

TWO DIFFUSION STEP SELECTIVE EMITTER: COMPARISON OF MASK OPENING BY LASER OR ETCHING PASTE

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ABSTRACT: Two dimensional solar cell structures to form a selective emitter on the front side or back contact solar cells are often created with the aid of a selectively opened masking layer. In this paper we compare two methods of opening a PECVD SiN_x layer. A nanosecond laser with a wavelength of 355 nm was used to ablate a PECVD SiN_x layer. Alternatively, an etching paste was screen printed and subsequently heated to remove the SiN_x. Both methods were successfully applied for the formation of a selective emitter structure on standard Cz monocrystalline solar cells. The process sequence includes two diffusion steps and uses one SiN_x layer as a mask and also as an ARC. Since the front contact grid and the mask opening have the same shape, they have to be aligned accurately. The best cell efficiency of 18.1% was achieved on an industrial scale solar cell with a SiN_x ARC opened by the etching paste. Scanning electron microscope pictures showed that the laser ablation method melts the silicon underneath the SiN_x layer and thus a wet chemical damage etch must also be applied, whereas the screen printed etching paste removes the SiN_x without damaging the silicon.

Keywords: Selective Emitter, Etching, Laser Processing

1 INTRODUCTION

Advanced solar cell concepts often require a two-dimensional structuring of the front or back surface of the cell. This can be achieved by using a masking layer of SiO₂ or SiN_x, which has to be opened in selected regions. The opened regions can subsequently be doped, etched or contacted.

In this paper, two methods of opening a masking layer of Plasma-Enhanced Chemical Vapor Deposition (PECVD) SiN_x are compared: a nanosecond UV-laser (355 nm wavelength) was used to ablate the layer including several μm of the underlying silicon. Therefore, this process requires an additional damage etching step.

Alternatively the masking layer can be etched by an etching paste (isishape SolarEtchTM BES by Merck), which is screen printed and then heated in an IR belt furnace [1-3].

For a comparison of both methods, a processing sequence for the formation of a selective emitter by two diffusion steps on a screen printed monocrystalline Czochralski (Cz) solar cell was chosen [4].

2 CELL CONCEPT

The processing sequence used to obtain the selective emitter structure is based on the standard screen printing process widely used in industrial environment. It is illustrated in figure 1, the additional steps are marked in blue.

The process starts with a KOH/IPA texture to create a random pyramid structure. For the first diffusion, the sheet resistance is increased to 90-100 Ω/□ in order to reduce Auger-recombination at the emitter surface. After the P-glass removal, a PECVD SiN_x layer is deposited, which serves as a mask and as an Anti Reflective Coating (ARC). Since its thickness will be reduced by 5-10 nm during the following heavy diffusion, a layer of approximately 80 nm has to be deposited.

The mask opening steps include damage etching in case of a laser ablation, or the removal of the etching paste. The pattern for both opening methods has the same

shape as the metallization screen. This guarantees a minimal area of unpassivated and heavily doped illuminated regions, but also requires a very exact alignment of the front side metallization, since the emitter should only be contacted in the opened area. Furthermore, the sintering parameters have to be adapted in order to prevent shunting of the lowly doped regions in the case that unwanted metal is besides the openings. The rear contact was formed by a full area aluminum BSE.

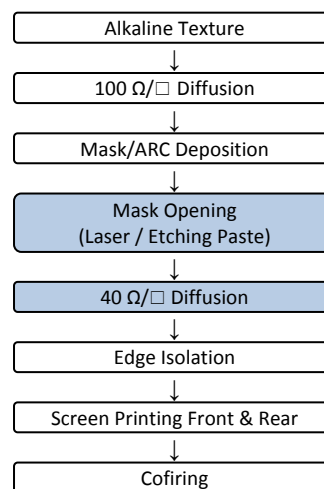


Figure 1: Processing sequence for the formation of a two diffusion step selective emitter. The additional steps to the standard screen printing process are marked in blue.

3 MASK OPENING BY LASER ABLATION

The laser ablation of a SiN_x layer is induced by the melting and evaporation of the underlying silicon, since the absorption coefficient of silicon is very high compared to the one of SiN_x. This leaves a molten and damaged surface. Engelhart et al [5] have shown, that for ultra short (ps) pulses, the damage is negligible and the opened area can be contacted without damage etching. For the ns laser we used for our experiments, this is not

the case. The heavily damaged surface resulting from the laser intensity necessary to completely remove the SiN_x is shown in figure 2. The effect of ns laser pulses on the minority carrier lifetime and dopant concentration has been investigated by Correia et al. [6] for various laser intensities and wavelengths. A reduction of lifetime was observed for high intensities, while the dopant atoms were driven into the wafer, leaving a lower concentration at the surface.

