Further improvements in surface modification of MC silicon solar cells: comparison of different post-PSG cleans for inline emitters

Arno F. Stassen & **Martien Koppes**, ECN Solar Energy, Petten, The Netherlands; **Johan Hoogboom**, Mallinckrodt Baker B.V., Deventer, The Netherlands

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ABSTRACT

Insufficient removal of phosphosilicate glass (PSG) after inline emitter formation for crystalline silicon solar cells reduces cell efficiency. With additional chemical steps, the surface can be modified to increase both short-circuit current and open-circuit voltage. In this paper we demonstrate that the efficiency can be increased by at least 0.4% absolute by using a simple surface modification process. The process is compatible with standard crystalline silicon production processes.

Introduction

For inline processing, the standard method of fabricating an emitter is by applying a phosphor-containing solution (either by spraying, sonic evaporation or by other methods), followed by a heating step. The phosphor present on the wafer dehydrates to form $(P_2O_5)_n$ which subsequently reacts with silicon and oxygen to form a phosphosilicate glass (PSG).

In order to obtain a high efficiency, this PSG layer has to be removed completely before applying a passivating anti-reflection coating (ARC), normally SiN_x:H. The standard method of removing PSG is by submerging the wafer in an aqueous hydrofluoric acid bath for one to two minutes.

Our paper previously published in *Photovoltaics International* [1] has shown that this process does not completely remove the PSG and that additional cleaning, or 'surface modification' will result in a higher efficiency.

"The presence of PSG-remains can be seen as either white spots or as a white glow over the wafers in SiN coating."

A thorough cleaning process can be divided into four steps: 1. removal of the PSG layer; 2. removal of particles such as dust from the surface; 3. removal of part of the dead layer; and 4. modifying the surface layer of the emitter. The standard PSG removal works poorly; the surface still contains large amounts of PSG remains and particles and the surface concentration of phosphor is often very high (over $3 \times 10^{21}cm^{-3}$) [2].

The presence of PSG-remains can be seen as either white spots or as a white glow over the wafers in SiN coating. This leads to more absorption, because the PSG is not fully transparent for visible light, and passivates poorly. The top layer of the emitter contains a very high amount of phosphor, the majority of which is not electrically active because the concentration is far above the solid solubility. By removing a small part of this so-called 'dead layer' (step 3), the absolute amount of non-active phosphor is reduced and therefore the number of recombination centres is reduced.

"Parameters of influence are crystal orientation, absolute surface area and surface morphology."

Finally, the passivation also depends on the resulting surface (step 4). Parameters of influence are crystal orientation, absolute surface area and surface morphology. For example, pinholes will reduce passivation quality.

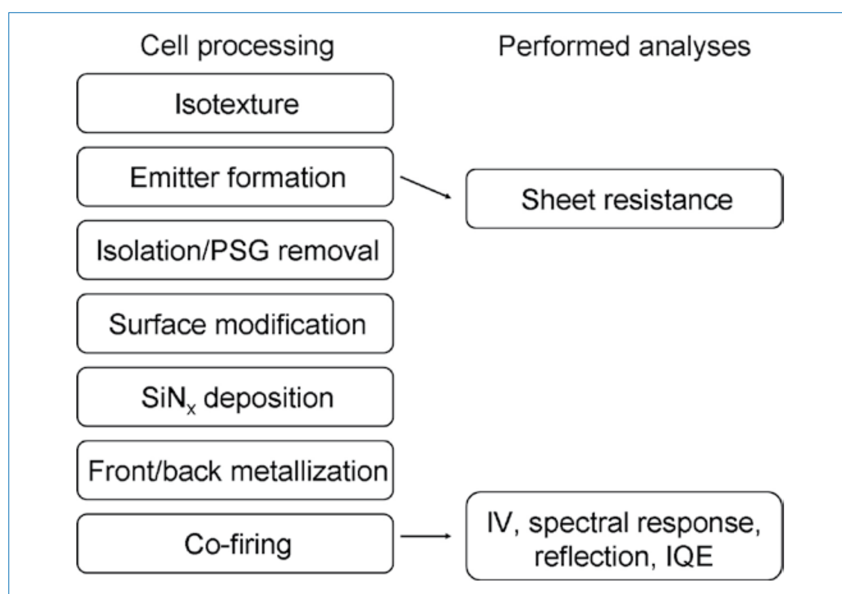

Figure 1. Process flow for fabricating solar cells and performed analyses. Groups 8 and 9 have isolation before surface modification, all other groups as final step.

