

A NOVEL APPROACH TO HIGH PERFORMANCE AND COST EFFECTIVE SURFACE CLEANING FOR HIGH EFFICIENCY SOLAR CELLS

A. Moldovan^{1A}, M. Zimmer¹, J.Rentsch¹, B.Ferstl², S.Rajagopalan², S.Thate², J.Hoogboom², M.Ross²

¹Fraunhofer Institute for Solar Energy Systems ISE, ²BASF SE

¹Heidenhofstraße 2, 79110 Freiburg, Germany

²Carl-Bosch-Straße, 67056 Ludwigshafen, Germany

^APhone: +49 (0)761 4588 5536, e-mail: anamaria.moldovan@ise.fraunhofer.de

ABSTRACT: In this work a novel one-step wet chemical surface cleaning approach with reduced cost of ownership for the industrial realization of high efficiency silicon solar cells is evaluated in a comparative study. For this purpose investigations concerning metal removal efficiency, impact on emitter sheet resistance change, carrier lifetime and on electrical cell data are performed. In all tests a comparable performance of SELURIS® to RCA [1] cleaning can be attained by an optimization of the SELURIS® formulation. On conventional Cz wafers of 156 mm size, peak efficiencies of 19.4 % for PERC devices with SELURIS® C-2000 series cleaning are achieved.

Keywords: wet chemical surface cleaning, silicon solar cells, selective emitter

1 INTRODUCTION

With introduction of the PERC (passivated emitter and rear cell) [2] solar cell concept that is currently transferred into industrial production [3-6], surface cleaning and conditioning is gaining an increasing importance. The quality of the interface between silicon substrate and passivation layer plays a significant role especially for high efficiency solar cells which are very sensitive to these impact factors. Therefore surface contaminations (organics, particles and metals) must be removed to secure effective passivation and avoid interlayer recombination sites. Supported by Fraunhofer ISE, BASF has evaluated a new cleaning recipe, which provides both effective cleaning performance and reduced cost of ownership.

In order to provide effective cleaning, an easy applicable, fast one-step cleaning solution was benchmarked, which is capable of simultaneously removing organics, particle and metal impurities, offering a cost-effective alternative to complex multi-bath, high temperature approaches like RCA-clean [1] which were derived from microelectronics. For this purpose, a comparative study of BASF's SELURIS® C-2000 series recipes with RCA cleaning was carried out to investigate metal solution capability, cleaning efficiency, effect on emitter sheet resistance change, carrier lifetime and on electrical cell data.

2 APPROACH

To ensure a complete metal removal, cleaning efficiency tests were conducted. For this purpose, RCA pre-cleaned test samples were contaminated with iron (Fe) and copper (Cu) solutions of a defined (0.1 mg/l or 1.0 mg/l Fe and Cu) concentration prior to RCA or SELURIS® C-2000 (standard composition, complexing agent variation SELURIS® C-2000a or C-2000b) cleaning. The concentration of metal on the surface in all states of the experiment was determined by DSE/AAS (droplet surface etching followed by atomic absorption spectroscopy). For the DSE surface scan, a freshly prepared solution of HF/H₂O₂ (both 2 wt. %) was used to ensure optimal metal collection efficiency.

Subsequent all pre-tests SELURIS® C-2000 and

RCA cleaning were compared within the scope of front and rear side lifetime samples according to the principle of a TOPAS (thermal oxide passivation all sides)-PERC [7] cell. A schematic cross section of a TOPAS-PERC device is depicted in Fig. 1.

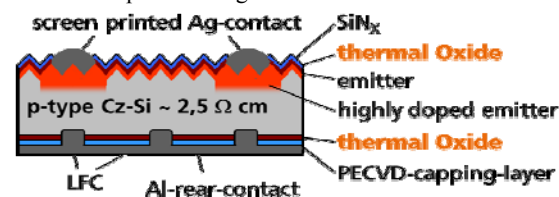


Figure 1: Schematic cross section of the TOPAS-PERC-type cell

For the PERC structure the textured surface of the rear side of the wafer is planarized by single-side wet chemical polishing etch in order to reduce the surface area and interface trap density [7, 8]. In the TOPAS approach both surfaces are passivated by a thin thermally grown oxide and are capped by a SiNx ARC on the front and a PECVD layer stack on the rear. Independent of the rear side, the implementation of a selective emitter [9] on the front side reduces carrier recombination in the emitter and enhances the blue response. A low doping level is chosen in the photoactive area for optimal charge carrier conversion and highly doped areas are placed underneath the metallization to ensure a low contact resistance. Contact formation is realized by screen printing and local point contacts on the rear side, created by LFC [10, 11]. Figure 2 shows the process sequence for the fabrication of TOPAS-PERC solar cells employed in this work.

