INFLUENCE OF DIFFUSION PARAMETERS ON ELECTRONIC QUALITY OF MULTICRYSTALLINE SILICON

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ABSTRACT: The presented work deals with phosphorus diffusion gettering of mc material. A significant improvement of electronic material quality after diffusion is reported. Additionally to $POCl_e$ diffusion some wafers undergo deposition and firing of PECVD SiN_x to study hydrogen passivation and to allow for a better comparability to solar cell results. Spatially resolved µPCD lifetime measurements provide insight into how various defect types react to different diffusion processes. 2x2 cm^2 solar cells produced in a photolithography based cell process allow detailed analysis of different defect regions. The interstitial iron content is lowered under the detection limit after $POCl_3$-diffusion. Both lifetime measurements and cell results indentify the diffusion process with low unloading temperature as the optimum one among processes without additional holding step at unloading temperature. Comparing processes with holding time at unloading temperature, the reference diffusion with higher unloading temperature turns out to be the best one.
Keywords: Diffusion, Gettering, Multicrystalline Silicon, High-Efficiency

1 INTRODUCTION

This study focuses on phosphorus diffusion as well as on hydrogen passivation of mc (multicrystalline) silicon. The experiment presented here is divided into two parts. The first part is the analysis of mc silicon material quality after varying post-diffusion parameters subsequent to a $POCl_3$ 80 Ohm/sq emitter as reference process. This is commonly known as post-diffusion gettering analysis [1]. The phenomenon of gettering is not well understood. A lot of scientific work has been carried out in this field of research, in particular studies about Fe gettering [2, 3]. In addition, the impact of hydrogen passivation from a fired PECVD (Plasma Enhanced Chemical Vapor Deposition) SiN_x:H is analyzed in this present study. Changes in the material quality are studied by lifetime measurements.
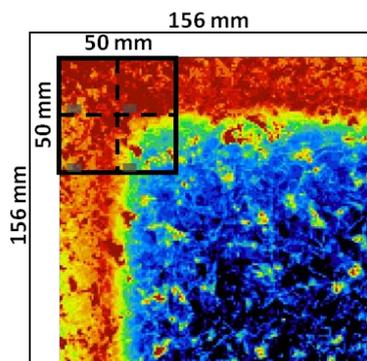
The second part of this study is the processing and characterization of solar cells on wafers adjacent to the lifetime samples with diffusion parameters that seemed to be promising in improving material quality according to previous lifetime measurements. It should be noted that the SiN_x passivated samples are more comparable to cell processed wafer material than non passivated ones.

2 INVESTIGATED MATERIAL

2.1 Wafer Selection

Figure 1: 5x5 cm^2 wafers under investigation are selected out of a 156x156 mm^2 mc wafer. (Red: low lifetimes; blue: high lifetimes)

Multicrystalline silicon wafers are selected so that one 5x5 cm^2 wafer preferably includes four different kinds of defect structures. After the solar cell process is completed, four 2x2 cm^2 solar cells are cut out of the original 5x5 cm^2 wafer so that each cell contains one of the four defect types.

Hence on cell level it is possible to investigate the influence of various diffusion steps on the respective defects. In Fig. 1 an example for wafer selection is shown. Here a 5x5 cm^2 wafer is depicted from the edge of the mc brick. This brick region is of special interest since most kinds of impurities diffuse from the crucible walls into the silicon matrix during block casting, form clusters, induce vacancies or simply remain as interstitial atoms. A lifetime map in Fig. 1 measured by µPCD (Microwave PhotoConductance Decay) clearly shows the low lifetime region resulting from the crucible edge. The wafer also includes a region of higher lifetime closer to the center of the mc brick. As a reference FZ material is included in the cell process.