At this moment, the ECN-Clean containing the J.T. Baker PV-160 surface modifier is the only commercial surface modification process used in the industry. We have looked at different processes for surface modification in order to improve on the existing system, and identified one process which results in improved cell performance for a small increase in cost. This process has been tested in different fabrication schemes.

Approach

All wafers are processed using an industrial firing-through process scheme (see Fig. 1). All tools are either identical to those used in the industry or scaled-down industrial tools.

The search for an improved method for surface modification has been divided in two parts. In the first part, six groups of 17 neighbouring wafers were used to test the effect of a wide range of different wet chemical surface modifications.

In group **1**, PSG is removed using only an aqueous HF solution without any additional chemical steps – a conventional PSG removal. The processing of group **2** is standard ECN-Clean using the PV-160 surface modifier. The modification performed on group **3** is an alternative processing sequence also using PV-160 as one of the active ingredients. This method is known to increase V_{oc}, J_{sc} and thereby efficiency compared to the standard ECN-Clean process, only for a much higher cost of ownership and has been previously published under the name "Pasha Clean" [2].

The surface modification steps performed on groups **4** and **5** are faster and cheaper versions of the processing used in group **3**. The processing time of group **4** is more than 15 minutes shorter than the processing time of group **3** and only a few minutes longer than the conventional ECN-Clean (group **2**). Group **6** is an alternative process not using the surface modifier as an active ingredient. The processing time is longer than that of the standard ECN-Clean, but only standard chemicals are used.

During each surface modification process, a very thin layer is removed from the top of the wafer. This is done in order to remove a part of the 'dead layer' (step 3) and to influence the surface (step 4). A result of this removal is an increase in sheet resistance R_{sheet}.

The wafers of each group were selected in such a way that each wafer has an almost identical 'neighbour' (sister wafer) in the five other groups. In this way, differences in material quality are excluded from the analyses. During all processing steps, except for the surface modification steps, the wafers were not processed per group but in order of position with the group (starting with all number 1s of each group, followed by all number 2s, and so on). By processing the wafer in this way, variation over time of the diffusion oven or the printing, for example, are excluded.

