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Industrial cleaning sequences for Al_2O_3-passivated PERC solar cells

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Abstract

In this paper, we investigate different industrial applicable cleaning sequences on test wafers and PERC solar cells in comparison to a laboratory type RCA clean. The cleaning sequences pSC1, HF/HCl, HF/O_3 and HF/O_3 show lifetimes between 1 ms and 2 ms which is comparable to a laboratory type RCA clean corresponding to a surface recombination velocity S_{pass} below 15 cm/s. The pSC1, HF/HCl clean achieves lifetimes around 1 ms, whereas the PSG-etch shows poor cleaning quality with lifetimes around 500 µs. Reference PERC cells using a rear protection layer before texturing and diffusion demonstrate efficiencies up to 20.4% for the cleaning sequence pSC1, HF/HCl prior to passivation which is comparable to the RCA clean. The HF/O_3 cleans result in lower PERC efficiencies up to 20.0% mainly due to a lower Fill Factor which is likely caused by etching of the emitter and hence increased contact resistance. Investigations of polished test wafers show that the cleaning sequences pSC1, HF/HCl, HF-Dip and pSC1, HF/HCl, HF/O_3 are able to sufficiently remove porous silicon from the front side and simultaneously allowing excellent rear surface passivation. A first batch of PERC solar cell results with polished rear surface post texturing and $POCl_3$ diffusion achieves efficiencies of up to 20.7% when applying an RCA clean. However, the pSC1, HF/HCl and pSC1 HF/O_3 still exhibit significantly lower efficiencies since in this batch the porous silicon of the emitter was not yet sufficiently removed, which is subject to further optimization.

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Keywords: Wet chemical polishing; screen-printing; PERC solar cells; cleaning sequences

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1. Introduction

A very promising process flow for industrial-type PERC solar cells includes double sided texturing, double sided $POCl_3$ diffusion and single sided wet chemical polishing [1]. Energy conversion efficiencies of 20.2% for PERC solar cells based on this process flow were recently reported [2]. However, these results were achieved using a laboratory type RCA clean after polishing and prior to ALD-Al_2O_3 deposition, which is costly in industrial process flows.

Vermang et al. [3] evaluated cleanings like SPM, HF, APM – including a sulphuric acid-hydrogen peroxide mixture (SPM) and an ammonia peroxide mixture (APM) – that result in a hydrophilic surfaces as well as cleanings like SPM, HF that result in hydrophobic surfaces prior to atomic layer deposition (ALD) of Al_2O_3 on lifetime test samples. Whereas both exhibited similar effective surface recombination velocities of around 100 cm/s using *p*-type Cz material, they favoured the hydrophilic cleanings due to its higher thermal stability and homogeneity. Other previous work [4] also reported good surface passivation with SPM, HF/HCl, HNO_3 cleans which form a hydrophilic surface and showed lifetimes around 300 µs using *p*-type Cz wafers and PERC cell efficiencies of up to 19.4%. More recent work [5] suggests, that with lifetimes around 1 ms, cleanings resulting in hydrophobic surfaces are superior in terms of cleaning efficiency. Using a Seluris® C solution, which aims at combining Standard Clean 1 (SC1) and Standard Clean 2 (SC2) in one step, they applied a Seluris, HF cleaning sequence prior to ALD-Al_2O_3 passivation to achieve an effective lifetime of 800 µs with p-type Cz material and PERC cell efficiencies of 19.9%. The reference applying a high quality SPM, HF/HCl clean yielded comparable values.

In this paper, we evaluate even shorter cleaning sequences e.g. HF/O_3 in a single step resulting in hydrophobic surfaces similar to the RCA clean. Due to the single step polishing process applied, these subsequent cleanings have the additional requirement of removing porous silicon at the wafer front side, that may originate from the polishing process.