3 EXPERIMENTAL SET UP

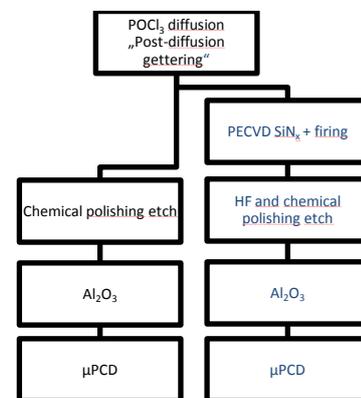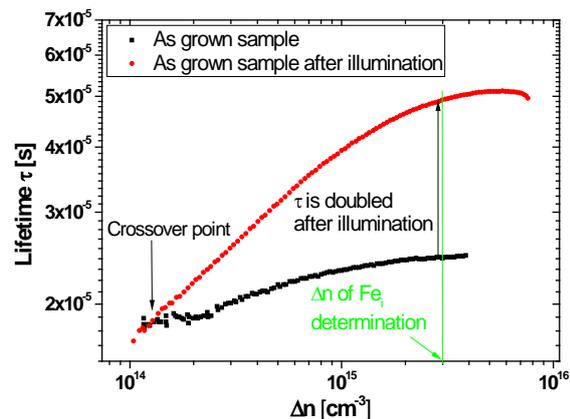### 3.1 Lifetime Measurements

Figure 2: Experimental sequence of lifetime measurements.

Fig. 2 gives an overview of the process flow for the lifetime measurements of 5x5 cm^2 wafers. Parameters like unloading temperature and holding time of the 80 Ohm/sq reference emitter with unloading temperature $T_{unload} = 700°C$ are varied (see Table 1) whereas the peak diffusion temperature was the same for all diffusions. Also a much shorter industrial diffusion is tested. It should be noted here that instead of diffusion with unloading temperature $T_{unload} = 500°C$, the diffusion of the lifetime samples was performed with $T_{unload} = 615°C$ because of a dysfunction of the POCl$_3$ furnace. The emitter is removed by a chemically polishing etch (~10 µm per side).

Table I: Investigated diffusion processes

Diffusion	1	2
	Reference ($T_{unload} = 700°C$)	Reference + 90 min holding time at T_{unload}
Diffusion	3	4
	Cool-down ramp ($T_{unload} = 500/615°C$)	Cool-down ramp + 90 min holding time at T_{unload}
Diffusion	5	6
	Industry ($T_{unload} = 700°C$)	Industry + 90 min holding time at T_{unload}

Then both wafer surfaces were Al$_2$O$_3$ passivated by ALD (Atomic Layer Deposition) in an Oxford Flex-AL tool (including a 30 min anneal step at 400°C). On some neighboring wafers PECVD SiN$_x$:H (direct plasma, low frequency) is deposited on both sides and fired in an industrial belt furnace to study the further improvement of material quality via hydrogenation. Before emitter etching, the SiN$_x$ layers of these samples are removed by diluted HF.


Figure 3: QSSPC lifetime before and after illumination of an as grown sample.

Lifetime measurements are performed using µPCD, QSSPC (Quasi Steady State PhotoConductance) and PL (PhotoLuminescence). Additionally, the Fe$_i$ concentration is determined. Iron is one of the strongest lifetime limiting impurities in mc silicon. It forms FeB complexes in the dark and dissociates within a few minutes under strong illumination (≥ 0.1 W/cm^2). This is accompanied by a change in lifetime which is proportional to the inverse concentration of Fe$_i$ atoms [4]. Fig. 3 shows an example of an as grown mc wafer that is measured before and after illumination. Phosphorus diffusion is well known to be a very effective way for Fe gettering and therefore the interstitial iron content is measured on samples that underwent different diffusions.

