

EMITTER PROFILE TAILORING BY GAS FLUX VARIATION IN TUBE FURNACE POCl_3 -DIFFUSION AND ANALYSIS OF THE PHOSPHOSILICATE GLASS

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ABSTRACT: We analyze possibilities and difficulties of forming POCl_3 -diffused emitters for industrial application with low recombination by reducing the maximum phosphorus concentration in the emitter. For this purpose we vary the concentration of reactants in the process tube furnace. Both life time samples and solar cells are processed with reference emitters and emitters of the proposed variation. During processing we take special care of a detailed characterisation of the phosphosilicate glass and assess its basic properties. We observe a gain in cell efficiency of 0.2% absolute on standard screen-printed silicon solar cells fabricated with the improved emitters. Diffusions with low concentration of reactants provide higher open circuit voltages and efficiencies. The fill factor level is maintained, since the contact resistance does not increase although the peak doping reduces from ~ 8 to $\sim 5 \times 10^{20} \text{ cm}^{-3}$. A correlation between peak doping and saturation current is observed. Increasing deposition time in expense of drive-in time allows mitigating the negative impact on sheet resistance homogeneity and homogeneity along the processing boat (suitable for 200 Wafers).

Keywords: Diffusion, Phosphorous, Emitter

1 INTRODUCTION

Emitters for industrial silicon solar cells have to comply with several requirements. Apart from building the p-n junction of the cell they also have to ensure a high lateral conductivity, enable a good contact with the screen printed front side metallisation and should cause only low recombination losses. Whereas the contact formation requires high dopant concentration, lower doped emitters should be preferred in view of recombination. Selective emitters are one option to meet these demands, however they require additional processing steps.

Currently, most industrial production lines apply a tube furnace diffusion using a liquid phosphorus oxychloride (POCl_3) source [1] for emitter formation. Optimisation of this process involves a large number of process parameters. Besides temperature, deposition- and drive-in time, the N_2 flux through the POCl_3 bubbler is an important parameter, which is investigated in this work. Our results reveal that this parameter allows adjusting the peak doping level, while maintaining a homogeneous sheet resistance distribution. Moreover we expand the characterisation to the phosphosilicate glass (PSG) as the intermediate step in order to better understand the whole diffusion process.

2 TUBE FURNACE POCl_3 -DIFFUSION PROCESS

Tube furnace diffusion is a batch process in which wafers, normally textured and cleaned, are exposed to an atmosphere of POCl_3 , O_2 , and N_2 at high temperatures in the range of 800 °C to 900 °C. Usually, the diffusion process consists of a deposition step with active POCl_3 -flux followed by a drive-in step in which the wafers are kept at peak temperature in a N_2 ambient. During deposition P_2O_5 forms on all surfaces of the wafers by the reaction [2]



The phosphorus pentoxide P_2O_5 immediately reacts with the silicon, by



resulting in in-diffusion of phosphorus and formation of the phosphosilicate glass (PSG). Apparently, a reduction of the partial pressure of POCl_3 leads to a lower supply of reactants in the tube furnace so that the reactions (1) and (2) and the subsequent in-diffusion processes take place more slowly.

As the wafers are closely arranged in the processing boat during the process, a variation of the reactant concentration in the gas mix might lead to a depletion of the reactants especially in the central part of the wafers, aggravating the problem of radial in-homogeneity. Furthermore, the gas flows from one side (gas zone) of the tube to the other (load zone) so that special care has to be taken that the supply of reactants is ensured also at the load zone of the tube. All these issues have to be considered when assessing the gas flux.

3 EXPERIMENTAL

In this work, we investigate the impact of the N_2 flux through the POCl_3 bubbler on the emitter properties. We use an industrial quartz tube furnace with 36 cm tube diameter and a diffusion boat that holds 200 wafers placed at a distance of 4.8 mm next to each other.

In a first step, we fabricate symmetric lifetime samples using 125x125 mm² (pseudo square) boron-doped float zone (FZ) silicon wafers with a resistivity of 1 Ωcm and a thickness of 250 μm , either shiny etched or textured with random pyramids. Several groups are processed each containing two shiny etched and two textured samples surrounded by dummy wafers to simulate a loaded boat. For each group the process parameters during diffusion are varied. Before and after diffusion and again after PSG etch we weigh the samples to determine the mass gain during diffusion and the mass

Table I: Process parameters and measurement results for emitters A, B, and C. Times increase from t_1 to t_2 and t_3 , so that A has a longer total process time than B and C. For R_{sheet} the mean value and standard deviation from the 10x10 FPP-maps are quoted, measured on planar samples after PSG removal. For J_{0e} the mean value and standard deviation from several measurements at different locations on one sample are listed. In both cases systematic measurement uncertainties are not included. All J_{0e} -samples receive an ARC onto both surfaces and are fired at a set temperature of 850 °C.