For the preparation of the lifetime samples 4'', boron doped Floatzone (FZ)-Si wafers with a resistivity of 1Ωcm and a thickness of 250 μm were used.

As an adjusted emitter sheet resistance is very important for the persuade cell concept, the impact of the composition of the cleaning solution and testing conditions on emitter sheet resistance change was investigated by 4-point-probe measurements.

Furthermore two batches of TOPAS-PERC solar cells with comparison of different cleaning processes were fabricated to investigate the impact on electrical cell data. Boron doped Cz-Si wafers with a resistivity of around 2 Ωcm, 156 mm dimension and a thickness of 200 μm

served as starting material.

Finally - as cost of ownership and process relevant - the stability of H_2O_2 was determined in different cleaning solutions. For this purpose, a freshly prepared SC1 (ammonia peroxide mixture) or SELURIS® C-2000 solution is heated to process temperature (65°C), then H_2O_2 is added and immediately after a sample is taken and analyzed by titration to determine the H_2O_2 concentration in the solution. Following further samples are taken and analyzed at intervals of 3 minutes to record the H_2O_2 decomposition.

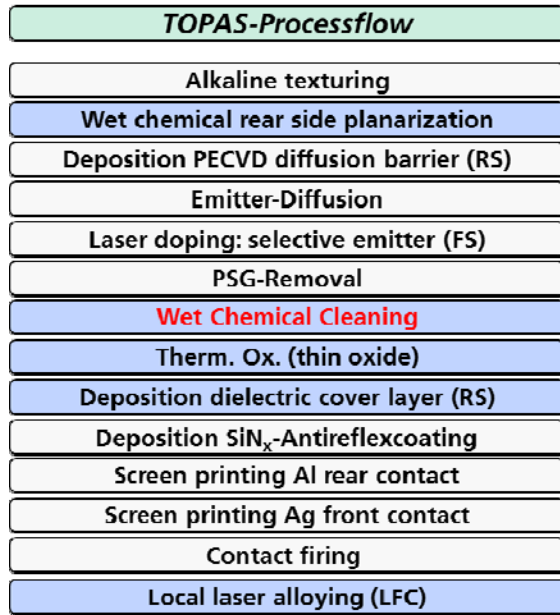


Figure 2: Process sequence for the fabrication of TOPAS-PERC solar cells employed in this work

3 RESULTS

3.1 Metal removal efficiency and symmetrical rear side lifetime samples

As pictured in Fig. 3, both tested cleaning approaches show a good and comparable metal surface contamination removal. After cleaning, the metal surface concentration mean value can be reduced for Fe from values above $1E13$ at/cm², to maximum values of $5E10$ at/cm², and for Cu from values above $1E12$ at/cm², to maximum values of $5E10$ at/cm².

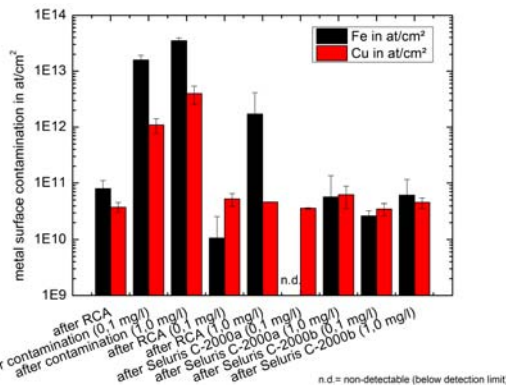


Figure 3: Metal surface contamination after RCA pre-cleaning, contamination in a solution of defined metal (0.1 or 1.0 mg/l Fe and Cu) concentration and subsequent

RCA or SELURIS® (standard composition, complexing agent variation) cleaning determined by DSE/AAS

The promising results on metal removal efficiency are also reflected in the high minority carrier lifetime of the simultaneously processed symmetrical rear side lifetime samples, which correspond to the structure of the TOPAS-PERC cell depicted in Fig. 1. The comparison of the metal removal efficiency and minority carrier lifetime values for SELURIS® C-2000a and b indicate the significance of additive selection.