3.2 Cell Process

Fig. 4 shows all applied processing steps for solar cell fabrication. It is a cell process based on photolithography for precisely defining front contacts allowing for small 2x2 cm^2 cells. Full sized wafers are cut by a laser and cleaned by a polishing etch consisting of HF, HNO$_3$ and CH$_3$COOH.
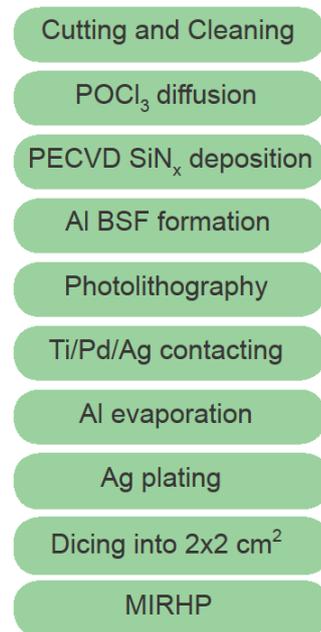
Figure 4: High efficiency cell process for mc wafers.

The emitter diffusion is carried out in an industrial-type POCl$_3$ diffusion furnace. After emitter formation surface passivation and hydrogenation is achieved by deposition and firing of PECVD (Plasma Enhanced Chemical Vapor Deposition) SiN$_x$. The Al BSF (Back Surface Field) is achieved by screen printing Al paste and firing together with the SiN$_x$ layer. Next step is the front grid definition via photolithography and evaporation of Ti, Pd and Ag. After Ag plating cells are diced into 2x2 cm^2 and annealed within a hydrogen atmosphere using MIRHP (Microwave Induced Remote Hydrogen Plasma).
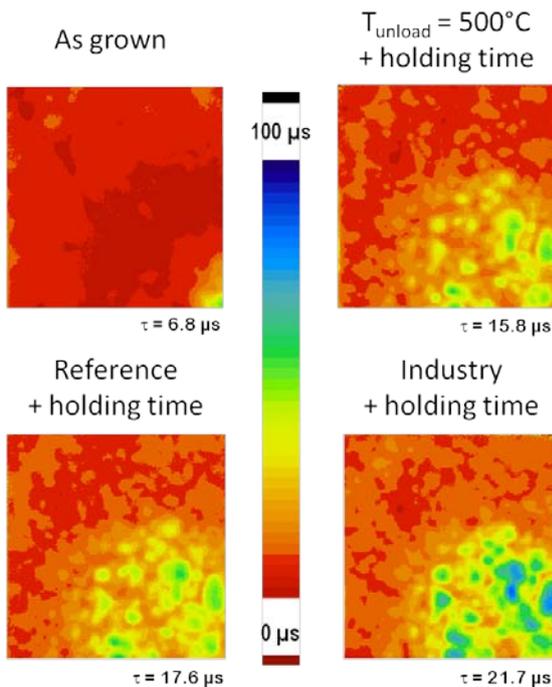
4   RESULTS

4.1 Characterization of bulk material

Four sets of wafers (with four wafers per set) are shown here: lifetime maps measured by µPCD of an as grown wafer together with its three sister wafers diffused in three different POCl$_3$ diffusion processes and the same with additional holding time at the respective unloading temperatures (see Fig. 5 and 6). These two comparisons

are repeated with wafers that underwent an additional SiN$_x$ deposition and firing step (see Fig. 7 and 8). The mean values are given in the pictures. In previous studies it was found that regions with the lowest lifetimes limit cell efficiency and can hardly be improved by phosphorus gettering [3].

In Fig. 5 the highest mean lifetime value $\tau = 19\,\mu s$ belongs to the industrial diffusion process. Reference and lower unloading temperature of $T_{unload} = 615°C$ lead to comparable material quality.

