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CO	Confidential, only for members of the consortium (including the Commission Services)	

EU-RES	Classified Information: RESTREINT UE (Commission Decision 2005/444/EC)	
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Abstract

Solar cell results of a process using only one etching and one cleaning step are reported. Solar cells were produced from p-type Cz (single crystalline) wafers. First data is presented that shows superior performance of a phosphorus diffusion process for the formation of the pn junction that does not require subsequent phosphosilicate glass (PSG) removal. Thus, the PSG etching step, commonly performed in diluted HF can be left out. As the edge isolation is performed using common laser technology, the only remaining wet chemical steps are the saw damage removal, pre-cleaning before texturing, texturing in diluted KOH (with additive) and post-texturing cleaning. The focus of the presented study the impact of reduced wet-chemical treatment of as-cut wafers using state of the art alkaline texturing additives. Only small losses were observed, when the saw damage etching and the pre-cleaning steps were left out.

Public introduction[1]

Dissemination level: PU

[1] All deliverables which are not public will contain an introduction that will be made public through the project WEBsite

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1 INTRODUCTION

One of the key goals of the Eco-Solar project is to reduce the use of resources of solar module manufacturing. One of the approaches is studied in WP3 which deals with remanufacturing, resource efficiency and reuse in solar cell processing. A typical process route for sc (single crystalline) p-type solar wafers is displayed in Figure 1. Solar silicon bricks are cut by metal wire saws (either using loose abrasive particles in an organic slurry matrix or fixed abrasive particles). The sawing process leaves the surface of the resulting silicon slices (wafers) highly damaged on a depth scale of 7 – 10 µm. Furthermore, wafers carry inorganic and organic residues from the sawing/handling process. While the first – if not completely removed – may interfere with solar cell efficiency, as metal contamination may serve as recombination site for charge-carrier pairs,[1] the latter tends to interfere with subsequent etching processes. Especially the homogeneity of alkaline surface structuring (texturing with random pyramids) may be affected.[2]

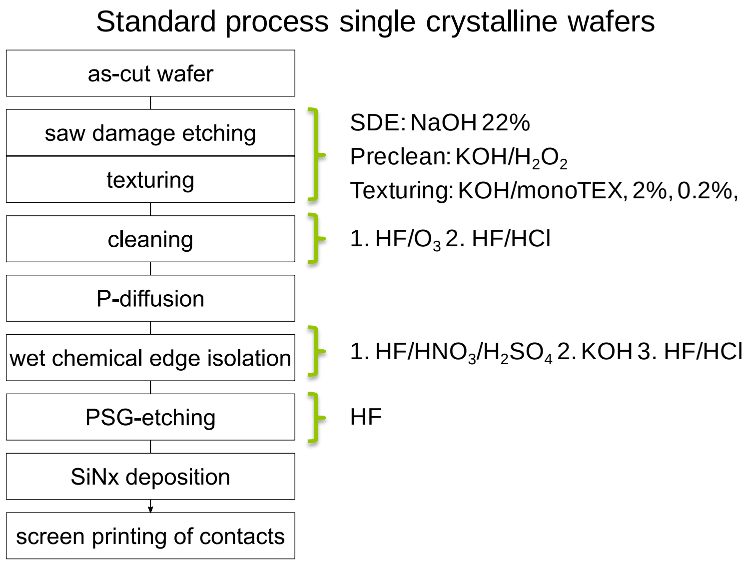


Figure 1: Typical process route for the fabrication of solar cells from single crystalline p-type silicon wafers.

Due to its superior properties of quickly removing silicon oxide, hydrofluoric acid is an essential process chemical for etching and cleaning of silicon surfaces. However, due to its high toxicity[2] and corrosive nature it poses and imminent danger on the workers. Furthermore, concentrated hydrofluoric acid waste requires expensive on site waste water treatment. In addition to that rinsing extensively in high purity water, which is required after etching and clean steps, negatively contributes to the ecological footprint.

[2] Hydrofluoric acid poses a great risk at workers due to its ability of quickly penetrating the skin barrier causing destruction of deep tissue layers, including bone. Pain associated with exposure to solutions of HF (1-50%) may be delayed for 1-24 hours. If HF is not rapidly neutralized and the fluoride ion bound, tissue destruction may continue for days and result in limb loss or death. HF is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid (http://web.utk.edu/~ehss/training/has.pdf)

In the following we report experimental solar cell results of a process sequence with a minimum amount of wet chemical etching steps. The process steps that may be deleted and / or replaced are indicated in Figure 2. First of all, process steps may be proven to be not absolutely necessary and may thus be simply left out – especially in the initial surface treatment section (saw damage removal and pre-clean) are expected to be of mostly “cosmetic” necessity – yielding a nice looking homogeneous surface structure. The saw damage that would impact due to its strong electrical recombinational activity expected to be removed in the alkaline texturing step.

