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PROGRESS IN LASER CHEMICAL PROCESSING (LCP) FOR INNOVATIVE SOLAR CELL MICROSTRUCTURING AND WAFERING APPLICATIONS

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ABSTRACT: In this paper we report progress in Laser Chemical Processing (LCP) wafering and microstructuring applications. The LCP method was formerly known as Laser Chemical Etching (LCE) and has now been extended to further applications as laser doping e.g. Fundamental experiments show that damage-free silicon removal in one single LCP step is possible without the need of damage-etching. Additionally, the wafering proof-of-concept could be obtained in terms of 7 centimeter deep cutting, competitive initial cutting speeds and encouraging low energy consumption compared to the multi-wire slurry saw. Two microstructuring applications are investigated: The edge isolation and the selective emitter formation using a phosphorous containing liquid as the dopant source. We present the first solar cell results with selective LCP emitter showing that LCP can introduce a local selective emitter into a shallow industrial emitter without negative impact on the recombination in the space charge region.

Keywords: silicon solar cells, microstructuring, wafering, Laser Chemical Processing (LCP), Laser Chemical Etching (LCE)

1 INTRODUCTION

The strong market growth of photovoltaic energy conversion is supported by continuous optimization of the entire production chain. Also, the economy of scale allows decreasing production costs for solar modules. However, the largest impact on the costs can be expected when new technologies emerge that allow easier and more efficient manufacturing of improved solar cell structures. A good example for such a technology is the Laser Fired Contacts (LFC) [5], that makes possible the manufacturing of solar cells with dielectrically passivated rear sides. These have the potential of cell efficiency well above 20%.

Another technology capable of improving considerably the way that solar wafers and solar cells are produced is the Laser Chemical Processing (LCP). This method was invented by Kray and Willeke and its principle presented in 2001 [6]. At this time, the name was Laser Chemical Etching (LCE) due to the initial idea of damage-free silicon removal for wafering application. Recently the focus of interest was enlarged to microstructuring as local doping for selective emitters or metallization so that the new name LCP reflects this broader focus.

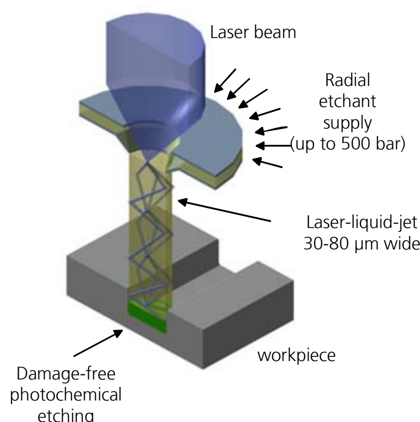

Fig. 1: Principle of Laser Chemical Processing (LCP).

The principle of LCP which is based on the waterjet-guided laser from Synova S.A. is shown in fig. 1: A hair-thin liquid jet is generated in a nozzle that has a transparent window on top. Through this window, a laser beam is focused into the jet and guided within via total internal reflection. Depending on the used liquid, the laser heating or evaporation can be combined with physical and/or chemical reactions as etching, doping or deposition.

In this paper, we first show the general result of damage-free removal of silicon before we review the status of the proof-of-concept of the wafering application. Then, the new microstructuring focus is presented by two applications: The edge isolation and the local doping for selective emitter formation.

2 DAMAGE-FREE SILICON REMOVAL

The most attractive property of LCP is the possibility to machine the silicon surface locally without the need to remove any damage afterwards. This increases considerably the process flexibility since the rest of the wafer does not necessarily have to be protected against the attack of a damage etch chemistry.

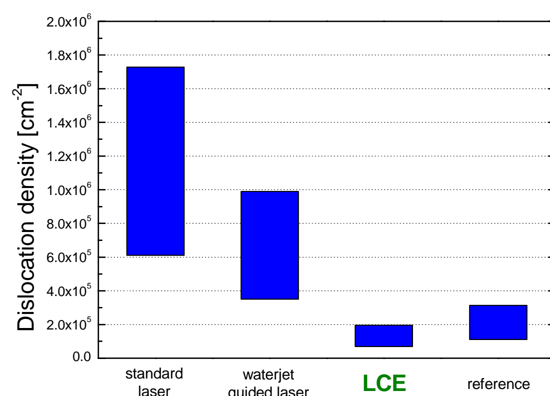

Fig. 2: Dislocation densities of Si samples grooved by different microstructuring methods, measured by x-ray diffraction.

