

Development of an Ozone-based Inline Cleaning and Conditioning Concept

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Abstract. In this work, a cleaning and conditioning process consisting of ozonized water, hydrofluoric and hydrochloric acid in concentrations below 1 wt% is implemented within an inline wet chemical processing tool. This inline process is characterized and compared to the cleaning and conditioning process inside a batch process tool. The resulting process homogeneity, the optical properties of the wafer surface after cleaning and conditioning inside the inline wet chemical processing tool and the resulting surface defects after passivation with intrinsic amorphous silicon is investigated. On large area Czochralski wafers a high degree of process homogeneity after an emitter etch back with standart deviation values below 5% are shown. Furthermore implied open circuit voltages above 740 mV after passivation with amourphes intrinsic Silicon are reached. In the end, system-specific optimization options are presented in order to achieve a more homogeneous process, which is capable of removing the phosphor silicate glass layer, perform an adjusted emitter etch back and leave a clean and defect free wafer interface in just one process step.

INTRODUCTION

For highly efficient solar cell concepts the requirements increase concerning the cleanliness and nature of the silicon surface, which becomes later the interface between the silicon base substrate and the passivation layer. Before passivation, a clean, defect-free and specifically H- or oxide-terminated silicon surface is necessary [1]. The ozone-based cleaning enables a good cleaning effect at room temperature and short process times of one minute [2]. Furthermore, the ozone-based cleaning allows to achieve a controlled emitter etch back in case of Passivated Emitter and Rear (PERC) based solar cell processing [3] as well as rounding of the pyramid tips of textured surfaces, which is preferable in case of Silicon Heterojunction (SHJ) solar cells[4]. Since inline processing can increase production throughput and yield, the ozone-based cleaning and conditioning process is implemented within an inline based wet chemical processing tool.

In contrast to standard wet chemical inline equipment, the wafer gets transported through the inline tool resting on eight pins (Fig. 1.), which minimizes the contact area between the conveyor system and the wafer. To keep the wafer in place during transport, four pins for lateral fixation are added. The wafer is transported through the process bath, in which the rear side (RS) of the wafer immerses into the process solution. To have a complete coverage of the wafer by the process solution, the front side (FS) of the wafer gets sprayed by a flood register from above (Fig. 2a.). After the process bath, a spray rinse cascade follows. Since the cleaning and conditioning process leaves a oxide layer on the wafer surface, the first part of the rinse has a short distance HF spray to remove this oxide layer. The second rinse is a DI-water spray. Finally, the wafer is transferred from the pocket onto O-rings and passes through the dryer module (Fig. 2b.).