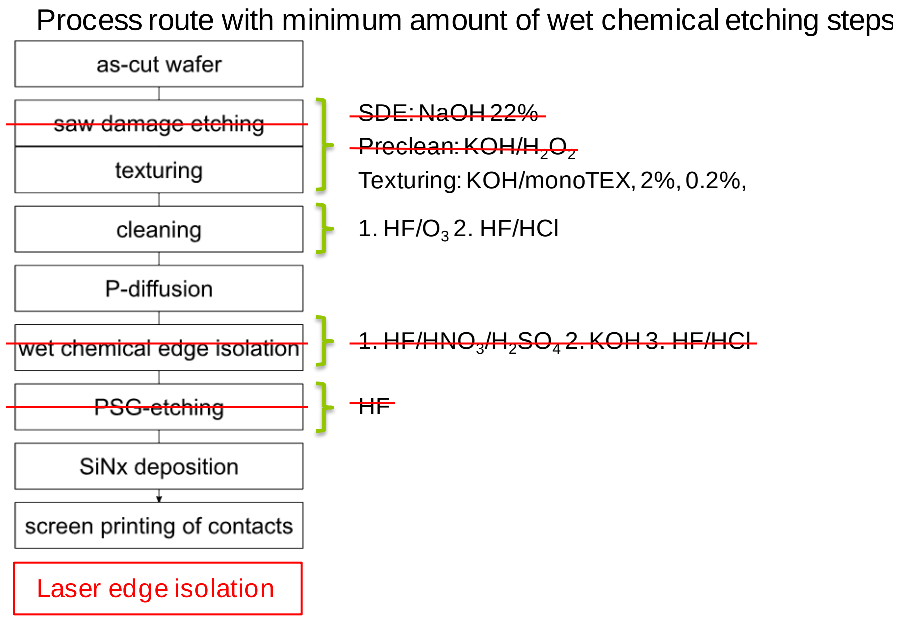


Figure 2: Process sequence with a minimum amount of wet chemical etching and cleaning steps.

Second, some processes may be replaced by “dry” alternatives. It is a well-known fact, that the wet chemical edge isolation can be replaced by a laser process at the end of the solar cell processing sequence.

The last process step that may be left out is the removal of the phosphorus silicate glass after the phosphorus diffusion. Within the project an alternative diffusion recipe has been developed that proved to be even superior to existing phosphorus diffusions, using the same equipment. The advantage of the developed process is that the PSG is not removed but used as passivating layer with superior properties. Results are shown in the following.

2 EXPERIMENTAL DETAILS

2.1 The diffusion recipe

In the work towards this goal of reducing the number of etching steps a phosphorus diffusion process has to be developed that allows good passivation quality without the need of the removal of the phosphorus silicate glass (PSG). Instead the PSG is used as surface passivation layer in combination with an amorphous SiNx antireflection film (a-SiNx:H) capping.
The measured sheet resistance and the emitter recombination current J_{0E} of the reference diffusion (without PSG) and the new diffusion recipe (at that point not quite tuned to the desired sheet resistance, yet) are plotted in Figure 3. While the sheet resistance indicates the dopant concentration, the J_{0E} is a sum parameter for the passivation quality and emitter recombination – which suffers from higher doping (lower sheet resistance). The superior passivation quality compared to a standard emitter is demonstrated, even when not fully tuned to the desired sheet resistance of 90 Ohm/sq. Despite the higher doping density much lower J_{0E} values are obtained.