In our experiments, we used a 355 nm YVO₄-laser (Trupf Vc6) with a peak power of 8 kW, a pulse frequency of 10 kHz and a pulse duration of approximately 20 ns. The laser intensity was optimized to remove most of the SiN_x without completely melting the texture. Subsequently the damage was removed in a 23% NaOH bath at 80 °C for 8 min. Scanning Electron Microscope (SEM) pictures show the complete removal of the random pyramid structure. Since the SiN_x layer was not etched, the silicon underneath the SiN_x was removed several μm from the edge, leaving a fragile skeleton SiN_x structure (figure 3).

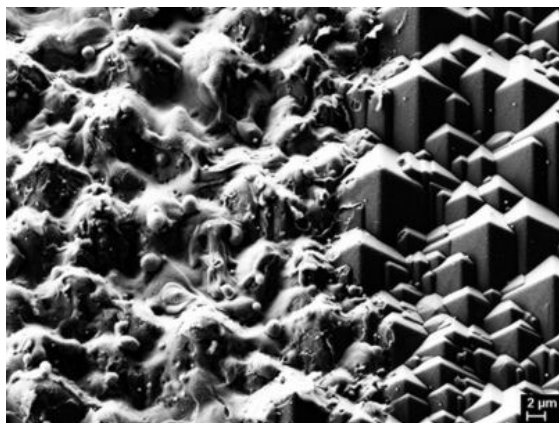


Figure 2: SEM-picture of severe laser damage (left side) at 35% intensity on an alkaline textured Cz-wafer before damage etching.

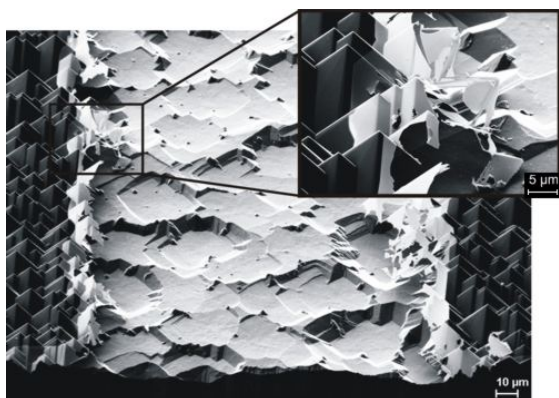


Figure 3: SEM-Picture of laser opened grid line after 8 min of damage etching in 23% NaOH solution at 80 °C. An underetch of several μm can be observed.

4 MASK OPENING BY ETCHING

The etching paste was printed with the same screen as the front side metallization paste later on (100 μm grid line opening width), to ensure optimal matching of both

patterns. The etching process was induced by heating in an IR belt furnace. For alkaline etched Cz silicon wafers, a spreading of the paste by 100-200 μm to each side of the grid lines was observed, which is caused by the capillary effect of the random pyramids. The SiN_x close to the etched regions therefore was thinned a bit after etching (figure 4).

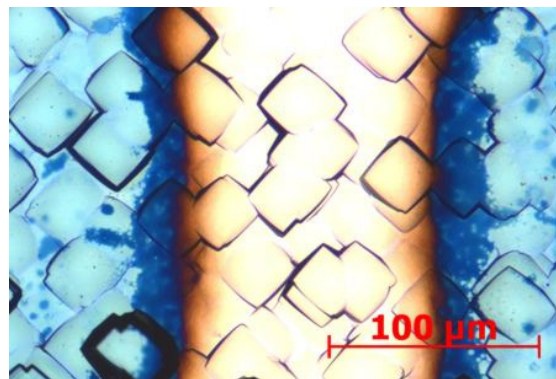


Figure 4: Optical microscope picture of grid line opening by the etching paste on an untextured Cz wafer. The initial SiN_x layer thickness was 110 nm.

Finally, the etching paste was removed in an ultra sonic bath. The cleaning time could be reduced by adding few KOH to the cleaning water. The NaOH etched Cz wafers were completely cleaned after 30 s, while for random pyramid textured wafers approximately 1 min cleaning time was necessary. The ultra sonic bath poses a mechanical stress to the wafer, which can lead to wafer breakage after a cleaning time of several minutes. This could possibly be prevented by using less power and placing the wafers into carriers instead of using tweezers for wafer handling. Bähr et al applied ultra sonic cleaning in KOH (0.1 wgt.%) and reported no problems [2].