Since this property is of general interest for all LCP applications, we performed tests on bare wafers and structured grooves using different technologies. Photolithography with wet-chemical etching (KOH) served as damage-free reference process. After the grooving, the dislocation density was measured via x-ray diffraction, cf. fig. 2. Since the measured dislocation density of the LCE/LCP sample is in the same range as the reference, we conclude that the silicon removal was damage-free. More details on this subject can be found in [7].

3 WAFERING

The initial idea of LCP, the cutting of silicon wafers out of large blocks, is a very challenging process since it competes with a well established high-throughput technology, the multi-wire slurry saw. Therefore we have to check different aspects if LCP can compete in general with the status quo. In detail, we have to address three first order questions:

- Are centimeter deep cuts possible?
- Is the cutting speed competitive?
- Is the energy consumption acceptable?

In the following sections, we will answer these questions.

Centimeter deep cuts

In order to test the ability of the liquid jet to maintain its laminarity even in very narrow and very deep grooves, we used a high-power infrared laser (Nd:YAG, λ=1064 nm) with 0.5 ms pulse length. With this system and water as carrier-liquid (jet width 83 µm) we tried to cut off silicon wafers from thick plates. As shown in fig. 3, we reached a maximum cutting depth of 7 cm, the largest wafer area produced so far is approx. 45x45 mm^2. The cut width was ≈100 µm which corresponds to an aspect ratio of impressive 700:1. This is a clear proof-of-concept that the guiding of laser inside a liquid jet in deep and narrow grooves is possible.

Cutting speed

In another set of experiments, we performed single

Fig. 3: Silicon wafers cut off thick Si plates via LCP (with water as carrier liquid) using a high-power ms-pulse laser. The liquid jet was orientated vertically in the pictures so that the cutting depth was 7 cm (left) and 4 cm (right).

Process	Conditions	Etch rate / cutting speed [µm/min]	Ref
HF/HNO_3 (CP-4A)	Basin, 25°C	80	[2]
Cl_2 plasma	Ar laser, cw, 7W, p=200 Torr	360	[3]
KOH	Basin, 100°C	6,4	[4]
MWSS		500	
LCP (10% KOH)	Single pass at 250 mm/s, IR laser 80W	9600	

Tab. 1: Comparison of etch rates / cutting speeds of different wet chemical reactions, typical wire saws and LCP.

cuts in thick wafers and measured the cut depth for different laser parameters. With a 1064 nm Nd:YAG laser with a pulse length between 600 and 1500 ns and 10% KOH as carrier liquid, we could measure a 100 µm deep cut after a single pass with 250 mm/s scan speed. This corresponds to a theoretical cutting speed of 160 µm/s through a 156 mm wide block. In tab. 1, a comparison of different cutting speeds is shown. Clearly, pure wet-chemical etching cannot compete with the feed rate of a wire-saw. In contrast, the laser ablation rate of LCP is more than one order of magnitude faster than the wire-saw even at this early stage. However it is to note that this high initial removal speed cannot yet be maintained at larger cutting depths and that the parallelization of LCP is a technological challenge. But the second proof-of-concept is observed, competitive LCP cutting speeds can be expected in principle.

Energy consumption

Since solar electricity is intended to reduce the emission of greenhouse gases, the energy payback time is of great interest [1]. Therefore LCP wafering must also compete in terms of demand of primary energy per produced wafer surface. In order to determine an estimation of LCP energy consumption we measured the *ablation efficiency* η_{abl}

$$\eta_{abl} = E_{abl,theor} / E_{abl,exp}$$

defined as the relationship between theoretical (50 J/mm^3 calculated from bond energy and bond density of Si) and experimental ablation energy in units of J/mm^3. The experimental value is calculated by measuring the ablated silicon volume and the used laser energy for the groove. Together with the *electro-optical efficiency* $\eta_{el.opt.}$ of the laser (the relationship between optical laser power and electrical power taken from the grid) and the width of the kerf d, the electrical energy demand per wafer surface can be calculated. Using the data in [1], the primary energy demand per wafer surface D_p is then calculated using a mean primary-to-electrical-energy conversion efficiency of $\eta_{prim.el.}$=31%:

$$D_p = \frac{E_{abl.theor} \cdot d}{\eta_{abl} \cdot \eta_{el.opt.} \cdot \eta_{prim.el.}}$$

As a reference, we evaluated data from our wire-saw where we performed a cut of a 100x100x275 mm^3 block with 0.5 mm/min cutting speed. The total energy consumption of this cut was 45.2 kWh which translates to a primary energy demand of 9161 J/cm^2. This value does not include the energy demand for consumables like SiC or the wire which is much higher than the process energy as shown in [1]. In fig. 4, the primary energy demands of different scenarios are shown. The standard wafering is plotted as the literature data from [1] as well as our experimental data with calculated SiC primary energy demand according to their relative shares.