As grown — $\tau = 6.8\,\mu s$
$T_{unload} = 615°C$ — $\tau = 16.7\,\mu s$
Reference — $\tau = 15.8\,\mu s$
Industry — $\tau = 19\,\mu s$
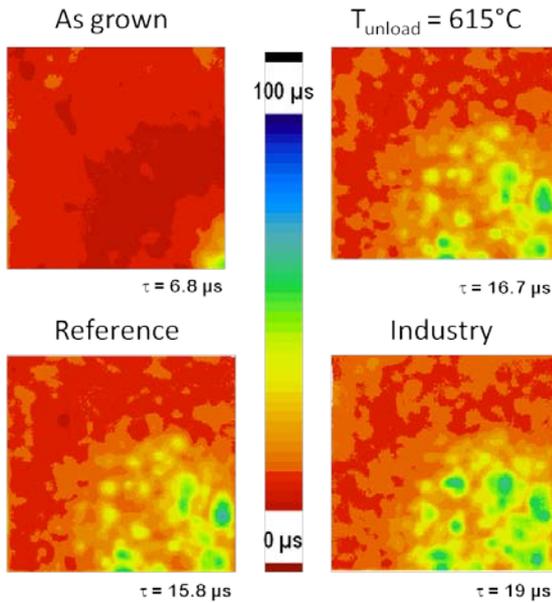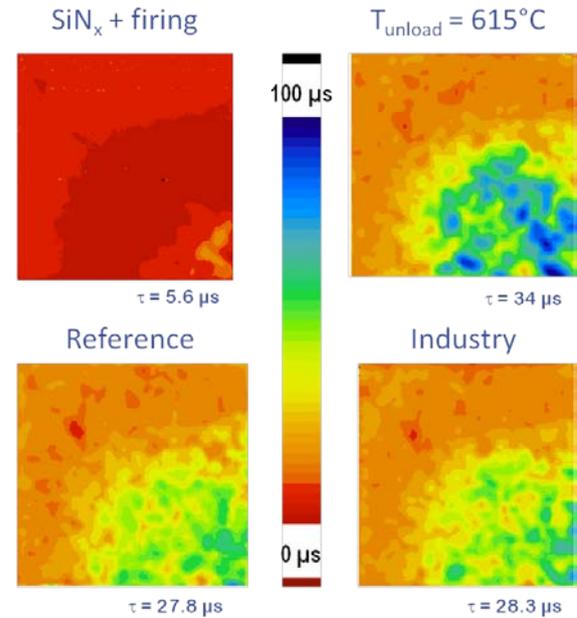
Figure 5: μPCD lifetime comparison of an as grown mc wafer with three sister wafers that are diffused in three different diffusion processes. Given are the mean τ values.

As grown — $\tau = 6.8\,\mu s$
$T_{unload} = 500°C$ + holding time — $\tau = 15.8\,\mu s$
Reference + holding time — $\tau = 17.6\,\mu s$
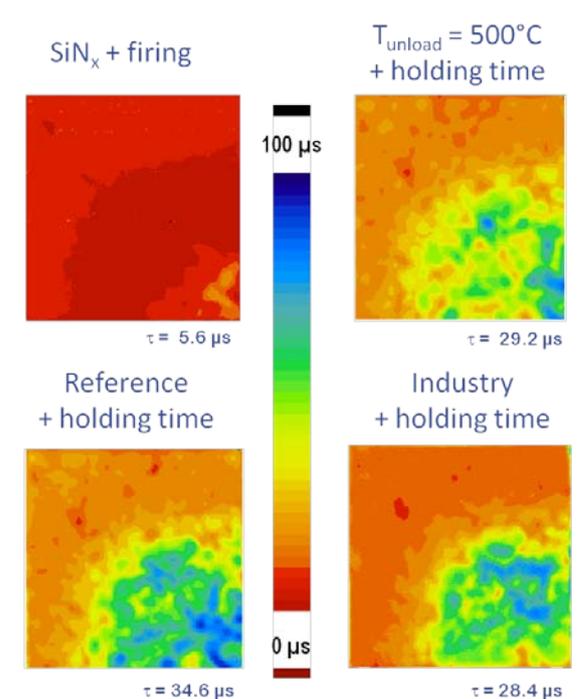Industry + holding time — $\tau = 21.7\,\mu s$

Figure 6: Same comparison as in Fig. 5 except that diffusion processes include a holding step at the respective unloading temperature.