2. Cleaning sequences for PERC cells with rear protection layer

We evaluate four different cleaning sequences targeted for industrial application prior to AlO_x/SiN_y passivation: 1) pSC1, HF/HCl; 2) pSC1, HF/HCl, HF/O_3; 3) HF/O_3; 4) PSG-etch (1% HF) and compare the results to a laboratory type RCA clean. The cleaning sequences 1 and 2 are designed as shortened versions of the RCA clean. The pseudo-SC1 (pSC1) clean applies KOH/H_2O_2 chemistry and aims at removing organic contamination similar to the SC1 in the RCA clean. The HF/HCl clean removes metallic contaminants similar as the SC2 clean in the RCA clean sequence. Both, the pSC1 and HF/HCl clean, are well known as typical industrial cleans prior and post texturing, respectively. In cleaning sequence 3, SiO_2 formed by ozone is removed by HF chemistry. The resulting etching of the silicon wafer surface might remove contaminants from the surface. The PSG-etch (clean 4) is chosen because it is the typical clean of a standard full-area Al-BSF production process applied after phosphorus diffusion and before Al screen-printing. To evaluate the impact of a cleaning sequence on the subsequent rear side passivation only, we fabricate test wafers for measurement of the effective lifetime τ_{eff} as shown in Fig. 1a). Using 1.5 Ωcm float zone (FZ) material these wafers are cleaned with the 5 cleaning sequences as described above. Then the ALD-Al_2O_3/PECVD-SiN_x passivation layer stack is deposited on both sides. After a firing step τ_{eff} is measured using a Sinton lifetime tester.

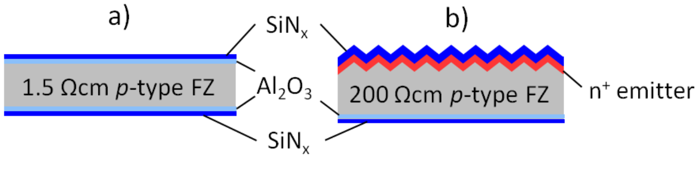

Fig. 1. Schematic drawing of test wafers for measurement of the effective carrier lifetime τ_{eff} (a) and of test wafers for measurement of the emitter saturation current J_{0e} and emitter sheet resistance R_{sh} (b).

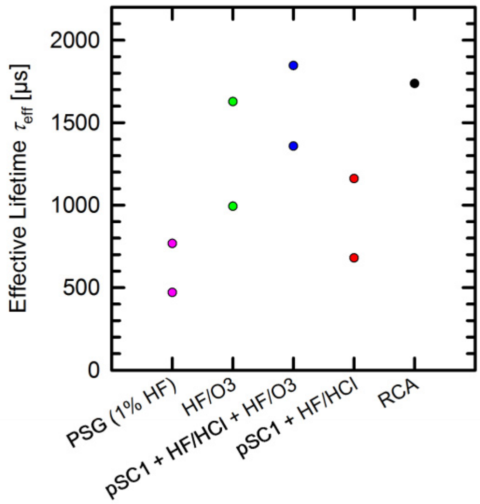

Fig. 2. Effective carrier lifetime $\tau_{eff.}$ of test wafers according to Fig.1a) cleaned with different cleaning sequences prior to passivation.

Figure 2 shows, that highest lifetimes of 1-2 ms are achieved using the RCA clean or one of the HF/O_3 based cleaning sequences. Using $S_{pass}=W/2^* \tau_{eff}$ this corresponds to a surface recombination velocity (SRV) of 8-15 cm/s. The two wafers cleaned with pSC1 + HF/HCl show lower lifetimes of 700 µs and 1200 µs yielding S_{pass} values of 12-20 cm/s. The lowest lifetime of around 500 µs – corresponding to an S_{pass} of 30 cm/s – is obtained for the PSG etch, probably due to insufficient removal of metallic contaminants.

