metallized to test whether the oxide was isolating the silicon from the metal. Except for the missing field on wafer #2 all three wafers have



**Figure 2:** The first four out of eight metal contacts of the TLM test structure

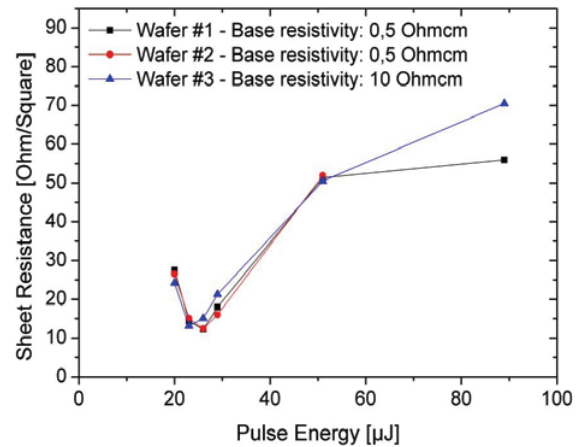
been processed equally with a variation of the pulse energy. The nozzle to produce the liquid jet had a diameter of 60  $\mu\text{m}$ . The pulse frequency was 35 kHz and the axis speed 50 mm/s. The number of lines on each field has been chosen such that the sum of the line widths yielded between 2 mm and 4 mm.

For the metallization 50 nm of titanium, 50 nm of palladium and 100 nm of silver have been evaporated and structured photolithographically using the lift-off approach. The resulting metal contacts with a TLM-length of 12  $\mu\text{m}$  have been subsequently thickened to approximately 30  $\mu\text{m}$  by silver plating. Figure 2 shows a microscope picture of the first four out of eight metal contact fingers positioned perpendicular to the LCP lines. The smallest distance between the metal contacts was 45  $\mu\text{m}$  and the highest 7,5 mm.

#### 4.2 Results

Before the TLM measurements the geometry of the structures had to be measured. The lengths of the contacts and their distances were measured with a microscope. The geometry of the LCP grooves was measured with a confocal microscope also accounting for the bending of the surface in the grooves.

The results of the sheet resistance measurements of all three wafers are shown in Figure 3 without error bars for clarity. Table I shows the values together with the measurement errors. On the fields with the lowest energy (17  $\mu\text{J}$ ) a measurement was not possible. Here the energy was so low that the silicon was hardly melted and the lines were partly interrupted. On all three wafers the



**Figure 3:** Measurement of the sheet resistance of LCP grooves

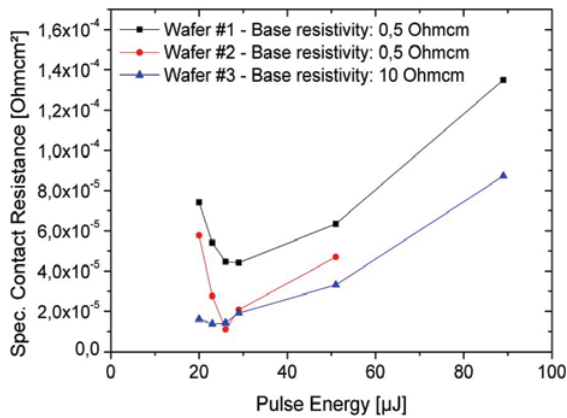
sheet resistance reaches a minimum of  $\sim 13 \Omega/\square$  in the low pulse energy range between 20  $\mu\text{J}$  and 30  $\mu\text{J}$ . For lower energies the sheet resistance increases, probably because the melt lifetime and the melt depth are reduced, which diminishes the doping, and because the lines are not homogeneous or even interrupted, which impairs the current flow. For higher energies the sheet resistance increases again. Obviously, a higher energy does not necessarily mean a better doping result. This result is in good agreement with our solar cell results [13] that achieve their best values in the same energy range where the sheet resistance measured here reaches its minimum and become worse for higher energies.

The results also show that on wafer #3 the minimum is reached at a slightly different energy than on wafer #1 and #2. This is probably due to the damage-etched surface of wafer #3, which has different optical properties than the shiny etched surfaces of wafers #1 and #2. Another difference can be observed for the highest energy (89  $\mu\text{J}$ ) between wafer #1 and wafer #3 (on wafer #2 this energy is missing as discussed above). The sheet resistance on wafer #1 is lower, which could be due to the leakage current mentioned above. However this effect should be confirmed by further measurements.

Figure 4 shows the results for the specific contact resistance from all three samples. Again the error bars are omitted for clarity and all values and measurement errors can be seen in Table II. The specific contact resistance is of the order of magnitude of  $10^{-5} \Omega\text{cm}^2$  to  $10^{-4} \Omega\text{cm}^2$  and follows the same trend as the sheet resistance. There is a minimum in the energy range between 20  $\mu\text{J}$  and 30  $\mu\text{J}$  and the resistance increases for higher energies.