A similar trend can be deduced from Fig. 6. Here the same diffusion processes as in Fig. 5 are shown with an additional holding time of 90 min at the respective unloading temperature. Among the longer lasting processes the industrial diffusion step is again the most efficient one. The process extension of 90 min has only a small positive effect on material quality. The highest improvement by 2.7 μs can be reported for the industry diffusion.

Fig. 7 and 8 represent the same comparisons as shown in Fig. 5 and 6 with an additional SiN$_x$ deposition and firing step for hydrogen passivation.


SiN$_x$ + firing — $\tau = 5.6\,\mu s$
$T_{unload} = 615°C$ — $\tau = 34\,\mu s$
Reference — $\tau = 27.8\,\mu s$
Industry — $\tau = 28.3\,\mu s$

Figure 7: Same as in Figure 5 with an additional SiN$_x$ deposition and firing step.

SiN$_x$ + firing — $\tau = 5.6\,\mu s$
$T_{unload} = 500°C$ + holding time — $\tau = 29.2\,\mu s$
Reference + holding time — $\tau = 34.6\,\mu s$
Industry + holding time — $\tau = 28.4\,\mu s$

Figure 8: Same as in Figure 6 with an additional SiN$_x$ deposition and firing step.

Due to this bulk passivation a material improvement up to $\Delta\tau = 17.3\,\mu s$ can be reached by the low unloading temperature diffusion. However, in case of non diffused material there is a degradation detected from $6.8\,\mu s$ of the as grown wafer down to $5.6\,\mu s$ of the SiN_x passivated one, which is possibly due to rearrangements of various defects during SiN_x deposition or firing. Similar trends have been reported before [5]. For the SiN_x samples without holding time the best diffusion seems to be the low unloading temperature process whereas for the long lasting processes it is the reference process which results in the highest lifetime. Additional holding at unloading temperature does not lead to a significant lifetime increase for all diffusions. While for the reference process lifetime raises by $7.2\,\mu s$, lifetime is reduced by $4.8\,\mu s$ in case of the low unloading temperature process. This is probably due to rearrangements of the low quality material regions during the exceedingly long process. Since there is no active cooling system, the wafers are already kept within the $POCl_3$ furnace tube for a quite long time until the low unloading temperature is reached. An additional holding time seems to give enough time for a more homogenous distribution of defects.

Besides µPCD lifetime mapping the interstitial iron concentration is determined from QSSPC measurements. In Fig. 9 the concentrations are shown for wafers originating from the lower and upper part of the brick without SiN_x passivation. The Fe_i concentrations of the gettered samples are clearly below the detection limit. The values shown below the detection limit are therefore most probably not to be trusted quantitatively. The measured difference in lifetime is so small that it lies within measuring inaccuracy.
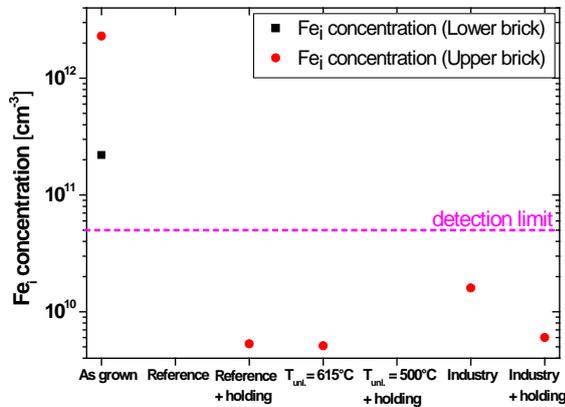

Figure 9: Determination of Fe_i concentration before and after Phosphorus gettering. Fe_i concentrations of gettered samples are below detection limit.