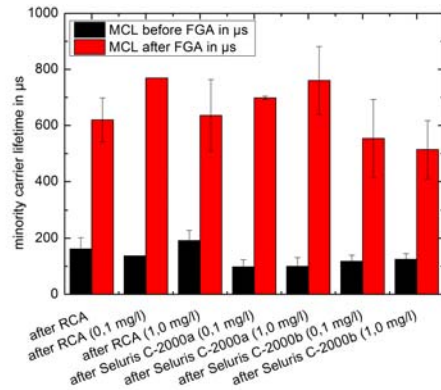


Figure 4: Minority carrier lifetime values of symmetrical rear side lifetime samples which were simultaneously processed with the metal removal efficiency test samples

3.2 IV-results of first cell batch

Fig. 5 shows the current-voltage (IV) parameters for the processed TOPAS-PERC solar cells with cleaning comparison (process sequence Fig. 2). The measurements of the fabricated cells are performed in the non-stabilized, as-processed state. Analysis of the results was carried out using the mean values of all tested firing temperatures (840, 860 and 880°C). Overall high median cell efficiencies of 19.3% and for SC1/SC2 and 19.2% for SELURIS® C-2000v1 could be achieved. Table 1 gives an overview of the median and the maximum values of the cell parameters for both cleaning approaches.

Table 1: Cell parameters measured after processing (not stabilised) using an industrial cell tester. All solar cells are fabricated from 156 mm pseudo-square sized Cz-Si wafers with a resistivity of ~2 Ωcm.

Cleaning group	Category	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	pFF (%)	η (%)
SC1/SC2	median (29)	650	39.3	75.6	83.2	19.3
	best cell	652	39.5	76.2	83.5	19.5
SELURIS® C-2000v1	median (34)	643	39.1	75.9	83.2	19.2
	best cell	646	39.4	76.6	83.4	19.4

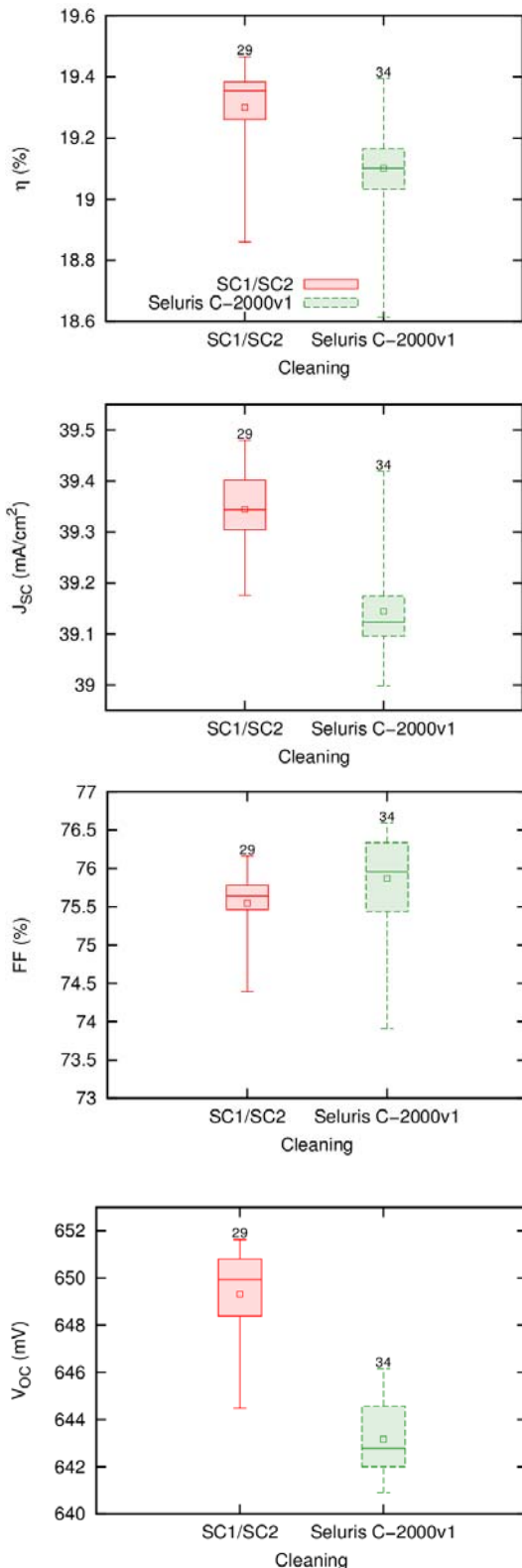


Figure 5: Current-voltage (IV) parameters for the processed TOPAS-PERC solar cells with cleaning comparison (first cell batch)

Despite the good cleaning performance demonstrated in the experiment described in the previous section lower cell efficiencies are obtained for SELURIS® C-2000v1 compared to SC1/SC2 cleaning. Lower J_{sc} and V_{oc} values indicate that the difference between the

efficiencies results from losses on the front side due to insufficient emitter etch-back. These findings can be confirmed by internal quantum efficiency (IQE) data. Losses resulting from the emitter can be observed in the lower blue response of the cell with SELURIS® C-2000v1 cleaning.