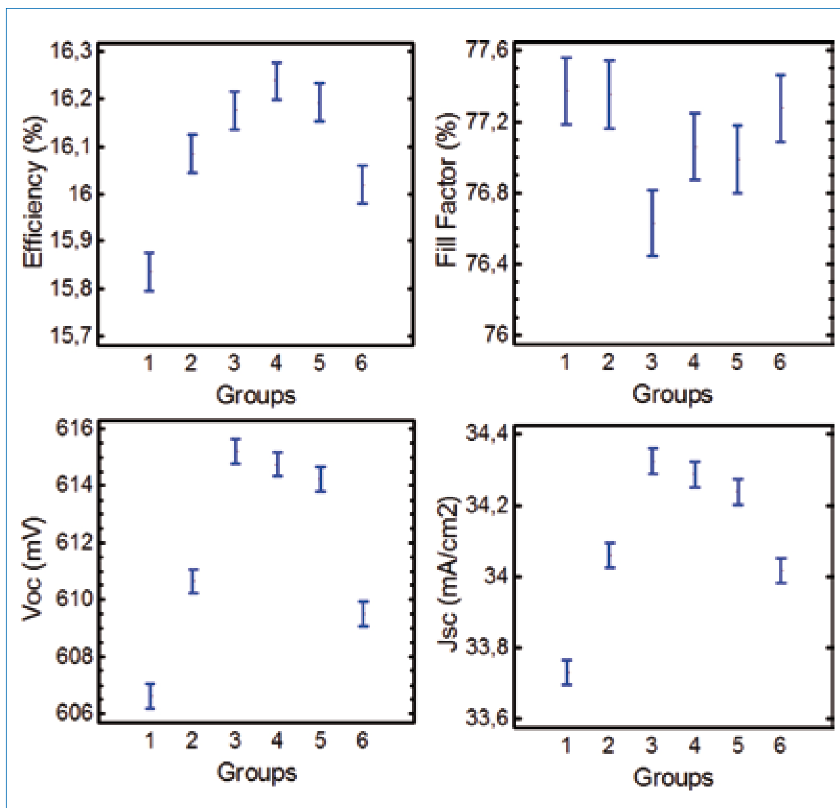

Figure 2. Means and 95.0% Tukey HSD Intervals of efficiency, current, voltage and fill factor of the six different mc-Si groups. **1**: only HF; **2**: ECN-Clean; **3**: Pasha Clean; **4**: very short variant on Pasha Clean; **5**: short variant Pasha Clean; **6**: alternative without PV-160 surface modifier.

	J_{sc} (mA/cm2)	V_{oc} (mV)	FF (%)	ETA (%)	max ETA	$J_{sc} \times V_{oc}$
1	33.731	607	77.4	15.836	15.997	20.463
2	34.060	611	77.3	16.085	16.199	20.797
3	34.323	615	76.6	16.176	16.370	21.109
4	34.288	615	77.1	16.238	16.386	21.074
5	34.238	614	77.0	16.193	16.326	21.034
6	34.017	609	77.3	16.020	16.150	20.731

Table 1. Cell parameters from an average of 17 neighboring mc Si cells.

	J_{sc} (mA/cm2)	V_{oc} (mV)	FF (%)	ETA (%)	max ETA	$J_{sc} \times V_{oc}$
7	33.703	607	77.7	15.901	16.015	20.460
8	33.992	609	78.1	16.163	16.214	20.698
9	34.156	613	77.9	16.300	16.348	20.928

7: only PSG removal with HF
8: WCJI with ECN-Clean
9: WCJI with surface modification **4**

Table 2. Cell parameters from an average of nine neighbouring mc Si cells.

Wafers were processed according to the process sequence given in Fig. 1. Before and after the cleaning steps, sheet resistance was measured using a Sherescan [3]. After processing, IV curves, spectral response and reflection were measured and internal quantum efficiency (IQE) was calculated. All multicrystalline silicon wafers had an area of 156 × 156mm^2 with an average thickness of 180μm.

The texture was the inline ECN-iso-texture, and the emitter was formed using a Despatch spraycoater and a Despatch IR heated belt furnace. SiN_x was used as ARC and deposited by an R&R SINA system. The wafers were screen printed using a Baccini printer. Firing was conducted in a Despatch IR firing belt furnace. All surface modification process steps are wet chemical steps in which only water-based chemistry is used.

After selecting the best industrial process, this chemical process (group **4**) was tested in combination with wet chemical junction isolation (WCJI) (group **9**) versus our standard process combining wet chemical edge isolation and ECN-Clean (group **8**) and a reference group with isolation by mechanical isolation and no surface modification (group **7**). Each group consisted of nine wafers: each wafer with sister cells in the other two groups. The WCJI is performed before the PSG removal to prevent surface damage from vapours formed during the WCJI process.