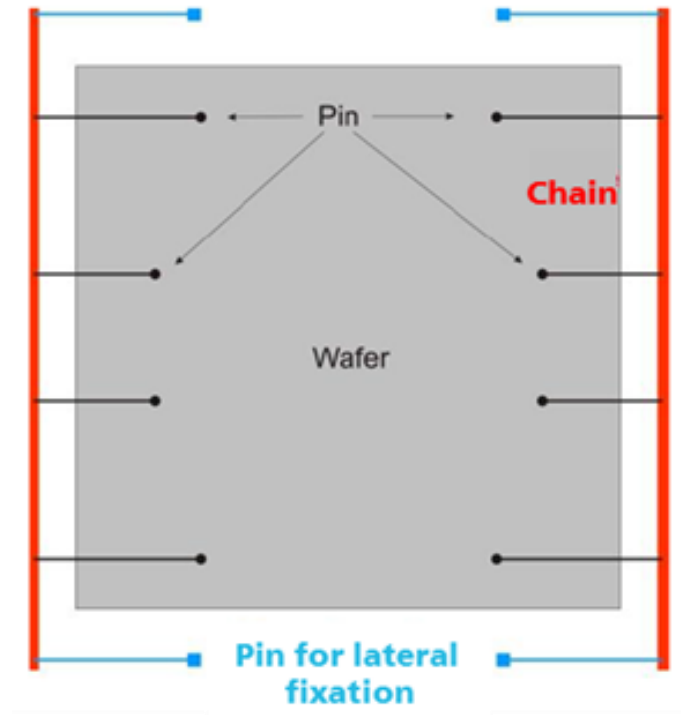


FIGURE 1. Sketch of transport pocket

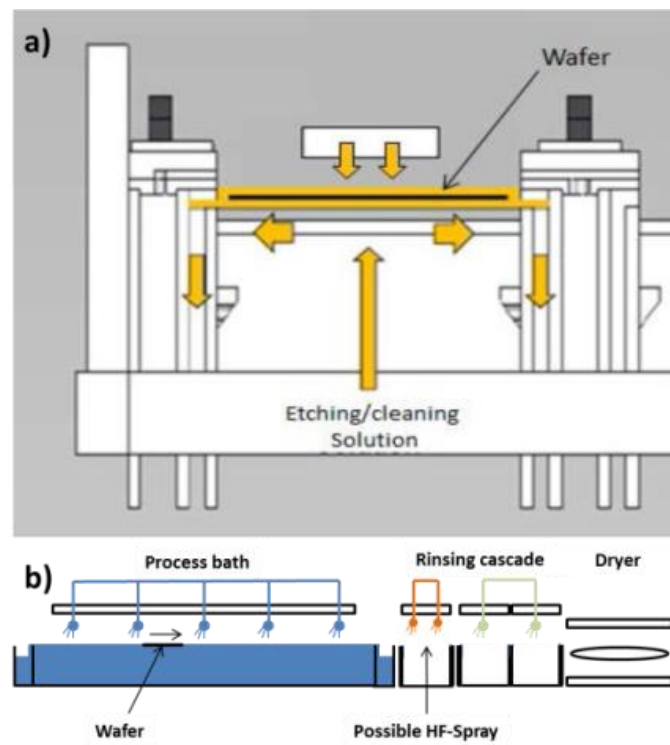


FIGURE 2. Sketch of cross section of the process bath (a), Sketch of process sequence (b).

EXPERIMENTAL APPROACH

For each Experiment, the same concentration for the ozone-based cleaning and conditioning solution were used. The experiments were carried out at room temperature and the cleaning and conditioning solution consisted of 2.7 g/l HF, 4.5 g/l HCl and 30 mg/l O₃. In the first experiment (Fig. 3.) the etching homogeneity at the front side (FS) and rear side (RS) was analyzed as a function of selected process parameters. A textured sample was provided with a diffused POCl₃ emitter. The emitter sheet resistance was measured by four point probe measurement (20 x 20 point mapping of the FS and RS) before and after the cleaning and conditioning process and can be used to analyze the process homogeneity on FS and RS of the wafer. Furthermore, the reflection at $\lambda = 600$ nm was determined before and after the process and compared to the same cleaning and conditioning process in a batch tool. For the cleaning and conditioning process, a time variation of $t = 2, 4$ and 6 minutes was performed.

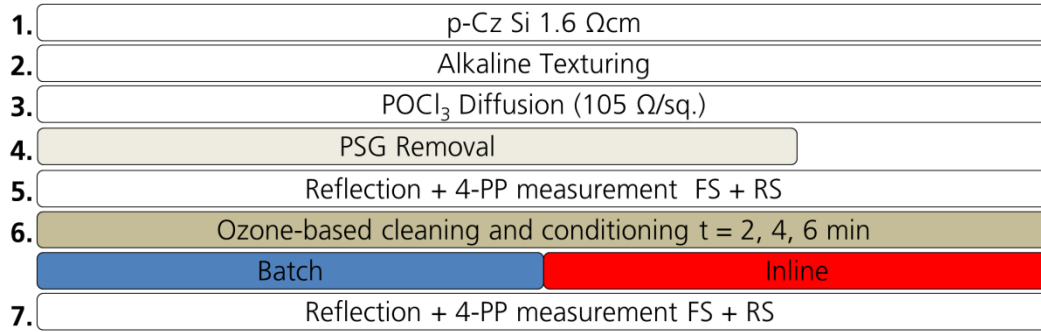


FIGURE 3. Process sequence of the first experiment

In the second experiment (Fig. 4.), the influence of the inline ozone-based cleaning and conditioning process and of the associated homogeneity differences were further investigated by determining the passivation quality with intrinsic amorphous silicon (a-Si:H(i)) and comparing it to the batch reference process. The oxide layer remaining after the cleaning and conditioning process was removed by means of an HF dip. The HF dip was either carried out in a batch tool or realized as a HF spray within the inline system. An approx. 12 nm thick a-Si:H(i) passivation layer was deposited by inline PECVD [5]. The resulting effective lifetime and implied open circuit voltage were measured by quasi-steady-state photo conductance (QSSPC) [6] at an injection level of 10^{15} cm⁻³. Lifetime-calibrated photoluminescence imaging were done to visualize surface defects. For the ozone-based process, a time variation of $t = 2, 3$ and 4 minutes was carried out.