4.2 Cell Results

After characterization of bulk material this chapter focuses on cell results. Fig. 10 shows a µPCD lifetime measurement of a gettered wafer from the lower brick region. Four different cell areas are marked by a, b, c, and d. Area c turns out to have the best bulk quality. This is also visible in IV and SR (Spectral Response) data (see Fig. 11-16). All data points are averaged values from two cells, originating from two neighboring wafers and therefore showing a very similar crystal structure. Magenta data points (area c) show highest efficiency η, open circuit voltage V_{OC} and short circuit current density j_{SC} (Fig. 11-13). Parallel to higher V_{OC}, which is a

sign for better bulk quality, j_{01}, deduced from fitting IV curves using the two diode model, is lower. A lower j_{01} value means less recombination within the emitter and base region. That is in accordance to improved bulk quality. These IV results are supported by the highest IQE and L_{eff} data calculated from the IQE data, which is a measure for bulk quality besides V_{OC}. By comparing IV data of different diffusion types the reference diffusion with holding time at unloading temperature is identified as the most efficient gettering process. This applies to all four wafer regions.
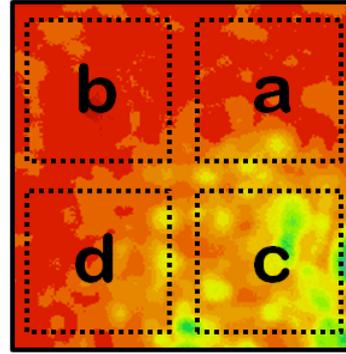
Figure 10: Positions of four cells onto a 5x5 cm^2 wafer. Area c can be identified as the best cell material.
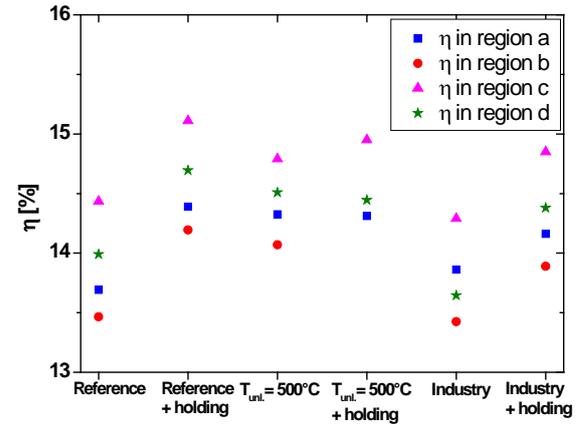
Figure 11: Efficiencies η versus six diffusion processes summarized in Table I. Each color resembles one of the different wafer regions a, b, c and d.
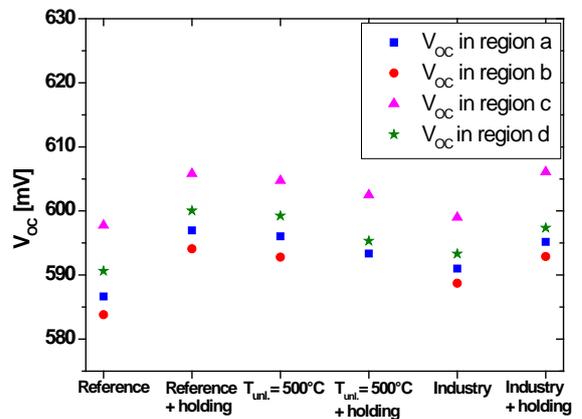
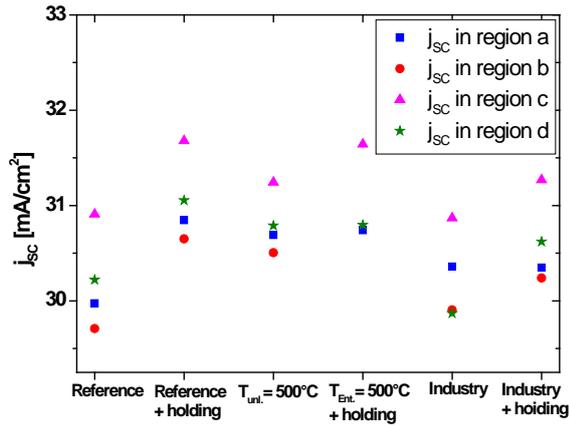**Figure 12:** Open circuit voltage V_{OC} versus type of diffusion.