In addition to the test wafers we fabricate PERC solar cells according to the PERC process flow as shown in Fig. 3a) in blue boxes, which is described in detail in Ref. 6. The PERC cell process flow applies a rear protection layer before single sided alkaline texturing and a $POCl_3$ diffusion aiming at a sheet resistance of 60 Ω/sq. After wet chemical removal of the PSG and the rear protection layer, we use the RENA Batchlab – a down-sized industrial cleaning tool – to carry out the five cleaning sequences as explained in the previous section. Then we deposit an ALD-Al_2O_3/PECVD-SiN_x passivation layer stack on the rear side and a PECVD-SiN_x on the front side. We locally ablate the rear passivation stack via laser contact openings (LCO) to form line shaped contacts. After Print-on-Print (PoP) Ag screen printing on the front and Al screen printing on the rear side, the wafers are fired in a conveyor belt furnace.

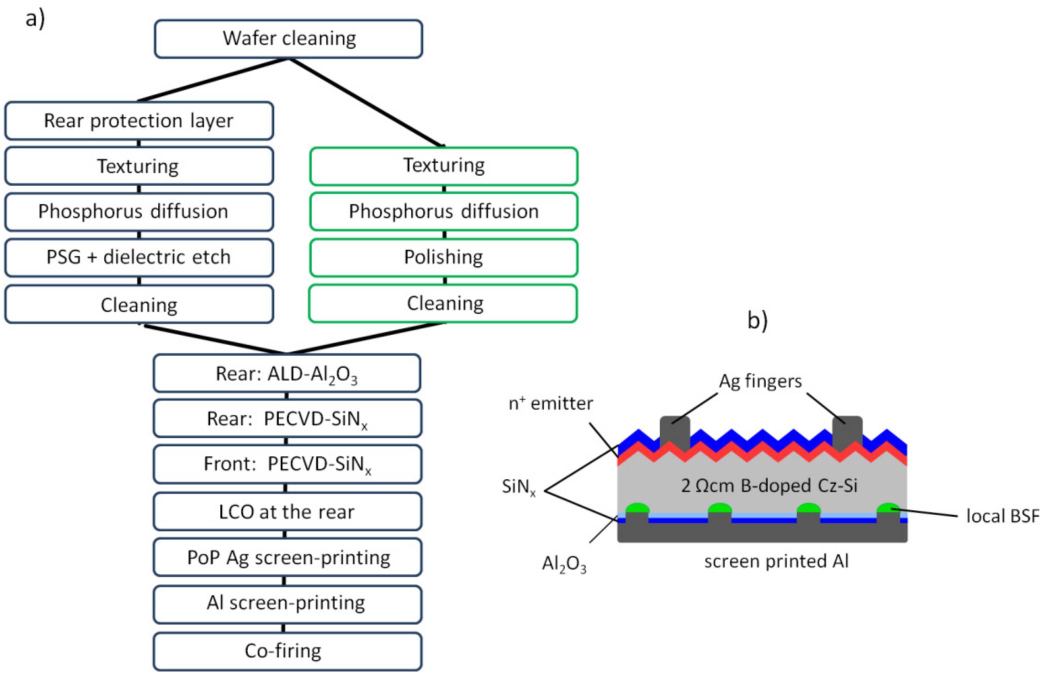

Fig. 3. (a) Process flows for PERC solar cells applying a rear protection layer (blue) and polished PERC cells (green/blue); (b) Schematic drawing of the PERC solar cells resulting from the process flows shown in a).

Figure 4a) shows the resulting energy conversion efficiencies η of the PERC solar cells for all 5 cleaning sequences. The best efficiencies of up to 20.4% are achieved using the pSC1, HF/HCl cleaning sequence. The cleaning sequences pSC1, HF/HCl, HF/O_3 and HF/O_3 show efficiencies of around 20.0%, and the PSG etch of up to 19.4%. Figure 4a) also shows the results of identically processed PERC cells from another batch that applied a laboratory type RCA clean before passivation with a best efficiency of 20.3%. The different cell efficiencies primarily result from different open circuit voltages V_{oc} that range from lowest values around 630 mV for the PSG-etch up to 657 mV for the RCA clean. The lower V_{oc} of the PERC cells with PSG clean is in accordance with the low lifetimes as shown in Fig. 2. However, the root cause of the slightly lower V_{oc} of the PERC cells applying HF/O_3 terminated cleans is not yet understood. The PERC cells cleaned with the HF/O_3-based sequences show lower fill factors *FF* (see Fig. 4b) when compared to the cells cleaned with pSC1, HF/HCl or RCA. The EL-images of the HF/O_3 cleaned PERC cells show dark spots, hinting to an increased contact resistance of the Ag fingers to the emitter which might be caused by a too strong etching of the HF/O_3 chemistry of the emitter on the front side.