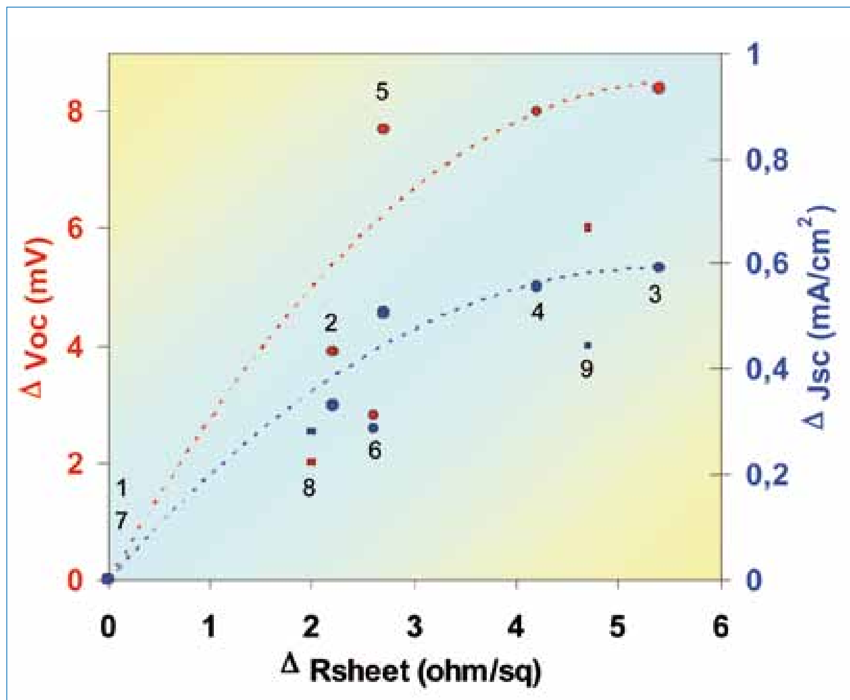

Figure 3. Increases in V_{oc} (red) and J_{sc} (blue) plotted versus the increase in R_{sheet}. The group number is plotted above or below the markers; the dotted lines are meant as guides for the eye. The circles correspond with Part 1 and the squares with Part 2.

The wafers selected for Part 1 and Part 2 are of a comparable material quality but there is no direct relation between the wafers selected for the two parts.

Results Part 1

The average cell results of groups **1** to **6** are shown in Table 1 and the statistical comparison in Fig. 2. The internal quantum efficiency and the increase in IQE compared to conventional PSG removal are shown in Fig. 4.

Results Part 2

The process used in group **4** has been tested in combination with wet chemical junction isolation **9** with as reference groups **7**: PSG removal with HF and mechanical edge isolation, and group **8**: WCEI followed by the ECN-Clean process. The average cell results are shown in Table 2.

Discussion

In groups **1** to **6**, all groups with additional surface modification show a significant increase in efficiency, J_{sc} and V_{oc}

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compared to conventional PSG removal. No significant reduction in fill factor was observed, except for group **3**, which underwent the most elaborate surface modification.

With respect to J_{sc} and V_{oc}, three levels can be distinguished. For group **1**, both J_{sc} and V_{oc} are significantly lower than for all other groups. Groups **2** and **6** show higher values than group **1**, but are still below the results observed in groups **3**, **4** and **5**.

As expected the use of ECN-Clean (group **2**) results in an absolute increase of 0.3% in efficiency. In group **3** even higher values for V_{oc} and J_{sc} are reached.

The novel surface modification steps of groups **4** and **5** shows that a J_{sc} and V_{oc} can be reached comparable to group **3** without a significant loss in fill factor. The efficiency gain of group **4** compared to group **1** (conventional PSG removal) is 0.4%.

Group **6** shows that it is possible to increase the efficiency by 0.2% absolute using only standard chemicals. However, this increase is significantly lower than using processing based on the PV-160 surface modifier. The main difference between group **6**'s results and the other groups is a lower gain in V_{oc}.

A direct relation exists between the increase in sheet resistance and resulting cell parameters changes for groups **2**, **3**, **4** and **5** (see Fig. 3). A higher increase in Rsheet not only results in higher values for J_{sc} and V_{oc} but also in a (except for group **3**) non-significant decrease in fill factor (see Table 1). The reason that group **4** has a higher efficiency than groups **3** and **5** (which have a higher product of $J_{sc} \times V_{oc}$) is that this reduction in fill factor is smaller.