SEM pictures of the cleaned surface of a random pyramid textured Cz wafer demonstrate only small remains of SiN_x and no visible damaging of the silicon (figure 5).

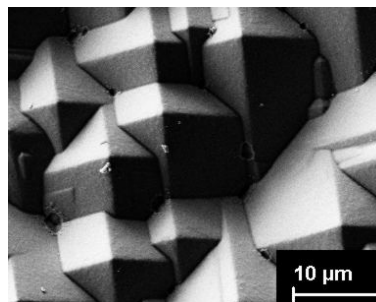


Figure 5: SEM-picture of an area opened by the etching paste on an alkaline textured Cz wafer. No silicon surface damage is visible.

5 CELL RESULTS

Both SiN_x opening methods were applied to form a selective emitter structure for industrial-type silicon solar cells. Since the laser working range was too small for industrial-scale solar cells, the cell size for comparing the opening methods was chosen to be 50x50 mm².

Additionally, large cells (125 mm semisquare) opened by the etching paste were produced to evaluate the potential of the cell concept.

5.1. Small area cells (50x50 mm²)

The small cells were processed according to the scheme in figure 1. In order to eliminate a possible effect of the rear side texture, the cells opened by the etching paste were also etched in NaOH before mask opening. The mask opening and the front side metallization were manually aligned with a high resolution optical camera system. Edge isolation was performed by a dicing saw between the heavy diffusion and the P-glass removal. The IV measurement results are shown in table 1.

Table I: Average and best IV measurement results of 50x50 mm² cells with a two diffusion step selective emitter ($R_{\text{sheet, heavy}} \approx 40 \Omega/\square$, $R_{\text{sheet, low}} \approx 150 \Omega/\square$).

Opened by		FF [%]	V _{oc} [mV]	J _{sc} [mA/cm ²]	η [%]
laser	avg.	74.6	630.0	35.7	16.8
	best	75.5	630.3	35.8	17.0
etching paste	avg.	75.8	628.2	36.2	17.2
	best	75.8	629.3	36.4	17.4

Average values are taken from five cells. A simulation of the IV curves by the two diode model reveals a shunt resistance higher than 4000 Ωcm^2 and a series resistance of 0.5 Ωcm^2 . The fill factor is limited by a high second diode saturation current density j_{02} caused by two effects: Transfer Length Method (TLM) measurements revealed a sheet resistance of approximately 150 Ω/\square , which represents a spreaded series resistance due to a not adapted finger distance and can be fitted also by a high j_{02} . An additional effect that may lead to a high j_{02} is the recombination at the cell's unpassivated edge. The high edge length to cell area ratio is worse compared to larger area cells (125 mm or 156 mm edge length).

The laser opened cells show a 0.5 mA/cm² lower short circuit current density, which is caused by wider grid lines compared to cells opened by the etching paste (figure 6). The groove left after damage etching is completely filled with Ag paste. For cells opened by the etching paste, the opening width is the same, but the Ag grid lines are thinner because no damage etching was performed and therefore no groove exists.

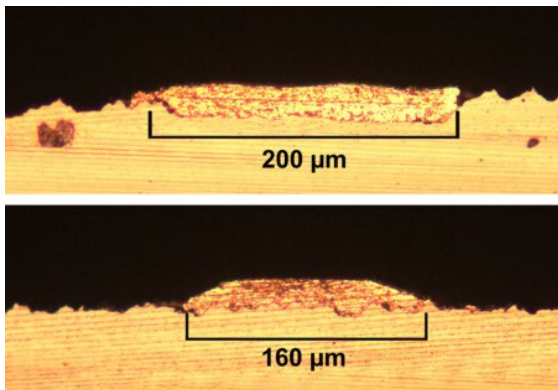


Figure 7: Optical microscope picture of the Ag grid line on laser opened cell (top) and a cell opened by the

etching paste (bottom). The groove left after damage etching on laser opened cells is completely filled with paste, which increases the Ag grid line width.

5.2. Large area cells (125 mm semisquare (ssq))

Due to problems with the high sheet resistance diffusion, we used a 50 Ω/\square standard emitter for the lowly doped regions, which was homogeneously etched back to 90 Ω/\square using a wet chemical process developed at UKN for a single diffusion selective emitter [7]. For the large cells, edge isolation was performed after the cofiring using a wafer dicing saw. Reference cells with a homogenous 50 Ω/\square emitter were processed separately.

