FURTHER IMPROVEMENTS IN SURFACE MODIFICATION OF MC SILICON SOLAR CELLS: COMPARISON OF DIFFERENT POST-PSG CLEANS SUITABLE FOR INLINE EMITTERS

Arno F. Stassen[1], Martien Koppes[1], Yuji Komatsu[1] and Arthur Weeber[1]
Johan Hoogboom[2], Jan Oosterholt[2], Sabrina Ritmeijer[2], Luuk Groenewoud[2]
[1] ECN Solar Energy, P.O. Box 1, 1755 ZG Petten, The Netherlands, Tel: +31 224 56 49 85, Fax: +31 224 56 8214,
[2] Mallinckrodt Baker EMEA, P.O. Box 1, 7400 AA, Deventer, The Netherlands
Email: Stassen@ecn.nl

ABSTRACT: Insufficient removal of phosphosilicate glass (PSG) after inline emitter formation for crystalline silicon solar cells is a limiting factor in reaching high efficiencies. With additional cleaning steps, the surface can be modified to increase both short-circuit current and open-circuit voltage without decreasing the fill factor. In this paper we demonstrate that the efficiency can be increased by at least 0.4% absolute by using simple surface modification processes.

Keywords: Chemistry, Surface Modification, Multicrystalline Silicon

1 INTRODUCTION

For inline processing, the standard method of fabricating an emitter layer is by applying phosphor from a solution (either by spraying, sonic evaporation or by other methods), followed by a heating step. The phosphor present on the wafer dehydrates to form $(P_2O_5)_n$ and 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 before applying passivating anti-reflection coating (ARC), in most cases silicon nitride. The standard method of removing PSG is by submerging the wafer in an aqueous hydrofluoric acid bath for one to two minutes.

We have shown before (1) that standard PSG removal is not complete and that additional cleaning, or “surface modification” will result in a higher efficiency.

A thorough cleaning process can be divided in four steps: [1] removal of the PSG layer, [2] removal of particles such as dust of 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, even for step [1]; the remaining surface still contains large amounts of PSG, particles and the surface concentration of phosphor is often very high (often over 3×10^{21} cm^{-3}).

The presence of PSG-remains can be seen as either white spots or as a white glow over the wafers. The result is 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 is not electrically active because the concentration is far above the solid solubility. By removing a small part of this so-called ‘dead layer’ [3], the absolute amount of non-active phosphor is reduced which means that also the number of possible recombination centers is reduced.

Finally, the resulting surface [4] is also of influence on passivation. Parameters of influence are crystal orientation, absolute surface area and surface morphology. For example, pinholes will reduce passivation quality

2 APPROACH

All wafers are processed according to a production firing-through process scheme which is similar to that used in industry. All tools are either identical to those used in industry or scaled down lab tools.

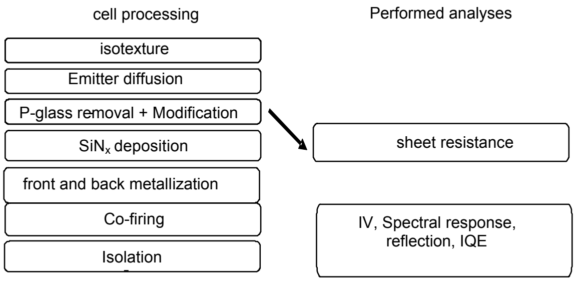

Figure 2.1. Process flow for fabricating solar cells and performed analyses.

Six groups of 17 neighboring wafers were used to test the effect of different wet chemical surface modifications

In group **1**, PSG is removed using only an aqueous HF solution without any additional chemical steps, so, a conventional PSG removal

The processing of group **2** is standard ECN-Clean using BakerClean PV-160® as performed in industry.

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 Voc, Jsc and thereby efficiency compared to the standard ECN-Clean process, only for a much higher cost of ownership and has 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 even more than 15 minutes shorter than the processing time of group **3** and only some minutes longer than the concentional ECN-Clean (group **2**).

Group **6** is an alternative process not using BakerClean PV-160® 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 ‘neighbor’ (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 (first all number 1s of each group, followed by all second wafers, etc.). By processing the wafer in this way, variation over time of e.g. the diffusion oven or the printing are excluded.

Wafers were processed according to figure 2.1. Before and after the cleaning steps the sheet resistance was measured using a Sherescan (3). After processing, IV curves, spectral response and reflection were measured from which the internal quantum efficiency (IQE) was calculated. All multi crystalline wafers used had an area of 156x156 mm^2 with an average thickness of 180 µm.

The texture was the inline ECN-iso-texture, emitter formation by using the Despatch spraycoater and the Despatch belt furnace. SiN_x was used as ARC and deposition by an R&R SINA system. The wafers were screen printed using a Baccini printer. Firing was conducted in a Despatch firing belt oven.

All steps in the surface modification process are wet chemical and only water based chemistry is used.

3 RESULTS

The average cell results are shown in table I and statistical comparison in figure 3.1. The internal quantum efficiency and the increase in IQE compared to conventional PSG removal are shown in figure 4.1.