The values of V_{oc} and J_{sc} of group **6** do not follow the trend observed in groups **2** to **5**. Although the increase in R_{sheet} is comparable to group **5**, the increases in J_{sc} and V_{oc} are much lower. This can be an indication that not only step 3 (removal of part of the dead layer), but also step 4 (modified surface) have a strong influence on the resulting I_{sc} and V_{oc}. The V_{oc} and J_{sc} increase due to the rise in R_{sheet} but are decreased simultaneously due to a less suitable surface for passivation.

The same trend is also seen in the internal quantum efficiency (see Fig. 4). Because both material and further processing are identical for all groups, except for the cleaning of the surface of the solar cell, the IQE is identical for both the bulk and the backside of the wafer (>600nm). The differences between 330 and 600nm coincide exactly with the voltage of the different solar cells (values given in Fig. 4b).

> **"The V_{oc} and J_{sc} increase due to the rise in R_{sheet} but are decreased simultaneously due to a less suitable surface for passivation."**

The second part, testing the surface modification with the shortest processing time and the highest gain in efficiency in combination with wet chemical edge isolation, has been performed with three groups of nine neighbouring wafers each.

The comparison between groups **1** and **7** indicates that processing differences can be neglected. Both J_{sc} and V_{oc} in the two groups are almost identical. Only the fill factor shows a difference, due to a further optimization of the processing. This increase in fill factor is even more pronounced in groups **8** and **9**. Where a small drop would be expected, a small (statistically insignificant) increase is observed (see Table 2).

The combination of WCJI and ECN-Clean results in an increase of approximately 0.25% absolute compared to no surface modification. The gain is in J_{sc}, V_{oc} and in fill factor.

The positive effects of the processing of group **4** versus those of a comparable group with the ECN-Clean as surface modification appear to be independent of the isolation method. Increases of 4mV and ~0.2mA/cm² are seen between both groups **2** and **4** and between groups **8** and **9**. Also, the reduction in fill factor of 0.2% is identical in both comparisons.

The relation between ΔR_{sheet} and ΔJ_{sc}, and ΔV_{oc} of group **9** is not in complete agreement with the relation found between groups **1** to **5** (see Fig. 3). In both groups, the J_{sc} and V_{oc} appear to follow a comparable trend versus the increase in R_{sheet}, but the absolute values are lower than in groups **2** to **5**. One explanation could be that, even though the PSG should act as an etching barrier, the emitter is slightly damaged during the WCJI without increasing the R_{sheet} observed. This damage results in a surface which is less ideal for surface passivation (step 4). If for group **9** comparable increases had been found as in groups **2** to **5**, average efficiencies of 16.5% would have been possible.

Conclusions

It is possible to increase the efficiency of solar cells produced with inline diffusion methods. This is done by using wet chemical steps after conventional PSG removal and before applying the anti-reflection coating (normally silicon nitride). Next to removal of PSG remains, particles and partial removal of the dead layer, surface morphology after the surface modification steps most likely influences the resulting cell performance.

The results from this paper show that an absolute increase of at least 0.4% in efficiency is possible by using a process suitable for industry.

Trends are observed in the increases in V_{oc} and J_{sc}. Groups with comparable processing (all containing J.T. Baker's