Measurements of the internal quantum efficiency (IQE) in the infrared regime as displayed in Fig. 5 show comparable values for most cleaning sequences except for the PSG-etch, which exhibits significantly lower values. Using our in-house developed silicon solar cell analysis software SCAN which is based on the analytical model for the QE introduced in [7], we model the experimental reflectance and IQE data to obtain the effective SRVs at the rear S_{rear}. For the PSG-etch we extract 330 cm/s, whereas the other cleaning sequences show values <50 cm/s indicating that the lower V_{oc} and J_{sc} values of the cells cleaned with the PSG-etch primarily result from higher recombination at the rear.

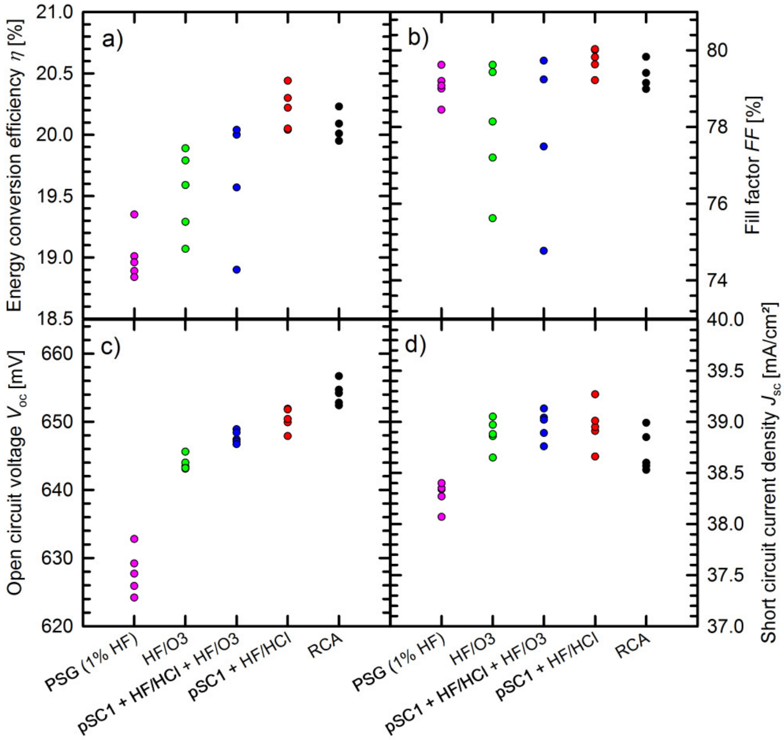

Fig. 4. Measured IV parameters of PERC solar cells cleaned with different cleaning sequences prior to passivation: (a) Energy conversion efficiency η; (b) Fill factor FF; (c) Open circuit voltage V_{oc}; (d) Short circuit current density J_{sc}. The spread of data is partly due to a variation of peak firing temperatures.

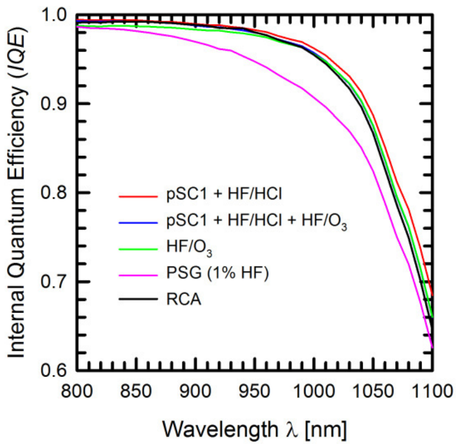

Fig. 5. IQE measurement in the infrared regime of the best solar cells shown in Figure 4.