On the right side of the graph, different LCP scenarios are depicted. An ablation efficiency of 60% is assumed (supported by experimental data) as well as an electro-optical efficiency of 20% (this can be realized already today by fiber lasers e.g.). It is obvious that the primary energy demands of LCP processes are very competitive to MWSS especially when the consumables are taken into account which are strongly reduced for LCP. By using smaller nozzles, thus yielding smaller kerfs, improving the ablation efficiency (e.g. by the usage of green lasers) and the electro-optical efficiency, the primary energy demand of LCP can easily fall below that of MWSS.

Since the primary energy demand of a mc-Si wafer is dominated by the raw material (62% share), the possible recycling of the kerf material in LCP processes gives an efficient possibility to further reduce the primary energy demand. Even a conservative estimation of 50% kerf recycling makes the cutting process a plus-energy-process, saving more than 90.000 J/cm^2 in the overall wafer energy demand. This shows that LCP could even contribute to a reduction of the energy payback time of solar cells.

4 MICROSTRUCTURING

Many different LCP microstructuring applications can be devised by choosing appropriate carrier liquids and lasers. In the following, we will present experimental results for the edge isolation and selective emitter doping.

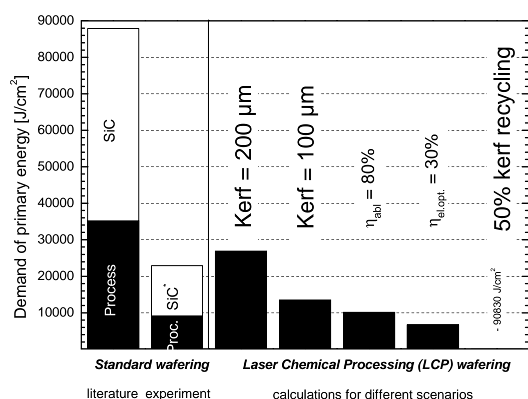

Fig. 4: Demand of primary energy in J per cm^2 wafer area. Standard wafering: Data taken from literature [1] and determined experimentally with calculated SiC contribution. LCP calculations for different scenarios. Initial assumptions (“kerf = 200 µm”): η_{abl} = 60%, $\eta_{el.opt.}$ = 20%. For details see text.

Edge isolation

Standard industrial solar cells need an isolation step after the completion of the electrical contacts to interrupt the electrical connection between front and rear contact from the emitter diffusion. This step is increasingly carried out by lasers. Therefore we performed a study with industrial solar cells (156x156 mm^2 size) and compared the isolation quality of the industrial reference, a UV dry laser and LCP with water. We observed in this study that the groove shape of LCP was much more homogeneous and the second ideality factors of the dark IV curves were consistently lower than for the dry laser samples. This indicates lower damage to the pn junctions as supported by the thermography maps in fig. 5. Clearly, the LCP laser shows much lower contrast to the rest of the cell (except the corners that were not isolated at all due to technical problems). More details on these issues have been published recently [8].

Selective emitter formation

Local high doping underneath the front contacts, known as selective emitter, can allow for shallower collecting emitter diffusions thus increasing the blue response as well as V_{oc}. This concept is industrially manufactured by BP Solar [9] in the laser-grooved buried contact cell. However, a damage-etch is necessary after the dry laser process and the entire wafer is diffused in an oven at elevated temperature. LCP could in principle simplify this process considerably: After SiN_x AR coating, LCP with a P containing liquid is used to open the SiN_x layer and introduce the local doping via laser heating and liquid-phase diffusion. No damage-etch and no oven process is needed at all.

To investigate if such a process is possible, we first used phosphoric acid H_3PO_4 as carrier liquid and cut grooves in bare silicon wafers with varying laser intensity. As shown in the Sheet Resistance Imaging (SRI) map [10] in fig. 6, local doping can be obtained and the sheet resistance can be influenced by the laser intensity.