Emitter	Temperature	POCl ₃ bubbler flux	Depos. time	Drive-in time	R_{sheet} planar [Ω/sq.]	$C_{P,\text{max}}$ [10 ²⁰ cm ⁻³]	J_{0e} planar [fA/cm ²]	J_{0e} textured [fA/cm ²]
A	T_A	high	t_1	t_3	60.7 ± 0.5	~8	360 ± 12	576 ± 5
B	$T_A + 10$ K	medium	t_1	t_2	58.1 ± 1.1	~6	356 ± 12	522 ± 6
C	$T_A + 10$ K	low	t_2	t_1	62.0 ± 1.0	~5	343 ± 7	577 ± 6

of the PSG layer. Measurements using inductive radio frequency (RF) coupling [3] performed before and after diffusion yield the sheet resistance of the diffused layer. Between diffusion and PSG etch an ellipsometry measurement gives the thickness of the PSG layer. Some of the planar wafers are cut into smaller samples after the PSG etch for later Secondary Ion Mass Spectrometry (SIMS) profiling. All wafers then receive a SiN_x anti-reflective coating (ARC) on both sides by means of plasma enhanced chemical vapour deposition (PECVD) and are fired in a conventional belt furnace to ensure comparison with cell level. The firing set temperature is 850 °C yielding about the same effective wafer temperature as for a metallised cell that is usually fired at set temperatures around 900 °C. After firing we measure the effective minority carrier lifetime τ_{eff} by the quasi steady-state photo-conductance decay (QSSPC) technique [4] and determine the emitter saturation current density

$$J_{0e} = \frac{qWn_i^2}{2(N_A + \Delta n)} \left[\left(\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{bulk}}} \right)^{-1} - \frac{W^2}{D\tau^2} \right]^{-1} \quad (3)$$

under low-level injection conditions [5,6] taking into account only Auger-recombination in the bulk. Here we use $\Delta n = 1 \cdot 10^{15} \text{ cm}^{-3}$, $\tau_{\text{bulk}} = 2.7 \text{ ms}$ [7], $D = 28.2 \text{ cm}^2/\text{s}$, $N_A = 1.5 \cdot 10^{16} \text{ cm}^{-3}$, $n_i = 9.5 \cdot 10^9 \text{ cm}^{-3}$. This saturation current limits the open circuit voltage V_{OC} of a solar cell to values below

$$V_{\text{OC,max}} = V_{\text{th}} \ln \left(\frac{J_{\text{SC}}}{J_{0e}} - 1 \right) \quad (4)$$

using the thermal voltage $V_{\text{th}} = 25.7 \text{ mV}$ and a short circuit current density value of $J_{\text{SC}} = 35 \text{ mA/cm}^2$ for a textured cell.

In a second step we proof the advantage of the novel emitter processes on solar cells made of 125*125 mm² (pseudo square) boron-doped Czochralski (Cz) silicon wafers with a resistivity of 1.5 Ωcm and a thickness of 210 μm, textured with random pyramids. After the diffusion a HF-dip removes the PSG and a PECVD SiN_x ARC is deposited onto the front side. Then we screen-print a standard metallisation consisting of AgAl-soldering pads and a full-area Al layer for later forming of the Al back surface field (BSF) for the rear surface and an Ag grid for the front contact. The cells go through firing at which a temperature variation is performed; groups of four to eight cells each are processed identically. Finally, laser edge isolation separates the p- and n-contact.

4 RESULTS

4.1 Emitter characterisation

Here, we present the results of three emitters A, B, and C, all with sheet resistances R_{sheet} of about 60 Ω/sq.. Table I lists the process parameters. Compared to the standard process A, the new processes B and C feature lower POCl₃-gas fluxes and a reduced total plateau time to meet the throughput requirements of industrial production. Moreover, we increase the plateau temperature for processes B and C by 10 K with respect to process A to reach the desired R_{sheet} . Deposition and drive-in times of emitter C are switched compared to emitter B to compensate for the further reduced gas flux. Table I also shows the measured R_{sheet} after PSG removal, the maximum phosphorus concentration $C_{P,\text{max}}$ obtained from the SIMS measurements (see Fig. 1), and the results of the J_{0e} analysis. The standard deviation of a spatial resolved four point probe (FPP) measurement on a 10x10 map covering the whole wafer is a measure for the homogeneity of R_{sheet} across the wafer surface. In case of the J_{0e} samples several measurements at different locations of the samples are performed, Table I lists the average value and the standard deviation.