3. Cleaning sequences for polished PERC cells

In this section we investigate different cleaning sequences prior to passivation for polished PERC cells with a process flow as shown in green boxes in Fig. 3a). Due to the requirement of etching porous silicon on the front side the choice of cleaning sequences is reduced to those including the pSC1 clean. Therefore we choose two cleaning sequences which are similar to the cleaning sequences 1) and 2) of the section above: 1) pSC1, HF/HCl, HF-Dip; 2) pSC1, HF/HCl, HF/O_3. The HF-Dip in the first sequence was added by mistake. However, we do not expect a strong impact compared to without HF-Dip. We apply the cleans to test wafers as displayed in Fig. 1b). The test wafers are processed applying double sided texturing and a $POCl_3$ diffusion with a sheet resistance of 45 Ω/sq. We then use the RENA InPilot tool [8] to apply a wet chemical single sided polishing process to remove the rear emitter and reduce rear surface roughness. We choose rear side polishing removals of 3 µm, 7 µm and 12 µm by adjusting the process time. The gas phase of the rear polishing process slightly increases the emitter sheet resistances from 45 Ω/sq to 50 Ω/sq (3µm), 60 Ω/sq (7 µm) and 70 Ω/sq (12 µm). After applying one of the pSC1, HF/HCl, HF-Dip and pSC1, HF/HCl, HF/O_3 cleaning sequences we deposit the AlO_x/SiN_y passivation layer stack on the rear and the SiN_y on the front side and conclude with a firing step. Test wafers as shown in Fig. 1a) are double sided textured and then subsequently polished with different removals on both wafer sides with the same polishing removals. Then we carry out the cleaning sequences, deposit the AlO_x/SiN_y on both sides and finish again by firing the wafers.

When moving from 3 µm to 12 µm polishing removal, the emitter saturation current densities decrease from 110-140 fA/cm² down to 70-95 fA/cm² for both cleaning sequences as shown in Fig. 6a). The improved J_{0e} values are very likely due to a reduced phosphorus concentration on the front surface caused by the longer gas phase etch during polishing [9]. The low J_{0e} values demonstrate, that both cleaning sequences sufficiently remove the porous silicon to allow a good emitter surface passivation while maintaining emitter sheet resistances below 70 Ω/sq as shown in Figure 6b), where both cleaning sequences only contribute about 2 Ω/sq sheet resistance increase as measured on reference wafers. The QSSPC measurements show effective lifetimes τ_{eff} around 1 ms for all polishing removals, where wafers cleaned with pSC1, HF/HCl, HF/O_3 obtain 100-150 µs higher lifetimes compared to the pSC1, HF/HCl, HF-Dip clean. Accordingly, both cleaning sequences allow an excellent rear surface passivation quality with SRVs $S_{pass} < 15$ cm/s when combined with an Al_2O_3/SiN_x rear passivation.