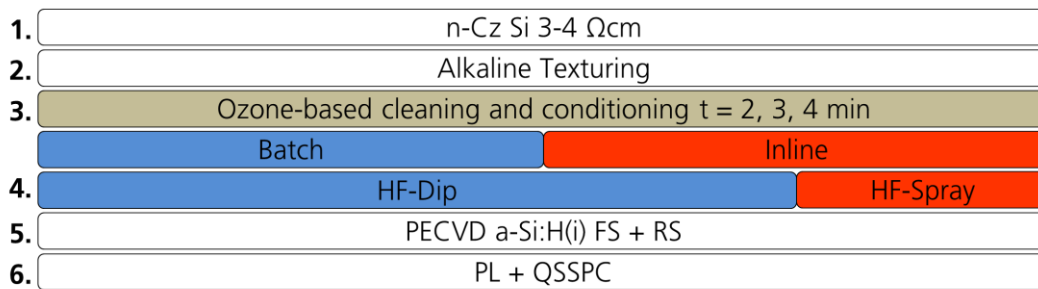


FIGURE 4. Process sequence of the second experiment

RESULTS

To visualize the etching homogeneity at the FS and RS of the wafer, the emitter sheet resistance of wafers without PSG were measured before and after the cleaning and conditioning process. With increasing process time, the emitter sheet resistance increased by approx. 10 Ω /sq. per minute, starting from 105 Ω /sq.. At the FS the emitter sheet resistance does not increase homogenously. The standard deviation of the emitter sheet resistance at the FS

increases with process time and is in the range between 5% and 11.2%. In comparison, the RS is very homogeneous, the standard deviation lies between 3.9% and 7.8%, also increasing with process time. The inhomogeneity expressed by means of a higher standard deviation at the FS can be attributed to the flood register, which sprays freshly ozonized process solution onto the FS of the wafer (Fig. 2). This spraying causes a higher etching rate at the impact area, right beneath the flood register. The etching rate at the edges of the FS is not as high, since the fresh ozonized process solution from the flood register, which is smaller than the wafer, does not cover the complete surface and is mixed with the process solution from the bath beneath. This behavior can be clearly identified in the sheet resistance mapping, where red lines are added as guide to the eye to visualize the position of the flood register (Fig. 5.).