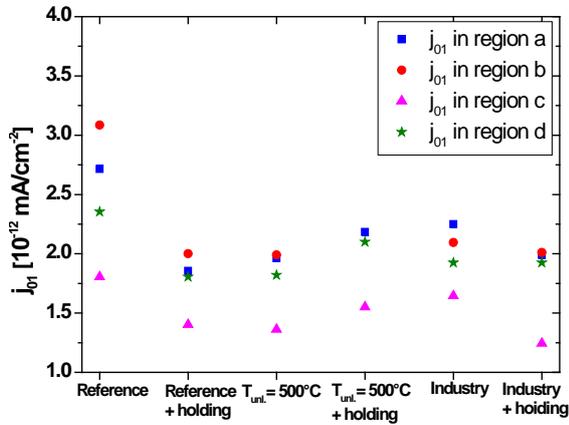**Figure 13:** Short circuit current density j_{SC} versus type of diffusion.

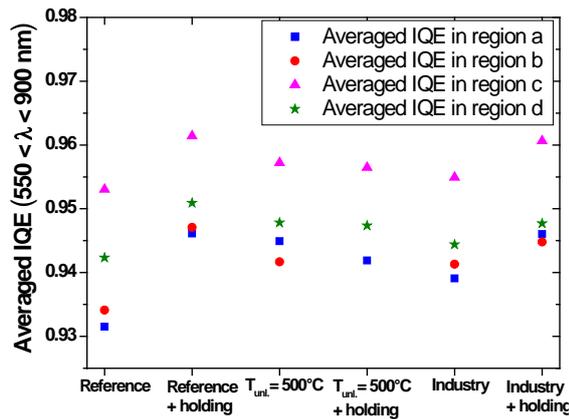**Figure 14:** Saturation current density j_{01} versus type of diffusion.

Figure 15: Averaged IQE within wavelength interval $550 < \lambda < 900$ nm versus type of diffusion.

Figure 16: L_{eff} versus type of diffusion.

Figure 17: IQEs vs. wavelength shown for mc wafers with different emitters. For comparison one FZ cell with reference emitter is added in black.

Figure 18: IQEs from 350 nm to 600 nm of data shown in Fig. 17.