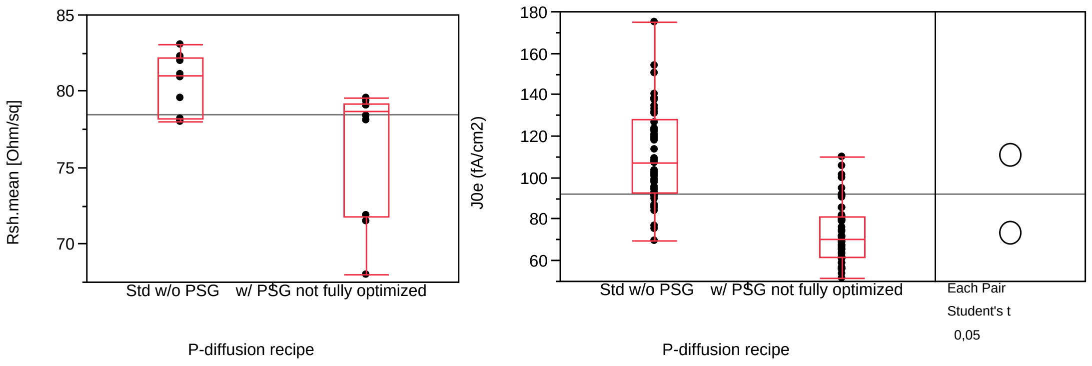


Figure 3: Sheet resistance and emitter recombination current of the “old” standard emitter, which requires PSG removal and the “new” emitter with PSG passivation (not fully optimized, e.g. sheet resistance lower than target (78 Ohm/sq instead of 90 Ohm/sq), Surface saw damage etched in 20% KOH.

Figure 4 four shows the emitter performance of the new emitter, now the final version, with and without PSG underneath the a-SiNx:H capping. The lower J_{0E} values for the PSG passivated symmetrical lifetime samples proves the excellent performance of the PSG passivation. Note that these samples have a random pyramid textured surface, while the values in Figure 3 were obtained on flat surfaces.

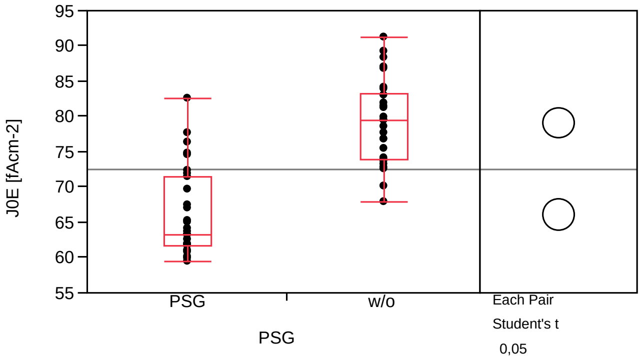


Figure 4: Emitter recombination current of lifetime samples with and without PSG passivation, 90 Ohm/sq. Surface textured with random pyramids.

In the following experiment this diffusion process was used.

2.2 Split table

In order to test if the latest generation of commercial texturing additives require the extensive pre-treatment before the actual texturing, solar cells were fabricated in three groups of 16 samples. The groups with stepwise simplified pre-treatment are summarized in Table 1.

Table 1: Split table of the three groups of the experiment.

Group 1 (reference)	**Group 2**	**Group 3**
SDE (5 µm)		
pre-clean (KOH/H_2O_2)	pre-clean (KOH/H_2O_2)	
Texture etch (5µm)	Texture etch (10µm)	Texture etch (10µm)
Post-clean (HF/O_3+HCl/HF)	Post-clean (HF/O_3+HCl/HF)	Post-clean (HF/O_3+HCl/HF)
P-diffusion		
SiNx deposition, metallization		

To compensate for the missing SDE etching, the texturing time was increased for groups two and three. The details about the rest of the process can be found in the following section.

2.3 Processing details

Details on the processing of the silicon wafers are listed below:

- 16 wafers / group
- p-type Cz wafers (2,5 Ohm*cm)
- SDE: ~20% KOH 220sec, etching depth: 5,8 µm
- Pre-clean: KOH/H_2O_2
- Texturing: 2% KOH, RENA monoTEX F @ 80°C,etching depth:
    - group 1: 6,0 µm

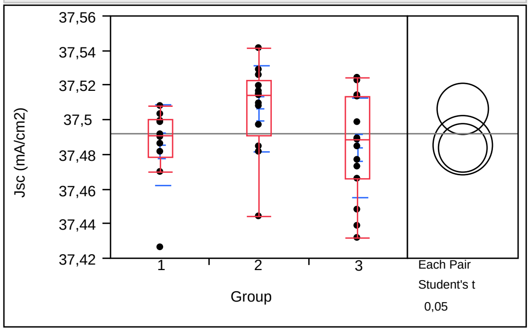
  - group 2: 8,6 µm
  - group 3: 8,7 µm
- Post-clean: HF/O_3 (0,1%/11 ppm, 10 min) + HCl/HF (2%/2%, 2 min)
- New P-diffusion recipe in atmospheric pressure quartz tube diffusion (91 Ohm/sq)
- SiNx passivation and anti-reflective coating: direct plasma PECVD (deposition time was adjusted to reach the typical dark blue cell color)
- No PSG-etching
- Front side metallization: commercial silver paste, three busbars, backside metallization: commercial full aluminum paste, no soldering pads
- Fast firing (peak 875°C)
- Laser edge isolation (standard parameters)