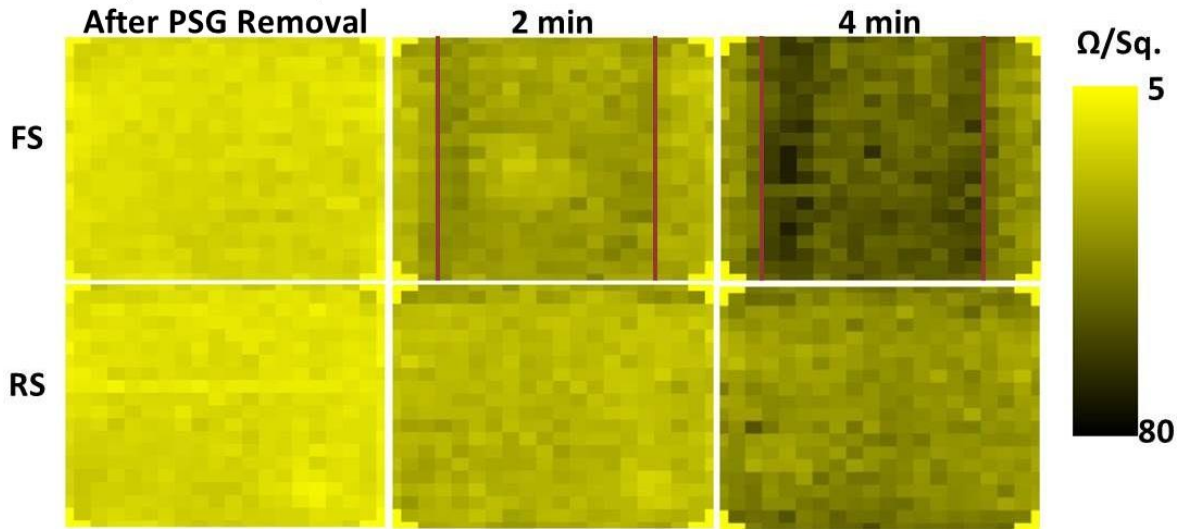


FIGURE 5. Change in emitter sheet resistance of inline processed substrates (red lines as guide to the eye of flood register).

The reflection values increase with process time as the pyramids are rounded during the ozone-based cleaning and conditioning process (Fig. 6.). By comparison of the reflection values of FS and RS for the inline process the homogeneity difference can also be seen. The reflection is higher at the FS than at the RS and is more pronounced with higher process times. This difference can be ascribed to the same root as the increasing emitter sheet resistance and is caused by the higher etch rate on the FS. The obtained total reflection values of the RS are comparable to the reflection values of the batch processed samples.

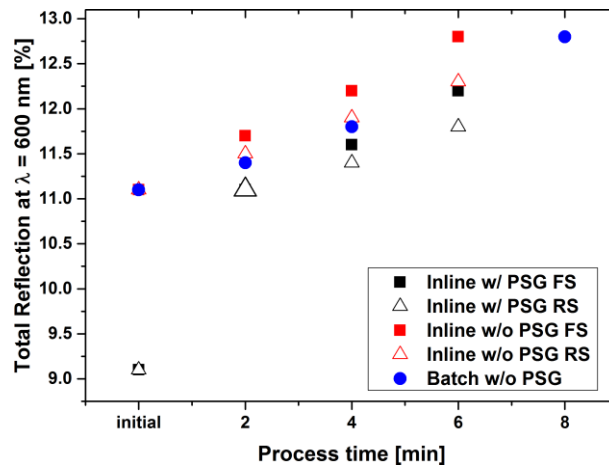


FIGURE 6. Total reflection measured at $\lambda=600\text{nm}$ in initial state and after ozone-based process.

In order to realize a homogeneous and comparable process on the FS and RS of the wafer in the inline process tool, the flood register must be changed or substituted by a dip system where both sides of the wafer get immersed. The etching behavior of wafers with PSG are delayed by the time it takes to remove the PSG, while the etching rates are the same after the removal. The reflection values are the same for samples with PSG and a process time of two minutes and samples after PSG removal in initial state. Out of this data it can be assumed that the ozone-based cleaning and conditioning process with its low HF (2.7 g/l) and HCl (4.7 g/l) concentrations is capable of a complete removal of the PSG within a two minutes process time.

To further investigate the influence of the inline ozone-based cleaning and conditioning process and of the associated homogeneity differences, the passivation quality with a-Si:H(i) was determined. For both, the inline ozone-based cleaning and conditioning process with following HF-Spray inside the tool or HF-Dip inside a batch tool, comparable values in τ_{eff} and iV_{OC} were achieved, as for the batch ozone-based cleaning and conditioning process (Fig. 7. and Fig. 8.). The mean values of τ_{eff} and iV_{OC} range for all process times above 4.5 ms or 736 mV, which indicates a good passivation quality and therefore a effective pretreatment of the wafer surface.