Figure 1 presents the SIMS profiles measured for the three emitters. Apparently, the peak doping $C_{P,\text{max}}$ decreases when reducing the gas flux, even if the temperature is increased as it is the case for emitters B

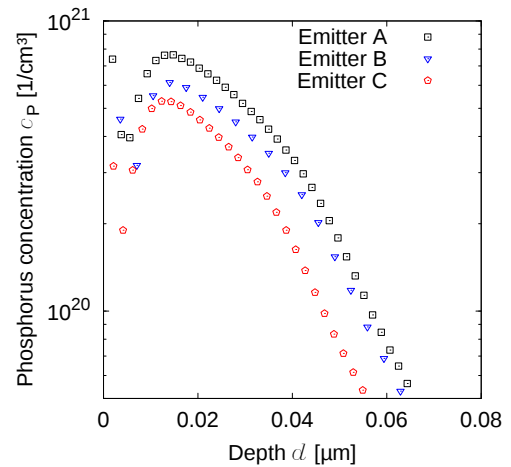


Figure 1: Phosphorus concentration profiles close to the surface for the three emitters obtained by SIMS measurements. Note that the peak doping reduces with decreasing gas flux from emitter A to emitter C. The decrease towards the surface is assumed to be an artefact of the SIMS measurement.

and C. Except for the peak doping, the profiles are quite similar, all three emitters feature the same junction depth. The decreased peak doping yields less recombination in the emitter, which slightly reduces J_{0e} compared to the standard process. Although the results on textured samples do not exhibit the same clear correlation, it seems that the approach works out. According to Eq. (4) a gain in V_{OC} of about 3 mV is expected when decreasing J_{0e} by 10%.

To assess the homogeneity throughout the tube, we process emitter C in a full loaded boat with 200 Cz wafers of 125*125 mm² (pseudo square) size and measure the sheet resistances by RF coupling. The geometry of the inductive measurement also enables a quantification of the sheet resistance homogeneity on each wafer by means of the standard deviation of all measurement points distributed over the wafer surface. Figure 2 shows the distribution of the average value and the standard deviation of R_{sheet} for each wafer plotted versus the position in the diffusion boat. From the gas zone to the load zone the sheet resistance slightly increases from 65 to 69 $\Omega/sq.$, the standard deviation for all boat positions is 1.5 $\Omega/sq.$ (2%). The standard deviation measured for the individual wafers increases from ~1.5 $\Omega/sq.$ (2%) for the gas zone to ~2.5 $\Omega/sq.$ (4%) for the load zone with maximum values of 3.5 $\Omega/sq.$ (5%). Thus, despite the low $POCl_3$ flux, we still achieve an acceptable homogeneity for both the distribution of the sheet resistance along the fully loaded boat and over the surface of the individual wafers. The higher values for the standard deviation compared to the 10x10 FPP-mapping (see Table I) result from different measurement geometries. The higher absolute values might originate from differences in the material and the increased number of wafers of the fully loaded boat compared to the previous experiments.

4.2 Analysis of the PSG layer

Besides the three above mentioned emitters a large number of process variations is carried out, which enables us to perform the characterisation of the PSG layer on a satisfying statistical basis. The measured ratio

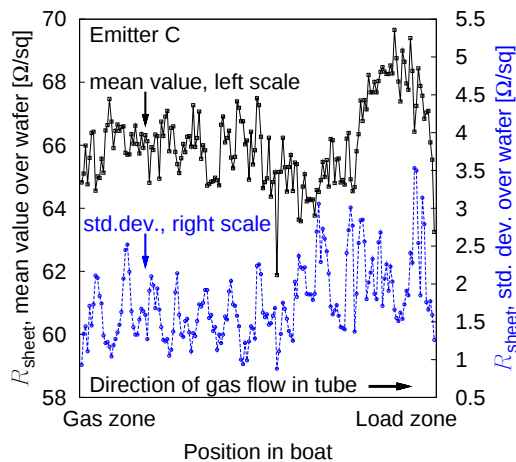


Figure 2: Average value (solid line, left scale) and standard deviation (dashed line, right scale) of the sheet resistance map measured for each wafer versus position in the diffusion boat for processing a fully loaded boat using process C.