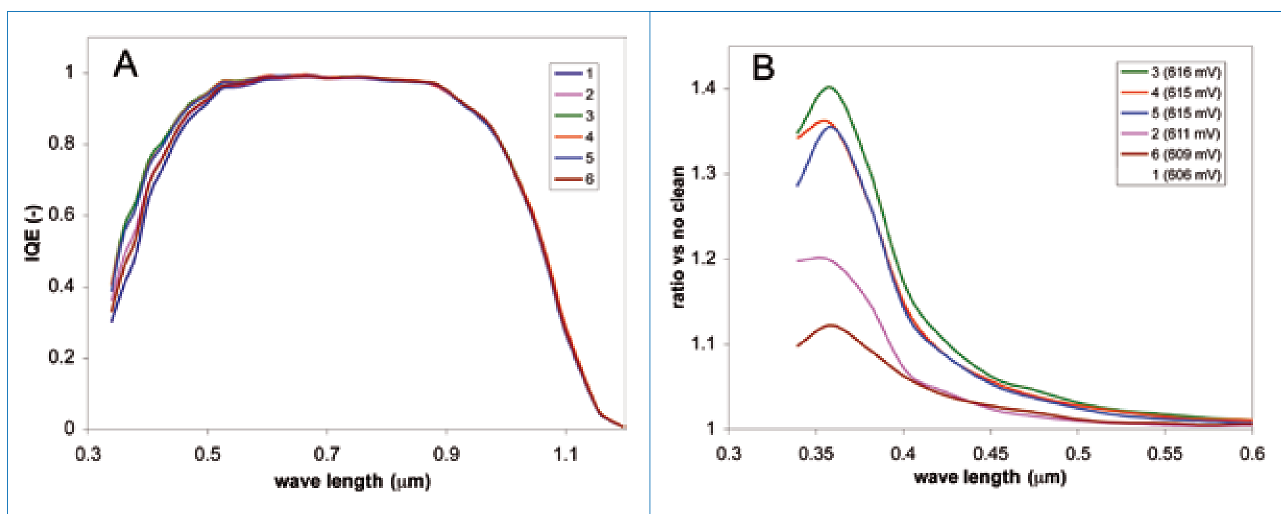

Figure 4. A: Internal quantum efficiency of a set of neighbouring cells with different surface modifications; B: the relative increase in blue response compared to no clean (included are the voltages of the individual cells).

PV-160 and no WCJI) show increases in V_{oc} and J_{sc} related to increasing ΔR_{sheet}. In groups with alternative processing (all containing PV-160 but with WCJI) a comparable trend is observed; only the actual increases in J_{sc} and V_{oc} are smaller.

The use of surface modification **4** instead of the ECN-Clean results in an increase in efficiency of 0.15% absolute. This increase is independent of the isolation method. In both tests, gains were seen of 4mV in V_{oc} and 0.2mA/cm^2 in Jsc and a loss of 0.2% in fill factor, resulting in this 0.15% increase in efficiency.

Acknowledgements

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About the Authors

Arno Stassen has worked as a research scientist in ECN's Silicon PV Technology group since 2006, addressing chemical etching, oxidation and cleaning of silicon wafers. As project leader, he is responsible for the ECN pilot line process. Stassen studied chemistry at the Radboud University Nijmegen and obtained his doctorate at Leiden University in 2002. From 2002 to 2006, he worked as a post-doctoral research fellow at the Technical University of Vienna, Leiden University, Technical University of Delft and ETH Zurich.

Martien Koppes has worked as a chemical specialist in ECN's Silicon PV Technology group since 1991. Koppes has been strongly involved in the development of multiple wet chemical processes such as the ECN-isotexture, the ECN T2 low reflection texture, the ECN-Clean, the Pasha Clean and wet chemical processes dedicated for n-type solar cells.

Johan Hoogboom obtained his Ph.D. in 2004 on physical-organic chemistry and solid-state physics from the Radboud University in Nijmegen, The Netherlands, focusing on self-assembled alignment layers for LCDs. After that, he moved to MIT as a postdoctoral fellow, working on polymer-based explosives sensors in a joint project with the US Army. In 2006, he moved back to the Radboud University as an assistant professor in organic electronics, coordinating material research into organic solar cells, LEDs, FETs, TFTs and nanowires. In early 2008, he joined Mallinckrodt Baker B.V. and is now the global R&D coordinator for silicon photovoltaics.

Enquiries

ECN Solar Energy
P.O. Box 1, 1755 ZG Petten
The Netherlands

Tel: +31 224 56 49 85
Fax: +31 224 56 8214
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