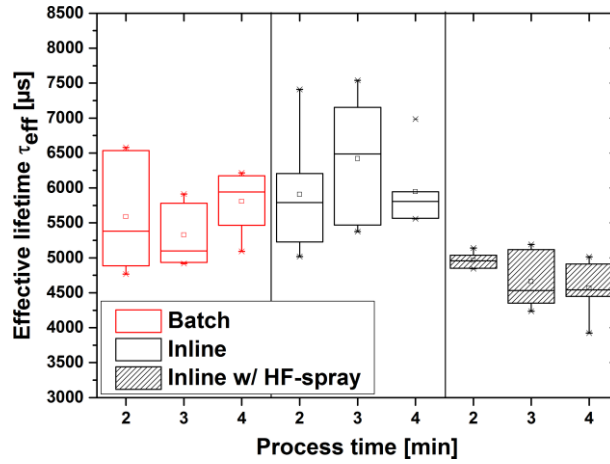


FIGURE 7. Effective lifetime measured by QSSPC

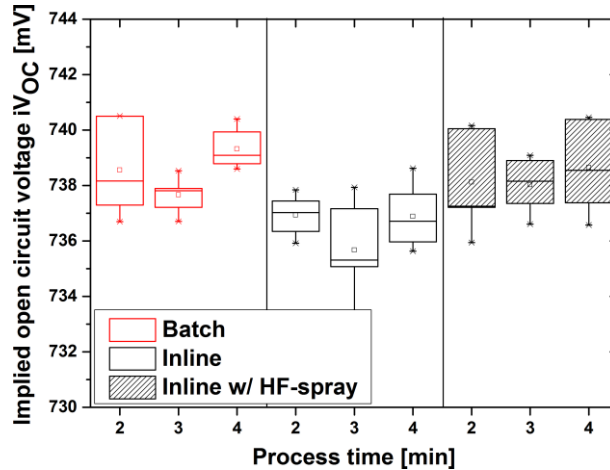


FIGURE 8. Implied open circuit voltage measured by QSSPC

When considering the life-time-calibrated photoluminescence image of the inline processed wafers (Fig. 9. (right)), stripe like structures can be observed. These stripe like structures have a considerable influence on the effective minority charge carrier lifetime of the a-Si:H(i) passivation. Due to their number and spacing, these structures can be assigned to the fluorocarbon rubber O-rings installed in the dryer module (Fig. 9. (left)). The fluorocarbon rubber O-rings are not abrasion resistant and leave particles on the wafer surface.

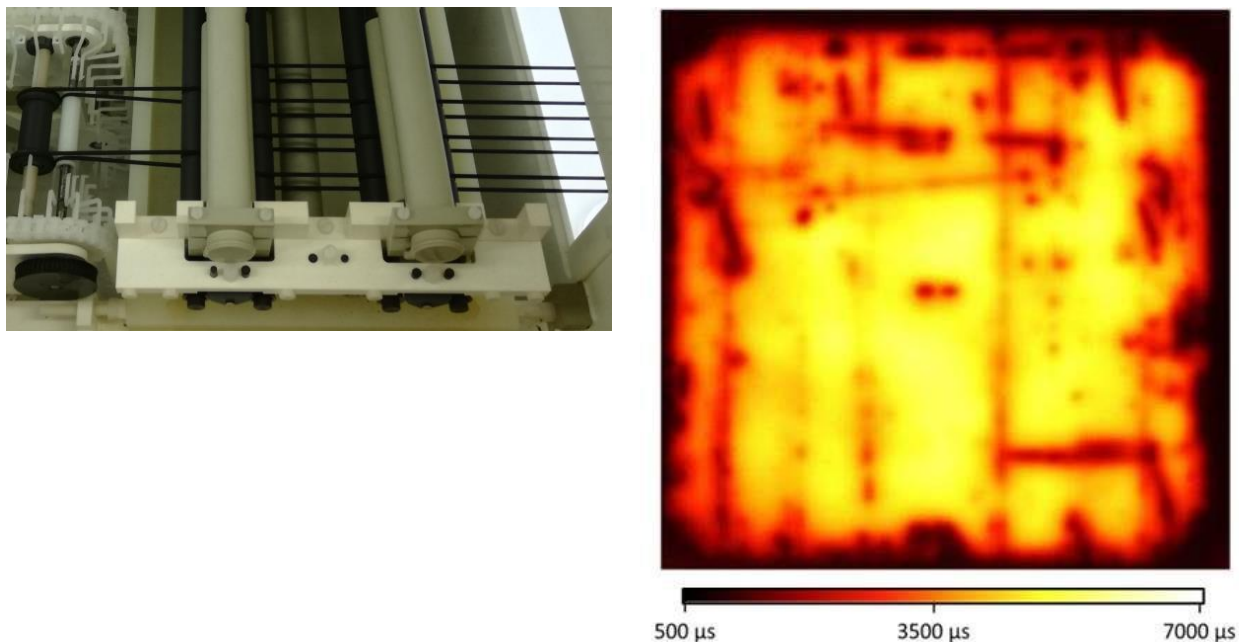


FIGURE 9. Dryer in initial state (left), PL image of inline processed wafer (right)

In order to reduce the stripe structures the existing O-rings in the dryer module were reduced in number and wrapped with Teflon tape (Figure 10. (left)). As shown in the life-time-calibrated photoluminescence image (Fig. 10. (right)), the strip structures could be minimized.