Table II: Probability values (P -value) from multilinear regression of mass gain and PSG thickness. Low values indicate high correlation. Significant values in bold font.

	Mass gain during diffusion	
	7	19
Nr. of observations	7	19
Temperature	0.321	$3.17 \cdot 10^{-5}$
$POCl_3$ gas flux	0.077	$4.99 \cdot 10^{-5}$
Deposition time	0.038	0.035
Drive-in time	0.413	0.694

of mass gain during diffusion on textured and planar samples is 1.6 ± 0.2 , a result in good accordance with the geometrical surface enlargement factor of 1.73 for random pyramids [8]. Multilinear regression yields a probability value (P -value) for the four process input parameters temperature, gas flux, deposition time, and drive-in time (see Table II). The smaller the P -value, the higher the significance of the independent variable in the linear model [9]. The results show that for the analysed processes, the mass gain correlates with deposition time and gas flux, whereas temperature and drive-in time do not significantly affect the mass gain. Measuring the thickness of the PSG by ellipsometry after 19 different diffusions we find a clear dependence on three of the four process parameters – temperature, deposition time, and gas flux. The mass loss of the wafers after PSG removal is quite accurately proportional to the PSG thickness, indicating a mass density of (2.46 ± 0.26) g/cm³ as a mean value with standard deviation; the systematic error will be higher. The ellipsometry data yield a value of 1.58 ± 0.03 (at a wavelength of 633 nm) for the refractive index, independent of processing conditions. The mass gain during diffusion is not proportional to the PSG thickness whereas mass loss during PSG removal indeed is, indicating a change in PSG composition with varying process parameters. A possible explanation would be, that reactions (1) and (2) show a different temperature dependence: While reaction (1), which is responsible for the mass gain, seems to be nearly independent of temperature, the PSG growth by reaction (2) is accelerated by higher temperatures. SIMS measurements on samples that still feature the PSG layer indicate that the phosphorus concentration in the PSG depends on the process parameters. However, the large noise of the data due to charging of the PSG layer during the measurement as well as the lack of standards with known phosphorus concentration do not allow a closer analysis at present.

4.3 Cell results

Figure 3 shows the measured IV-parameters plotted versus the firing set temperature T_{set} . After a first measurement of the electrical properties directly after the last process step (filled symbols in Fig. 3) some of the cells are illuminated for 10 h at ~0.3 suns and show a degradation of a few mV in V_{OC} and less than 0.1 mA/cm² in the short circuit current density J_{SC} . We attribute these changes to the formation of boron-oxygen complexes [10]. The fill factor FF shows no significant changes. On these cells we conduct a forming gas anneal (FGA) at 350 °C for 5 minutes, illuminate the cells again to reverse possible annealing of the Cz bulk and repeat the measurements (open symbols in Fig. 3).