The IQE and reflectance (R) of one solar cell of each group are depicted in Fig. 7.

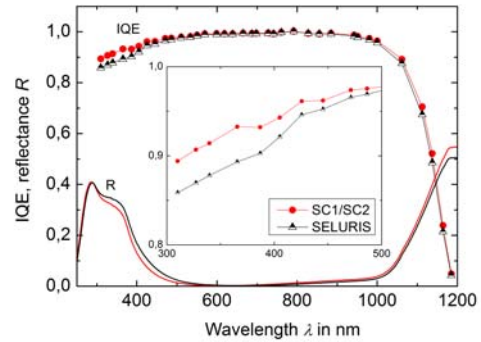


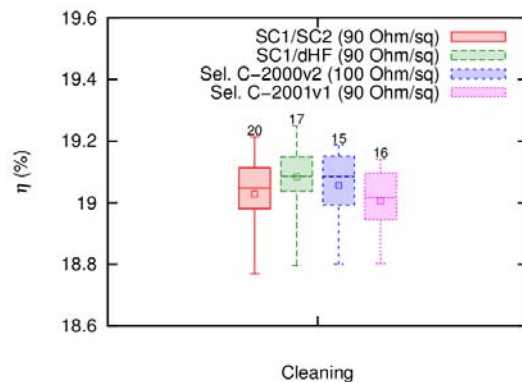
Figure 6: Internal quantum efficiency (IQE) and reflectance (R) of one solar cell of each group

3.3 IV-results of second cell batch

In an effort to improve the J_{sc} and V_{oc} losses resulting from insufficient emitter etch-back two new approaches were adopted for the fabrication of the second cell batch. On the one hand a new SELURIS® C2001v1 solution with an emitter adjustment capability equivalent to that of SC1/SC2 cleaning was tested under equal experimental conditions as for the first cell batch, on the other hand an improved SELURIS® C2000v2 solution (optimized complexing agent system) was tested with a 100 Ohm/sq start emitter in order to consider an approach independent of the etch rate. Further a second reference group with SC1 cleaning followed by a dip in diluted hydrofluoric acid (dHF) was included in the experiment.

In the second experiment high and equivalent overall median cell efficiencies of 19.0 or 19.1% could be achieved for all cleaning approaches. Even if the FF values are higher for the samples of the second experiment, the J_{sc} and V_{oc} values are somewhat lower. Possible reasons for that can be either the non-ideal alignment of the selective emitter structure during screen printing or the lower pitch used for the LFC process.

In Fig. 8 the IV parameters of the second experiment are presented in a summarized form.



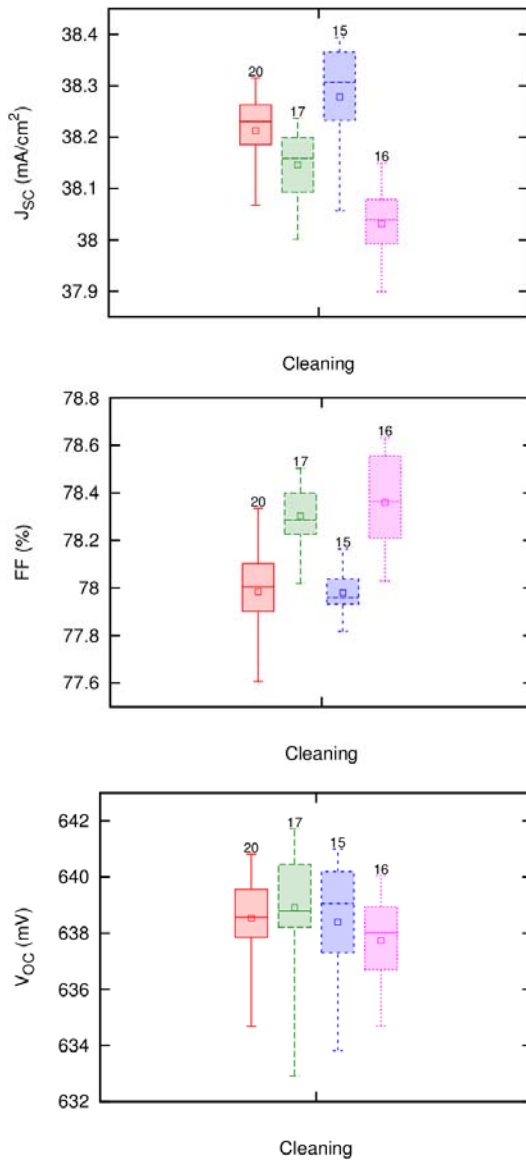


Figure 8: Current-voltage (IV) parameters for the processed TOPAS-PERC solar cells with cleaning comparison (second cell batch with optimized SELURIS® recipes C-2000v2 and C-2001v1)

3.4 H₂O₂ decomposition

The decomposition rate of H₂O₂ is reduced by a factor of 4 in SELURIS® C-2000v1 in comparison to that in SC1 solution (Fig. 9). Free metal ions in solution catalyzing the H₂O₂ decomposition are intercepted by the complexing agent system of the SELURIS® solution.