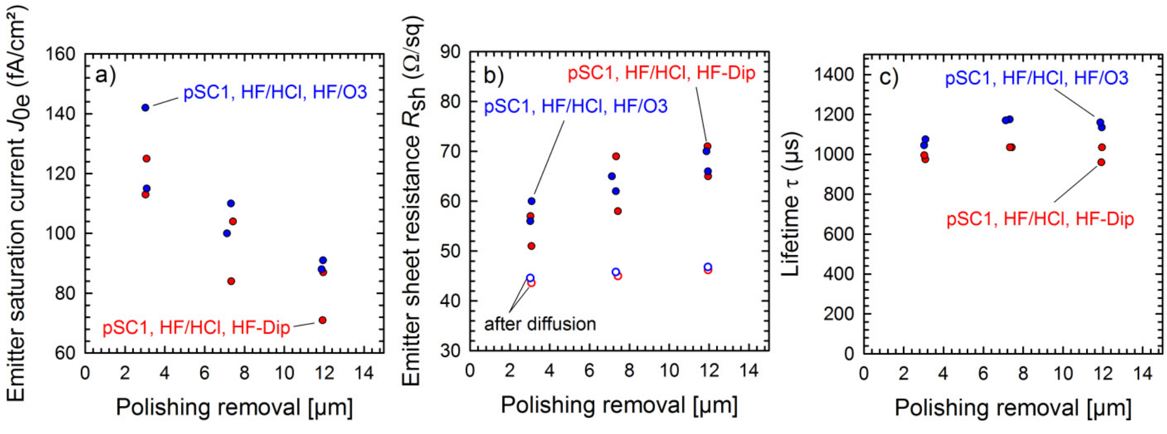

Fig. 6. Measured parameters of test wafers of type c) and d) in Fig.1: (a) Emitter saturation current density J_{0e}; (b) Emitter sheet resistance R_{sh}; (c) Effective carrier lifetime τ_{eff} at an injection level of 10^{15} cm^{-3}.

In a next step we process polished PERC cells according to the process flow in green boxes in Fig. 3a). The two cleaning sequences used in the test wafer experiment are now designed to be slightly shorter: 1) pSC1, HF/HCl; 2) pSC1, HF/O_3. The wafers apply double sided texturing and a phosphorus diffusion aiming at a sheet resistance of 45 Ω/sq. After the polishing process with a rear side polishing removal of 5 µm, we carry out the cleaning sequences. We deposit the AlO_x/SiN_y passivation layer stack and form line shaped contact via LCO. After PoP Ag screen printing on the front side and full area Al screen printing on the rear, the wafers are fired. The process flow is described in detail in Ref. 1.

Figure 7a) shows the energy conversion efficiencies η of the polished PERC solar cells for different cleaning sequences. The laboratory type RCA cleaning prior to passivation resulted in a polished PERC solar cell with an efficiency of 20.7%, a V_{oc} of 659 mV, a J_{sc} of 38.7 mA/cm² and a FF of 81.0%. PERC cells cleaned with the pSC1, HF/O_3 or the pSC1, HF/HCl cleaning sequence show significantly reduced efficiencies of up to 19.9% and 19.4%, respectively. The cause for this trend is revealed by the IQE measurements of the PERC cells as shown in Fig. 7b). Here the cells cleaned with pSC1, HF/O_3 or pSC1, HF/HCl show lower IQE values at short wavelengths when compared to the RCA clean indicating increased recombination at the cell's front side. Using our analysis software SCAN again, we fit the model in Ref. 7 to the experimental data to extract the diffusion length L_{em} and front surface recombination velocity S_{front}. Using

$$J_{0e} = \frac{qn_i^{\,2}}{N_A}\cdot\frac{D}{L_{eff}} \qquad \text{with} \qquad L_{eff} = L_{em}\frac{L_{em}S_{front}\sinh\left(\frac{W_{em}}{L_{em}}\right)+D\cosh\left(\frac{W_{em}}{L_{em}}\right)}{L_{em}S_{front}\cosh\left(\frac{W_{em}}{L_{em}}\right)+D\sinh\left(\frac{W_{em}}{L_{em}}\right)}$$

we obtain J_{0e} values of 85 fA/cm² (RCA), 200 fA/cm² (pSC1, HF/O_3) and 310 fA/cm² (pSC1, HF/HCl) which fit well to the results of test wafers (Fig. 1b) processed in parallel to the PERC solar cells. Whereas the J_{0e} value for the RCA cleaned PERC cells is comparable to the values shown in Fig 6a), the J_{0e} values of the pSC1, HF/O_3 and the pSC1, HF/HCl cleaned cells and second set of test wafers strongly exceed the J_{0e} values shown in Figure 6. The root cause of the missing porous silicon etching capability of the cleans when applied to the PERC cells and second set of test wafers is not yet understood. However, it is very likely not caused by the missing HF-Dip or the missing HF/HCl step, since these cleans should not significantly etch silicon. When extracting S_{rear} we obtain comparable values <40 cm/s for all three cleaning sequences, demonstrating that pSC1, HF/HCl and pSC1, HF/O_3 suffice to allow excellent passivation using an ALD-Al_2O_3/PECVD-SiN_x passivation layer stack.