The etching was performed in a manual wet bench (SDE) and in an automated wet bench (pre-clean, texturing and post-clean); both wet benches were manufactured by RENA. The ratio of wafers per batch and bath volume corresponds to typical industrial equipment. The etching and cleaning took place in circulated baths. The cleaning process step consists of an oxidizing O_3-containing bath with a very small amount of added HF to increase the ozone solubility. The wafer surface and remains of the texturing additive and noble metals such as copper are oxidized. Subsequently the wafers are dipped in HF/HCl mixture to remove the sacrificial silicon oxide and with it the remaining metal contamination from the wafer surface.
The diffusion and PECVD were performed in Centrotherm equipment, printing with Baccini printer and drying furnace, fast firing in a Centrotherm furnace.

3 RESULTS

The solar cell parameters of the three processing groups are plotted in Figure 5.

Oneway Analysis of Jsc (mA/cm2) By Group



Missing Rows 1

Excluded Rows 9

Quantiles

Level	Minimum	10%	25%	Median	75%	90%	Maximum
1	37,43	37,43	37,48	37,49	37,50	37,51	37,51
2	37,44	37,46	37,49	37,51	37,52	37,54	37,54
3	37,43	37,44	37,47	37,49	37,51	37,52	37,52

Means Comparisons

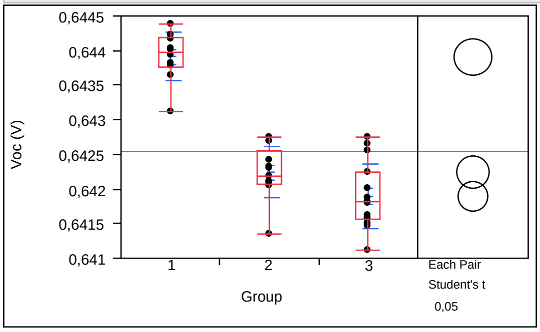
Comparisons for each pair using Student's t

Connecting Letters Report

Level			Mean
2	A		37,51
1	A	B	37,49
3		B	37,48

Levels not connected by same letter are significantly different.

Oneway Analysis of Voc (V) By Group



Missing Rows 1

Excluded Rows 9

Quantiles

Level	Minimum	10%	25%	Median	75%	90%	Maximum
1	0,6431	0,6432	0,6438	0,6440	0,6442	0,6444	0,6444
2	0,6413	0,6416	0,6421	0,6422	0,6426	0,6427	0,6427
3	0,6411	0,6413	0,6416	0,6418	0,6422	0,6427	0,6428

Means Comparisons

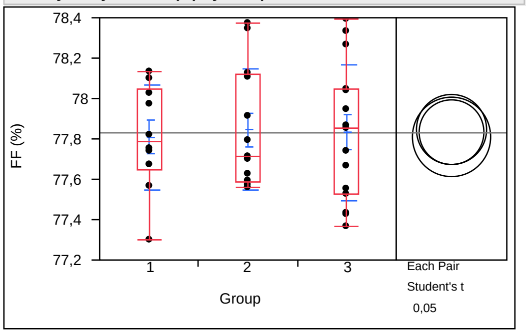
Comparisons for each pair using Student's t

Connecting Letters Report

Level				Mean
1	A			0,6439
2		B		0,6422
3			C	0,6419

Levels not connected by same letter are significantly different.

Oneway Analysis of FF (%) By Group



Missing Rows 1

Excluded Rows 9

Quantiles

Level	Minimum	10%	25%	Median	75%	90%	Maximum
1	77,30	77,33	77,65	77,79	78,05	78,13	78,13
2	77,56	77,56	77,58	77,71	78,12	78,36	78,38
3	77,37	77,40	77,53	77,85	78,04	78,36	78,39

Means Comparisons

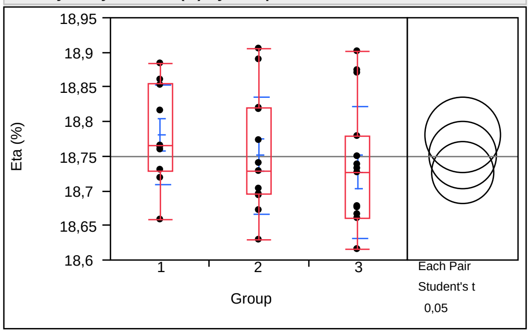
Comparisons for each pair using Student's t

Connecting Letters Report

Level		Mean
2	A	77,85
3	A	77,83
1	A	77,81

Levels not connected by same letter are significantly different.