This preliminary result encouraged us to fabricate first solar cells with a shallow industrial spray emitter with 50 Ω/sq sheet resistance. After rear side full-area Al screen-printing and firing, PECVD-SiN_x was deposited on the front side. Then, grid-shaped grooves where machined with LCP (H_3PO_4), TiPdAg was evaporated through a photoresist mask structured by

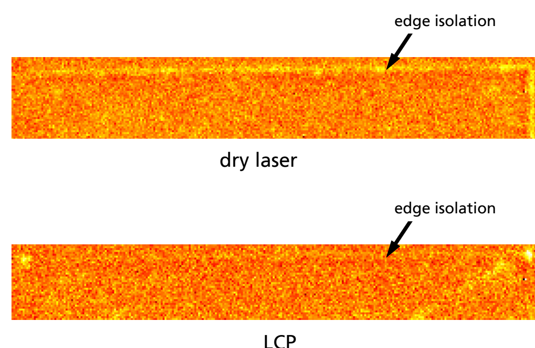

Fig. 5: Thermography maps of cell borders with edge isolation via dry UV laser (upper picture) and LCP with water and IR laser (lower picture).

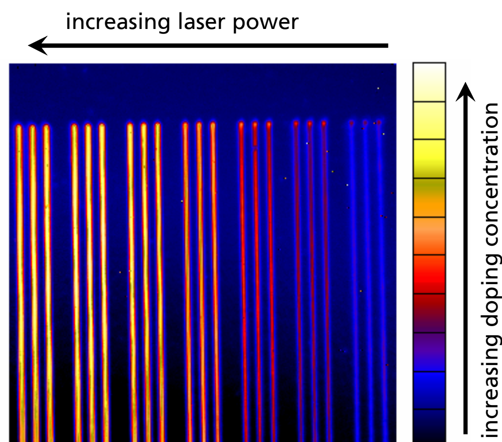

Fig. 6: Sheet Resistance Imaging (SRI) maps of bare silicon wafers grooved with LCP (IR laser, H_3PO_4 as carrier liquid). Lighter colors indicate higher doping. As the laser power increases from right to left, it becomes clear that the sheet resistance can be influenced by the laser power.

photolithography. After lift-off, the grid was thickened by Ag electroplating.

Most interesting in this experiment was to determine the LCP damage to the pn junction since the shallow emitter was only 0.2-0.3 µm deep. Extended defects from the laser irradiation could easily lead to pn shunting, thus increasing j_{02} or decreasing R_p. Therefore we performed Suns-Voc measurements [11] in different stages of the cell fabrication. Typical pseudo fill factors are well above 80% which prove that LCP processes with very good connections between the two emitters can be realized. LBIC measurements show that the cells are very homogeneous, which is also a very positive result, cf. fig. 7. More details on this issue can be found in [12]. Comprehensive cell characterization will be published elsewhere.

5 CONCLUSION

The Laser Chemical Processing (LCP), formerly named Laser Chemical Etching (LCE), is a flexible family of laser-assisted chemical processes. We could show that silicon wafering is a promising medium-term development since the proofs-of-concept have been conducted concerning centimeter deep cutting, high-speed cutting and low energy consumption. However, the initial high removal rates have to be maintained and the parallelization must be developed.

In much shorter time, microstructuring applications could be realized in production. We have shown that the edge isolation with LCP and water as carrier liquid could possibly perform better than with dry lasers. The selective emitter formation without oven process and masking layers shows high potential of increasing solar cell efficiency. Very encouraging first results indicate that local emitters can be grooved even into shallow emitters. These investigations will now be extended to high-efficiency structures to evaluate the selective LCP emitters further.

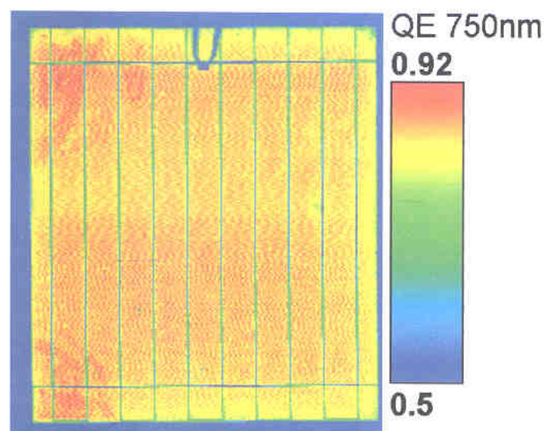

Fig. 7: LBIC measurement of a planar solar cell with selective LCP emitter. The homogeneous signal shows that no localized defects are introduced by the LCP process.

ACKNOWLEDGEMENTS

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