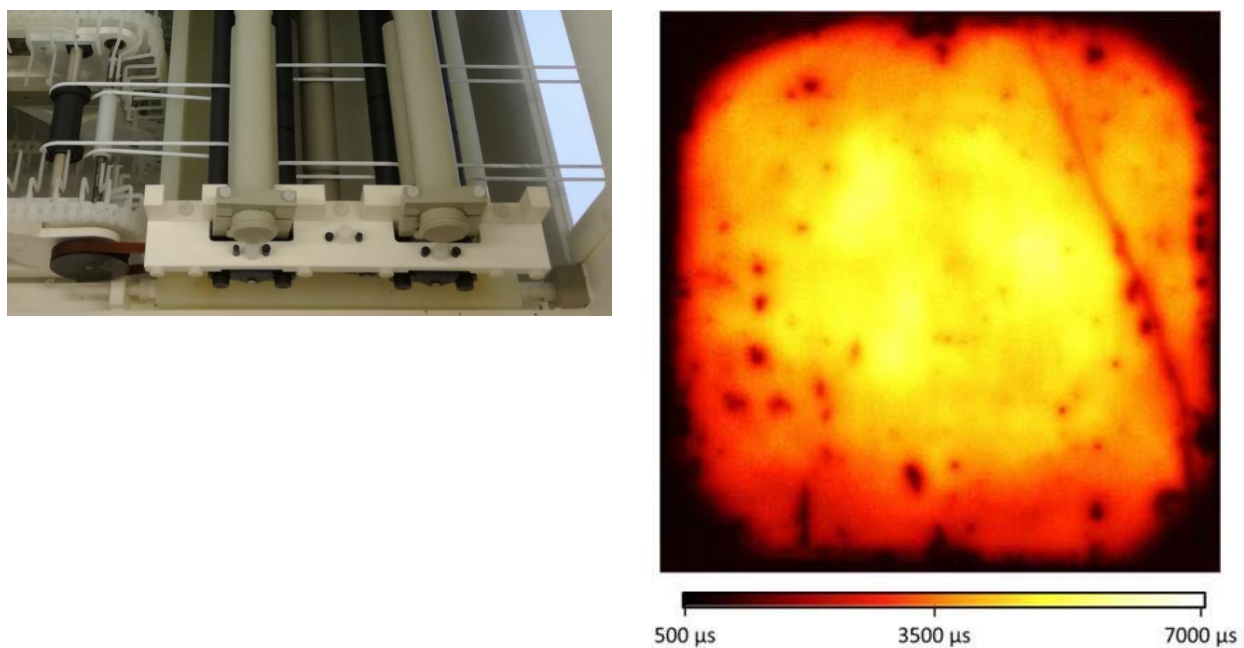


FIGURE 10. Dryer with Teflon wrapped conveyor belts (left), PL image of inline processed wafer (right)

SUMMARY

The ozone-based cleaning and conditioning process was transferred to an inline process tool. By four point probe measurement it was shown, that the RS of the wafer is processed homogeneously. An inhomogeneity on the FS, caused by a too narrow flood register, could be avoided by a modified flood register or by replacing it with a dipping system in which both sides are immersed. The obtained total reflection values were in case of the RS comparable to the reference batch process. Out of the reflection data it can be assumed, that the ozone-based cleaning and conditioning process is capable of removing the PSG layer by a two minute process. By a-Si:H(i) passivation after the ozone based cleaning and conditioning process it has been shown that with the inline process comparable values in τ_{eff} and iV_{OC} were achieved as for the reference batch process. With changing the too narrow flood register it is possible to receive a homogeneous process, which is capable of removing the PSG-layer, performing an adjusted emitter etch back and leaving a clean and defect free wafer interface in just one process step, while abrasion associated defects from O-rings can be avoided by using a abrasion resistant material.

ACKNOWLEDGEMENTS

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