Oneway Analysis of Eta (%) By Group



Missing Rows 1

Excluded Rows 9

Quantiles

Level	Minimum	10%	25%	Median	75%	90%	Maximum
1	18,66	18,66	18,73	18,76	18,85	18,88	18,88
2	18,63	18,65	18,69	18,73	18,82	18,90	18,91
3	18,61	18,62	18,66	18,73	18,78	18,89	18,90

Means Comparisons

Comparisons for each pair using Student's t

Connecting Letters Report

Level		Mean
1	A	18,78
2	A	18,75
3	A	18,73

Levels not connected by same letter are significantly different.

Figure 5 Solar cell results of the three experiment groups. The quantiles are displayed and the mean values are compared using the Student's test (significant differences are signified by non-overlapping circles, and different letters in the Connecting Letters Report.

The efficiency of the fabricated solar cells was found to be in the expected range of 18,75% (about 0,5% efficiency lower than stated in the ITRPV 2016[3] for current industrial efficiencies of this cell type, which as typical value research institutes without the ability of large scale process fine tuning can achieve).
The front surface of group 3 proved to have only a slightly inferior outcome to the other groups – only visible straight after texturing and no longer visible on finished solar cells with dark blue anti-reflective film and metal contact grid. Accordingly, no statistically significant differences in efficiency between the three groups could be detected within the chosen batch size.
However, a significant loss in open circuit voltage V_{oc} of 2 mV from group 1 to 3 (-0,3%rel) was recorded indicating that the saw damage etch step adds to the surface quality. One reason might be the overall smaller etching depth of the surface (~12 µm, when the saw damage was removed separately and ~9 µm when only texturing was performed). The smaller etching depth can be explained by the fact that the etching does not quite behave linearly with time, and thus the required time to achieve the same etching depth was underestimated by the operator.
As solar cell efficiency scales linearly with V_{oc} leaving out the SDE steps is expected to make a difference in larger scale production. A loss in efficiency of 0,06 %abs is to be expected. If this loss may be avoided, if longer texturing times and thus deeper etching is applied, needs further investigation.

[3]International Technology Roadmap for Photovoltaic (ITRPV) 2016
http://www.itrpv.net/.cm4all/iproc.php/ITRPV_seventh_edition_presentation_20160317.pdf?cdp=a

4 SUMMARY AND OUTLOOK

Solar cells from p-type single crystalline silicon were processed using only on etching and one cleaning step. The solar cell efficiencies (18,75%) were within the expected range.
A newly developed method for emitter formation and passivation proved to provide superior emitter performance allowing to skip the PSG removal.
Experimental results showed that only small losses in terms of solar cell efficiency are to be expected when, when in addition to the PSG step, SDE and pre-clean, before texturing are left out. The homogeneity and the visual outcome of the front side texturing suffer only slightly. However, the two steps pre-treatment are thought to reduce the deviation of the production outcome in case badly “treated” material is delivered by the wafer producers.
From the ecological point of view and, considering the reduction in capex and running costs, however a simplified treatment of incoming as-cut material may be considered, when the expected loss of 0,06%abs in efficiency can be tolerated (which may even be avoided, if longer etching during texturing is applied).
The wet chemical edge isolation step was replaced by a commercial lasering process step, which is well-known to perform inferior to the wet chemical step. One reason for the inferior performance is the loss in active area, when placing the laser groove near the edge on the front surface. One of the goals of this project is decrease this gap in efficiency by innovative new lasering processes.
In the next stage of this project the post-texturing clean will be studied to further reduce hydrofluoric acid consumption. Also, the PSG passivation diffusion so far only works reliably on single crystalline and not on multicrystalline wafers, an issue that will be further studied.
Another issue that will be addressed in this project is reduction of HF during the cleaning step.

5 LITERATURE

1. Buchholz, F., *Metal surface contamination in c-Si solar cell processing*, in *Fakultät für Chemie und Physik, Institut für Anorganische Chemie*. 2016, TU Bergakademie Freiberg: Freiberg.
2. Sonner, C., et al., *Influence of contamination and cleaning sequences on alkaline texturisation*, in *Proc. of the 26th European Photovoltaic Solar Energy Conference and Exhibition*. 2011: Hamburg. p. 1666-1670.