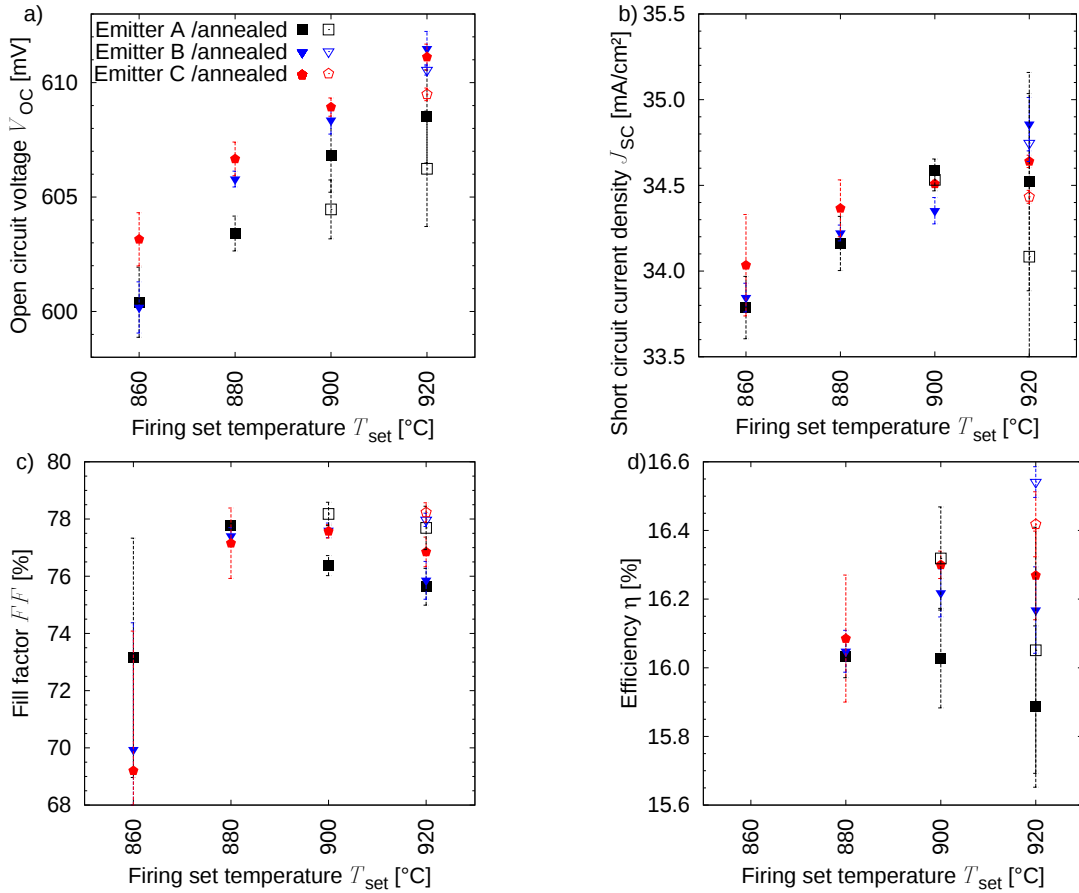


Figure 3: Solar cell characteristics for the four firing groups for each emitter measured after contact isolation (filled symbols) and after FGA and subsequent degradation by illumination (open symbols). Average value and standard deviation for each group are plotted. The legend of graph a) also applies to the other graphs.

The results confirm the expected advantages of the emitter processes B and C with reduced gas flux compared to process A. The reduced recombination in emitters B and C is clearly visible in the increased open circuit voltage V_{OC} . The gain is about 3 mV, as expected from the J_{oe} analysis performed in Section 4.1. Higher firing temperatures result in an increased V_{OC} , due to a thicker and higher doped BSF [11]. Both trends also appear in the data for the short circuit current density J_{SC} . The fill factors FF show no systematic impact of the diffusion process. Measurements by means of the transfer length method [12] on samples cut out of the cells yield identical specific contact resistances of $\sim 5 \text{ m}\Omega\text{cm}^2$ for all three emitters. After a FGA, all cells fired at $T_{\text{set}} = 920 \text{ }^\circ\text{C}$ reach fill factors around 78%, regardless of the diffusion process. The annealing step reduces the open circuit voltage V_{OC} of every group, which is partly due to more thorough degradation before the measurement after annealing with respect to the first measurement. The samples fired at $T_{\text{set}} = 920 \text{ }^\circ\text{C}$ improve notably in fill factor during annealing, which is a known effect of an increased conductance between silver crystallites and finger bulk [13]. Both before and after annealing the emitters B and C with lower gas flux show higher efficiencies of 16.5% and 16.4% for emitter B and C compared to 16.3% for emitter A (group average for $T_{\text{set}} = 920 \text{ }^\circ\text{C}$, measured after FGA). In combination with a FGA, higher firing temperatures might yield higher efficiencies, in particular for emitters B and C.

5 SUMMARY AND OUTLOOK

We adjust the peak doping of tube furnace diffused phosphorus-doped emitters by varying the N_2 flux through the POCl_3 bubbler. On both lifetime samples and solar cells we demonstrate that a reducing the peak doping from ~ 8 to $\sim 5 \cdot 10^{20} \text{ cm}^{-3}$ yields less recombination and enables $\sim 3 \text{ mV}$ higher open circuit voltages and $\sim 0.3 \text{ mA/cm}^2$ higher short circuit current densities. No increase in the contact resistance is observed and thus the fill factor remains at a high level resulting in increased cell efficiency of 0.2% absolute. Although the gas flux is reduced, we maintain a sufficiently homogeneous sheet resistance over wafer surface and boat position with standard deviations of 4% and 2% respectively for a diffusion boat fully loaded with 200 wafers of $125 \cdot 125 \text{ mm}^2$ (pseudo-square) size.

A better understanding of the formation of the PSG as the intermediate step in the process should allow to gain more insight into physical details of the diffusion process and give important information for process modelling. First results reveal that mass density and refractive index, are not affected by varying process parameters. Nevertheless composition seems to vary with gas flux thus causing different peak doping levels.

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