As mentioned before, especially V_{OC}, j_{01} and L_{eff} are a measure of bulk quality. All three quantities lead to the conclusion that the reference diffusion with holding time at unloading temperature is the most effective gettering process followed by the extended industrial process. Therefore an additional holding time in case of the reference and industry diffusion is reasonable. The additional holding time for the low unloading temperature process reduces V_{OC} and L_{eff} while j_{01} is
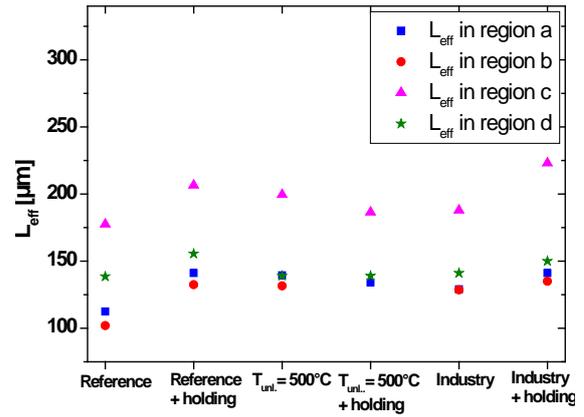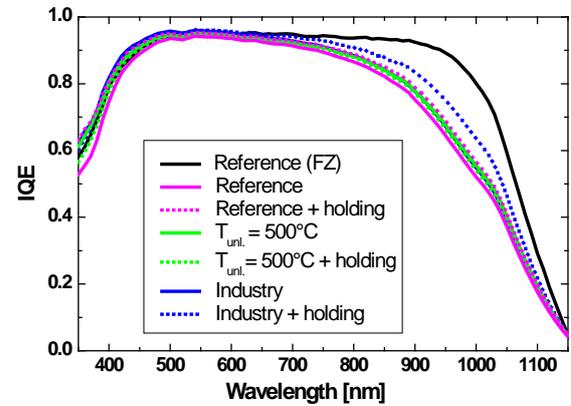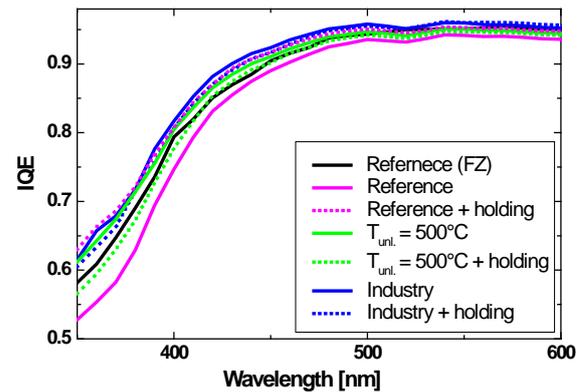
raised. That means that bulk quality is reduced by the process extension. This is in accordance with the lifetime results of SiN_x passivated samples where bulk quality of the extended low unloading temperature diffusion is reduced compared to its shorter version.

Fig. 15 shows the averaged IQE (Internal Quantum Efficiency) within wavelength interval $550 < \lambda < 900$ nm, corresponding to the bulk cell region. The material improvement for reference and industry between initial diffusion processes and their extended version is clearly visible. A similar trend can be observed for L_{eff} in

Fig. 16. IQEs versus wavelength taken from wafer region c are compared in Fig. 17 and 18 for different emitters and to one FZ cell shown in black.

From first sight mc wafers exhibit a strong loss at the backside compared to the FZ sample. This is most probably due to the low bulk quality of the wafers originating from the edge of the mc brick. In Fig. 18 a detail of Fig. 17 is presented which focuses on the low wavelength regime from 350 nm to 600 nm. The IQE values of the reference diffusion are below all other emitters which implies higher emitter recombination losses. This is in accordance with a higher j_{01} shown in Fig. 14.

5   CONCLUSION AND OUTLOOK

It is found that phosphorus diffusion leads to a strong improvement in electronic material quality leading to interstitial iron concentrations below the detection limit ($5 \cdot 10^{10}$ cm^{-3} [4]). The interstitial iron content of as grown material is measured to be $2 \, 10^{11}$-$2 \, 10^{12}$ cm^{-3}, depending on the height of the wafer in the ingot.

Due to hydrogen passivation from PECVD SiN$_x$ bulk quality can be improved significantly. The highest increase of $\Delta\tau = 17.3$ µs is reached by the low unloading temperature diffusion.

In accordance with the previous bulk analysis on 5x5 cm^2 wafers with SiN$_x$:H passivation, cell results identify the low unloading temperature process as the most effective one in gettering among the diffusion processes without additional holding time at unloading temperature. Cells from the region of highest lifetimes (area c), measured by µPCD, show the best cell results.

Comparing diffusion processes with holding time at unloading temperature, the reference diffusion leads to the best results both on Al$_2$O$_3$ passivated lifetime samples and on cell level. An unusually increased saturation current density j_{01} is reported for the reference diffusion process without additional holding time at unloading temperature. This might be due to lower bulk quality as well as due to a higher recombination in the emitter.

Experiments with the same types of diffusion processes on other mc material will be performed and compared to the presented results. In addition, POCl$_3$ diffusions with varied deposition temperature are planned and their gettering efficiency will be analyzed.

6   ACKNOWLEDGEMENTS

7   REFERENCES

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