Table II: IV measurement results of 125 mm ssq cells with a two diffusion step selective emitter structure ($R_{\text{sheet, heavy}} \approx 40 \Omega/\square$, $R_{\text{sheet, low}} \approx 90 \Omega/\square$, $R_{\text{base}} = 1.9\text{--}2.9 \Omega\text{cm}$, average over 13 cells) and reference cells ($R_{\text{sheet}} \approx 50 \Omega/\square$, average over 9 cells)

Cell		FF [%]	V _{oc} [mV]	J _{sc} [mA/cm ²]	η [%]
sel. emitter	avg.	79.3	629.9	35.4	17.7
	(etching paste) best	79.1	633.0	36.1	18.1
reference	avg.	79.0	626.5	35.0	17.3
	best	79.5	628.4	35.3	17.6

The IV measurement results are very similar to the ones obtained with the single diffusion selective emitter process [7]. For all cells the texture was inhomogeneous and blurry, so slightly higher short circuit currents could be achieved with an optimized texture.

5.3. Spectral response measurements

For the best large area cell, the external quantum efficiency (EQE) and the reflection curve were measured. A calculation of the internal quantum efficiency (IQE) reveals an excellent blue response (figure 7, IQE(400 nm) = 91 %).

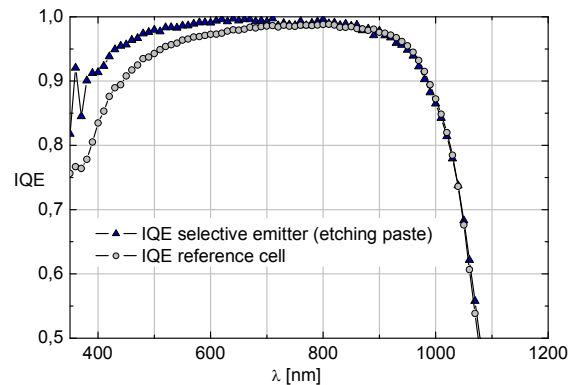


Figure 7: IQE of the best selective emitter 125 mm ssq cell compared to a 50 Ω/\square homogeneous emitter reference cell.

In order to evaluate the effect of the sheet resistance in the lowly doped area on the blue response, laser opened 50x50 mm² cells were processed with different doping levels in the lowly doped areas and a 10 Ω/\square heavy diffusion. The sheet resistance was adjusted by a variation of the maximum diffusion temperature, and was measured by the TLM method. The IQE was calculated

from measurements of the reflection and the EQE (figure 8). The relatively small difference between $67 \Omega/\square$ and $180 \Omega/\square$ leads to the conclusion, that for a very high sheet resistance the front side passivation becomes the limiting factor. A sheet resistance beyond approximately $100 \Omega/\square$ leads to a reduction of the fill factor due to the high spreaded series resistance, so best results should be achieved between 90 and $100 \Omega/\square$.

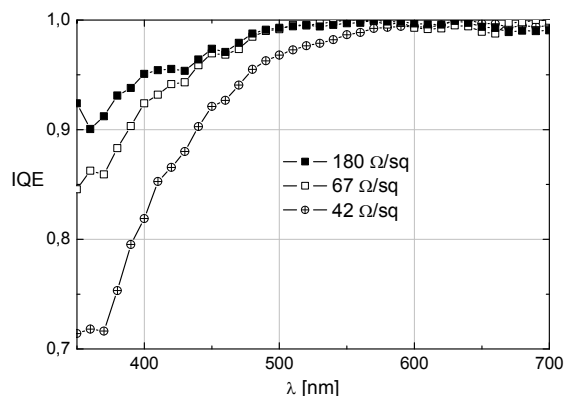


Figure 8: Blue response of $50 \times 50 \text{ mm}^2$ selective emitter solar cells with $10 \Omega/\text{sq}$ sheet resistance under the grid lines and different sheet resistance in the illuminated areas.

6 SUMMARY

We compared two methods of opening a masking layer of SiN_x . A nanosecond laser with a wavelength of 355 nm was used to ablate the SiN_x . The laser also melts the underlying silicon. Therefore, a damage etching is necessary, which also removes the emitter. Alternatively, an etching paste was applied using screen printing technology. The etching process was induced by heating in an IR belt furnace, afterwards the paste was removed in an ultra sonic bath. We observed no damaging of the silicon surface.

Both methods were applied in a selective emitter fabrication process. The Cz cells with the laser opened grid have a $0.5 \text{ mA}/\text{cm}^2$ lower short circuit current density due to wider grid lines compared to the cells opened by the etching paste. The best cell efficiency of 18.1% was measured on a 125 mm ssq cell using the etching paste for mask opening. An evaluation of the IQE for different doping levels in the lowly doped regions leads to an optimal sheet resistance between 90 and $100 \Omega/\square$.

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