Table I. Cell parameters, average of 17 neighboring mc-Si cells

	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	ETA (%)	max ETA	Jsc × Voc
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

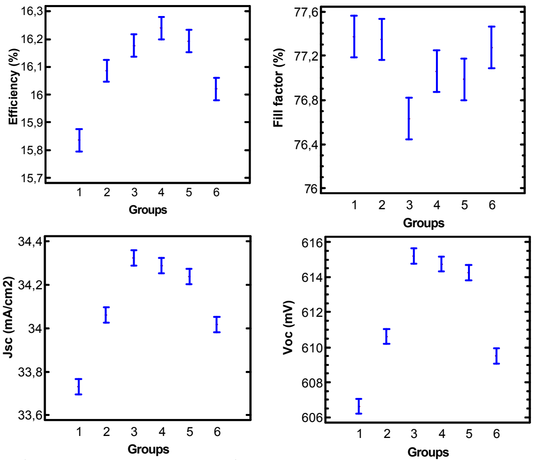

Figure 3.1. Means and 95.0% Tukey HSD Intervals of efficiency, current, voltage and fill factor of the six different mc-Si groups.

4 DISCUSSION

All groups with additional surface modification show a significant increase in efficiency, Jsc and Voc compared to conventional PSG removal.

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

Especially in Jsc and Voc three levels can be distinguished. For group **1** both in Jsc and Voc 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 Voc and Jsc are reached,

The novel surface modification steps groups **4** and **5** show that a Jsc and Voc 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 although the best results are obtained with processing using the BakerClean PV-160$^{®}$, it is possible to increase the efficiency by 0.2% absolute using only standard chemicals. The main difference between the results of group **6** and the other groups is a lower gain in Voc.

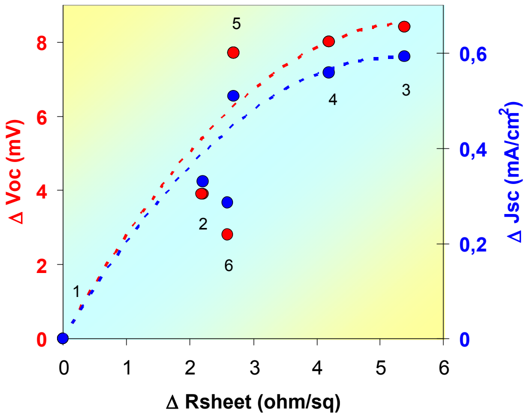

Figure 4.1. Increases in Voc (red) and Jsc (blue) plotted versus the increase in R_{sheet}. The number of the group is noted above or below the measured points, the dotted lines are meant as guide for the eye.

There is a direct relation between the increase in sheet resistance and the changes in cell parameters in the groups **2**, **3**, **4** and **5** (see figure 4.1). A higher increase in R_{sheet} 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 II). The reason that group **4** yields a higher efficiency than groups **3** and **5** (who have a higher product of Jsc×Voc) is that this reduction in fill factor is less strong. Group **6** does not follow this trend: although the increase in R_{sheet} is comparable to group **5**, the increases in J_{sc} and V_{oc} are much lower than would be expected. This can be an indication not only step [3] (removal of part of the dead layer), but also step [4] (modified surface) has an influence of the resulting Isc and Voc.

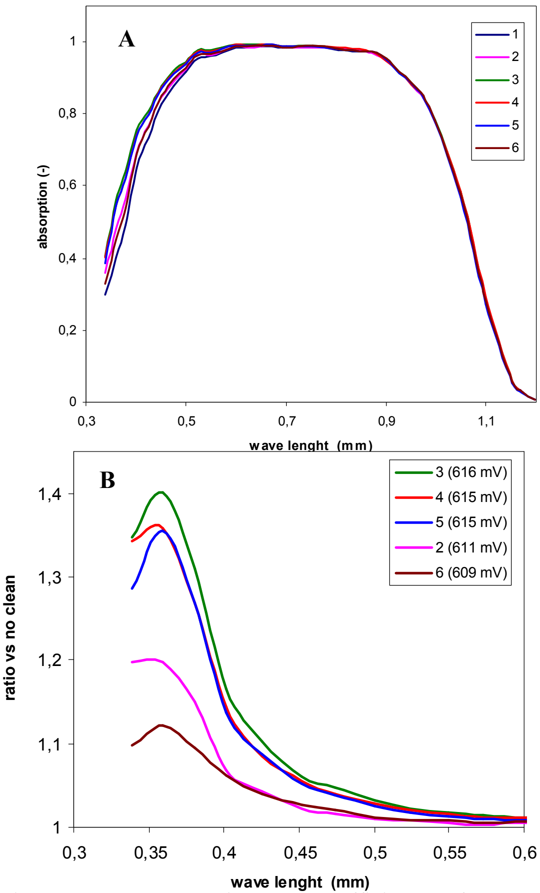

Figure 4.2: A: Internal quantum efficiency of a set of neighboring cells with different surface modifications ; (B) the relative increase in blue response compared to no clean (included are the voltages of the individual cells).

The same trend is also seen in the internal quantum efficiency (see figure 4.2). 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 (>600 nm). The differences between 330 and 600 nm coincide exactly with the voltage of the different solar cells (values given in figure 4.2B).

5 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, also the surface morphology after the surface modification steps probably influences the resulting cell performance.

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

It is also possible to increase the efficiency of solar cells with 0.2% absolute by using only standard chemicals, but the best results are all obtained using the BakerClean PV-160®.

5 ACKNOWLEDGEMENTS

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6 REFERENCES

(1) Hoogboom et al. PV International. Ed. 2, 2009
(2) I. Cesar et al., *Proc. 23nd EPVSEC*, Valencia, 2008
(3) http://www.sunlab.nl/sherescan/