**Table I:** Measured sheet resistance with measurement errors

|          | Pulse energy / $\mu\text{J}$       | 17 | 20   | 23   | 26   | 29   | 51   | 89   |
|----------|------------------------------------|----|------|------|------|------|------|------|
| Wafer #1 | $\rho_{sh} / \Omega/\square$       | -  | 27,6 | 14,4 | 12,2 | 18,0 | 51,3 | 56,0 |
|          | $\delta\rho_{sh} / \Omega/\square$ | -  | 9,9  | 2,6  | 2,4  | 3,0  | 6,9  | 2,0  |
| Wafer #2 | $\rho_{sh} / \Omega/\square$       | -  | 26,5 | 15,1 | 12,4 | 16,0 | 51,9 | -    |
|          | $\delta\rho_{sh} / \Omega/\square$ | -  | 10,0 | 2,5  | 2,5  | 2,3  | 6,5  | -    |
| Wafer #3 | $\rho_{sh} / \Omega/\square$       | -  | 24,2 | 13,1 | 15,1 | 21,3 | 50,5 | 70,5 |
|          | $\delta\rho_{sh} / \Omega/\square$ | -  | 6,2  | 2,8  | 2,9  | 2,7  | 1,9  | 3,0  |



**Figure 4:** Measurement of the specific contact resistance of metal contacts to LCP grooves

The resistance of the metal fingers causes a systematic error which is not accounted for. A correction of this error would lower the contact resistance. Therefore the values shown here have to be viewed as an upper limit for the contact resistance.

## 5 CONCLUSION

The goal of this work was to develop a method for characterization of the local doping of silicon wafers formed using the LCP process. The focus was put on measurement of the sheet resistance of the LCP doping and the contact resistance of metal contacts to LCP grooves.

A test structure for the characterization of the LCP process has been proposed and tested successfully. It can be used for future characterizations mainly for testing new doping chemicals but also for studying the influence of process parameters. With this structure it was for the first time possible to measure the average sheet resistance of single LCP grooves and the specific contact resistance of contacts to LCP grooves independently of other emitter diffusion.

With phosphoric acid (85 wt%) a sheet resistance of  $13 \Omega/\square$  and a specific contact resistance in the range of  $10^{-5} \Omega\text{cm}^2$  -  $10^{-4} \Omega\text{cm}^2$  for evaporated metal contacts have been achieved. For both sheet and contact resistance the minimum values are reached in the low pulse energy range between 20  $\mu\text{J}$  and 30  $\mu\text{J}$  (for a 60  $\mu\text{m}$  nozzle). For lower energies the sheet resistance increases rapidly, probably because of the reduced melt lifetime and melt

depth and because the lines are inhomogeneous or even interrupted, which impairs the current flow. Also the contact resistance increases at very low energies probably again because of the reduced melt lifetime and melt depth and because not all the oxide is opened, which reduces the contact area. The increase in sheet and contact resistance for high energies shows that higher energy does not necessarily mean a better doping result. These measurements confirm former solar cell results, which are best in the low energy range and worsen for higher energies.

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**Table II:** Measured specific contact resistance with measurement errors

| Pulse energy / $\mu\text{J}$ |                                    | 17 | 20                   | 23                   | 26                   | 29                   | 51                   | 89                   |
|------------------------------|------------------------------------|----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Wafer #1                     | $\rho_c / \Omega\text{cm}^2$       | -  | $7,4 \times 10^{-5}$ | $5,4 \times 10^{-5}$ | $4,5 \times 10^{-5}$ | $4,4 \times 10^{-5}$ | $6,4 \times 10^{-5}$ | $1,4 \times 10^{-4}$ |
|                              | $\delta\rho_c / \Omega\text{cm}^2$ | -  | $4,1 \times 10^{-5}$ | $4,3 \times 10^{-5}$ | $2,2 \times 10^{-5}$ | $2,2 \times 10^{-5}$ | $4,6 \times 10^{-5}$ | $1,1 \times 10^{-4}$ |
| Wafer #2                     | $\rho_c / \Omega\text{cm}^2$       | -  | $5,8 \times 10^{-5}$ | $2,8 \times 10^{-5}$ | $1,1 \times 10^{-5}$ | $2,1 \times 10^{-5}$ | $4,7 \times 10^{-5}$ | -                    |
|                              | $\delta\rho_c / \Omega\text{cm}^2$ | -  | $4,9 \times 10^{-5}$ | $1,5 \times 10^{-5}$ | $5 \times 10^{-6}$   | $1,0 \times 10^{-5}$ | $2,1 \times 10^{-5}$ | -                    |
| Wafer #3                     | $\rho_c / \Omega\text{cm}^2$       | -  | $1,6 \times 10^{-5}$ | $1,4 \times 10^{-5}$ | $1,4 \times 10^{-5}$ | $1,9 \times 10^{-5}$ | $3,3 \times 10^{-5}$ | $8,7 \times 10^{-5}$ |
|                              | $\delta\rho_c / \Omega\text{cm}^2$ | -  | $9 \times 10^{-6}$   | $1,0 \times 10^{-5}$ | $6 \times 10^{-6}$   | $1,0 \times 10^{-5}$ | $2,1 \times 10^{-5}$ | $1,3 \times 10^{-4}$ |

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