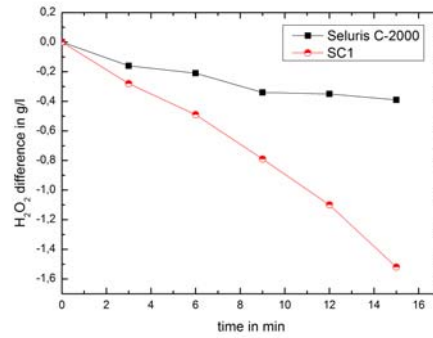


Figure 9: Decomposition rate of H₂O₂ in SC1 vs. SELURIS® C2000 solution at 65°C.

4 SUMMARY/CONCLUSION

In the present work a comparative study of BASF's SELURIS® C series recipes with RCA cleaning was carried out. The alkaline SELURIS® C cleaning solution with optimized complexing agent system enables metal removal efficiencies comparable to that of SC1/SC2 (RCA) cleaning in one process bath. The high minority carrier lifetimes resulting after cleaning also of in advance contaminated samples confirms the results of metal removal efficiency experiment.

Furthermore an extended bath lifetime, reduced process time and chemical consumption due to the stabilized multifunctional solution result in a significant lower cost of ownership.

The improved SELURIS® C-2000v2 and C-2001v1 recipes allow both a high cleaning performance without etching the surface (C2000v2) or with the possibility for emitter adjustment (C2001v1). The results of the second TOPAS PERC cell batch with cell efficiencies exceeding 19% indicate that SELURIS® C-2000v2 or C-2001v1 cleaning solutions can replace the complete SC1/SC2 (RCA) process providing equivalent cell efficiencies.

5 ACKNOWLEDGMENTS

We gratefully acknowledge the technical support by the PV-TEC co-workers and our project partners at BASF SE for funding of this work.

6 REFERENCES

1. Kern, W. and D. Puotinen, *Cleaning solutions based on hydrogen peroxide for use in silicon semiconductor technology*. RCA Review, 1970. **31**: p. 187-205.
2. Blakers, A.W., et al., *22.8% efficient silicon solar cell*. Applied Physics Letters, 1989. **55**(13): p. 1363-5.
3. Engelhart, P., et al. *Q.ANTUM - Q-Cells next generation high-power silicon cell & module concept*. in *Proceedings of the 26th European Photovoltaic Solar Energy Conference and Exhibition*. 2011. Hamburg, Germany.
4. Münzer, K.A., et al. *Towards 19.5 % industrial crystalline silicon solar cells*. in *Proceedings of the 26th European Photovoltaic Solar Energy*

- Conference and Exhibition. 2011. Hamburg, Germany.
5. SCHOTTSolar, *press release SOL2011-182*. 2011.
 6. Wolf, A., et al. *Pilot line processing of 18.6% efficient rear surface passivated large area solar cells*. in *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*. 2010. Honolulu, Hawaii, USA.
 7. Mack, S., et al. *Towards 19% efficient industrial PERC devices using simultaneous front emitter and rear surface passivation by thermal oxidation*. in *Proceedings of the 35th IEEE Photovoltaic Specialists Conference*. 2010. Honolulu, Hawaii, USA.
 8. McIntosh, K.R. and L.P. Johnson, *Recombination at textured silicon surfaces passivated with silicon dioxide*. *Journal of Applied Physics*, 2009. **105**: p. 124520.
 9. Jäger, U., et al. *Selective emitter by laser doping from phosphosilicate glass*. in *Proceedings of the 24th European Photovoltaic Solar Energy Conference*. 2009. Hamburg, Germany.
 10. Preu, R., et al. *Laser-fired contacts - transfer to a simple high efficiency process scheme to industrial production*. in *Proceedings of the 29th IEEE Photovoltaics Specialists Conference*. 2002. New Orleans, Louisiana, USA.
 11. Nekarda, J., et al. *LFC on screen printed aluminium rear side metallization*. in *Proceedings of the 24th European Photovoltaic Solar Energy Conference*. 2009. Hamburg, Germany.