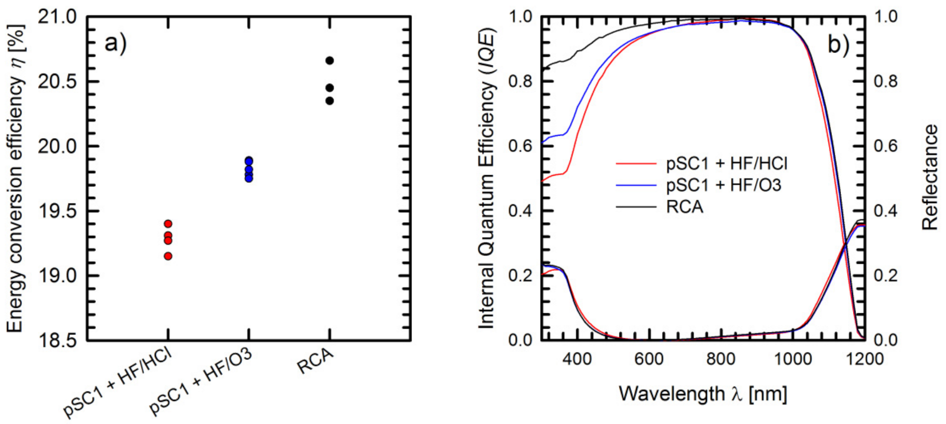

Fig. 7. (a) Energy conversion efficiencies η of polished PERC solar cells cleaned with different cleaning sequences prior to passivation. The spread of data is partly due to a variation of peak firing temperatures; (b) IQE and Reflectance measurements of the best solar cell shown in a).

4. Conclusion

We demonstrate on test wafers, that HF/O_3 terminated cleaning sequences such as pSC1, HF/HCl, HF/O_3 or HF/O_3 prior to Al_2O_3/SiN_x passivation result in effective lifetimes >1 ms and corresponding surface recombination velocities S_{pass}< 15 cm/s. Accordingly PERC solar cells applying these cleaning sequences show effective surface recombination velocities S_{rear} of <50 cm/s. However, the highest reference PERC cell efficiency of 20.4% was obtained with the cleaning sequence pSC1, HF/HCl on an industrial batch-type cleaning tool which is comparable to PERC cells applying a laboratory type RCA clean. The HF/O_3 terminated cleans results in slightly lower PERC cell efficiencies probably due to an unintended etch back of the emitter which is subject to further optimization. However, when using a process flow for polished PERC cells, the cleaning sequence prior to passivation layer deposition needs to remove porous silicon from the wafer front side as well. Using test wafer experiments we showed that cleaning sequences pSC1, HF/HCl, HF-Dip or pSC1, HF/HCl, HF/O_3 meet these requirements with emitter saturation currents J_{0e} of 80-140 fA/cm² and effective lifetimes τ_{eff} around 1 ms – both comparable to the RCA clean. Another experiment with similar cleaning sequences on polished PERC cells did not reproduce these J_{0e} values and resulted in efficiencies of 19.4% for cells with a pSC1, HF/HCl cleaning and 20.4% with a pSC1, HF/O_3 cleaning. The root cause of the insufficient removal of porous silicon in this batch of cells is not yet understood. However, the highest efficiencies with up to 20.7% for the polished PERC cells have been achieved using an RCA clean prior to Al_2O_3/SiN_x rear passivation.

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