

Applicability of screen-printable dopant pastes: gettering and selective emitters

T. M. Pletzer, H. Windgassen & H. Kurz, RWTH Aachen University, Institute of Semiconductor Electronics, Aachen, Germany

ABSTRACT

Phosphorus dopant pastes are an attractive alternative to the conventional phosphorus oxychloride (POCl_3) dopant source for emitter processing in solar cells, as they allow the fabrication of selective emitters on an industrial scale. In this paper it is demonstrated that single-sided uniform screen-printed emitters, processed with phosphorus dopant pastes, can getter multicrystalline silicon (mc-Si) wafers more effectively than conventional double-sided uniform POCl_3 emitters. This result is confirmed by minority carrier lifetime measurements with the quasi-steady-state photoconductance (QSSPC) method. Solar cells with selective emitters were processed using phosphorus dopant pastes on mc-Si wafers and were subsequently characterized. The current-voltage (I - V) results are improved compared to uniform POCl_3 emitter solar cells and an increased internal quantum efficiency (IQE) for selective emitter solar cells is demonstrated.

Introduction

The development of new industrial solar cell concepts is being accelerated by selective emitter technology [1]. Such emitters feature high doping ($\sim 30\Omega/\text{sq.}$) beneath the front contact grid and moderate doping elsewhere ($\sim 100\Omega/\text{sq.}$). Thereby selective emitters can increase the efficiency of solar cells by improving the IQE in the ultraviolet (UV) wavelength range due to reduced Auger recombination in the emitter [2,3]. Furthermore, selective emitters permit lower contact resistance values at the front-side metallization resulting in a lower series resistance compared to conventional solar cells [3].

Producing selective emitters by screen-printing of phosphorus dopant pastes [4–6] in combination [3,7] with conventional POCl_3 diffusion is an attractive fabrication method and is employed in this work. This article presents a summary of current and previous work to show the applicability of screen-printable dopant pastes in regard to gettering and selective emitter structures, which have been investigated in more detail by Pletzer et al. [7,8]. In order to successfully apply these selective emitter structures, it is crucial to investigate gettering [8–10] and emitter doping profiles [11,12]. During emitter formation, efficient gettering of impurities such as metal, is essential to improving the wafer quality, as these impurities lead to unwanted Shockley-Read-Hall (SRH) recombination.

Gettering of impurities occurs when phosphorus diffuses into the wafer from a phosphorus source such as a POCl_3 gas or a phosphorus dopant paste. Driven by the concentration gradient of phosphorus, the impurities diffuse towards the emitter surface during emitter formation at high temperatures. At the surface the impurities have a high solubility. Subsequently, the formed phosphorus impurity complexes are strongly bound in the emitter by

Coulomb forces. This binding is strong enough to prevent recontamination by, for example, metal silicide precipitation at grain boundaries [13]. Afterwards, these bound impurities have only negligible influence on the characteristics of the fabricated solar cells.

Conventional double-sided POCl_3 emitters allow the fabrication of uniform emitters and provide an effective double-sided gettering [9]. In contrast, screen-printed emitters, as presented in this study, provide only single-sided gettering. Thus, the formation of a parasitic p-n junction at the back side of the cell is suppressed [14], giving way to new cell designs, such as rear-side passivated cells [15].

This work focuses on the gettering efficacy in mc-Si wafers using uniform screen-printed emitters [7,8], the

measurement of selective emitter profiles and the investigation of solar cells with selective emitters.

For the second section, the gettering efficacy of uniform screen-printed emitters was obtained by minority carrier lifetime measurements using the QSSPC method [16] and has been compared with results of conventional uniform POCl_3 emitters, which were used as references in this work.

The best phosphorus dopant paste was used to process selective emitters on mc-Si wafers. These emitters were characterized to determine phosphorus doping profiles, compared to conventional uniform POCl_3 emitters.

Finally, entire solar cells with screen printed selective emitters were processed and characterized to explore their potential for industrial production.

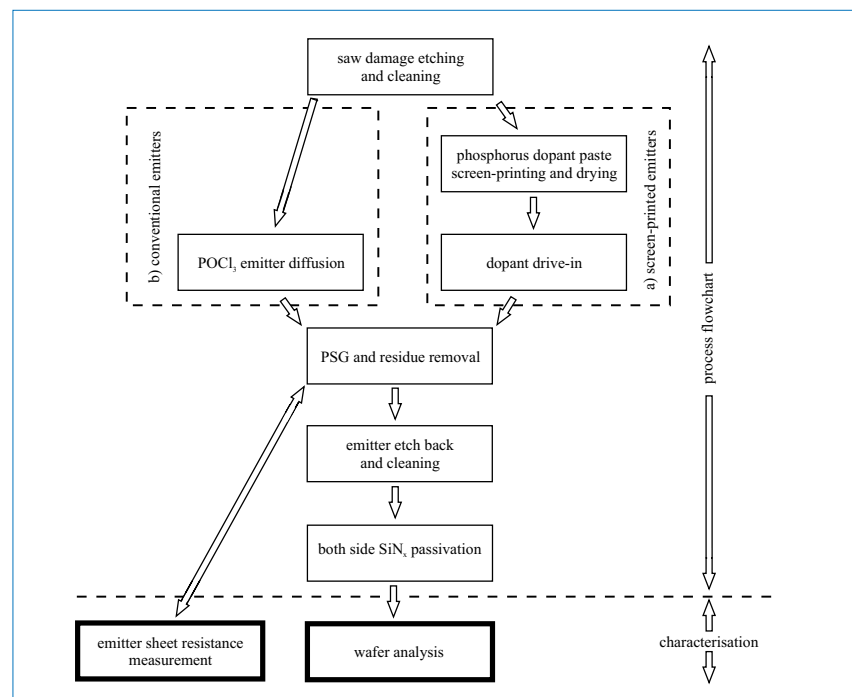


Figure 1. Process flowchart of the gettering investigation.

Process technology for gettering

Eleven dopant pastes with different phosphorus concentrations were compared in the fabrication process of single-sided emitters. All samples were processed on neighbouring mc-Si wafers from the same brick with boron doping (p-type). The process sequence and analysis steps are outlined in Fig. 1. An alkaline saw damage etch and a subsequent cleaning were followed by the emitter formation in two different ways: (i) screen-printing of different phosphorus dopant pastes on one side of the wafer, followed by diffusion (samples one to 11) and (ii) conventional batch POCl₃ diffusion on both sides of the wafer as reference (sample 12).

Control samples without emitter diffusion were included in the study to monitor the as-received material quality (sample 13).

The diffusion process was carried out in the same quartz tube furnace at a temperature of about 820°C with constant gas flow and time [5,11]. Later, the phosphorus silicate glass (PSG), formed as a by product of the diffusion process, was removed along with any residues by a dip in diluted hydrofluoric acid.

Emitter sheet resistance (R_{sh}) measurements (Fig. 1) were carried out using a four-point-probe technique. In Table 1, single-sided uniform screen-printed emitters with different phosphorus pastes, their respective R_{sh} and standard deviation (σ) are listed. An emitter is regarded as sufficiently uniform if $\sigma \leq 10\%$, so that local differences in the contact formation do not significantly influence the whole solar cell. The emitter R_{sh} of the samples one to three and the POCl₃ reference sample are in a typical range of emitters used in industrial solar cell production (approx. 50–60Ω/sq.). Samples four to eight show emitter R_{sh} , which is typical for weakly-doped emitters with low phosphorus concentration. Samples eight, 10 and 11 have $\sigma > 10\%$, apparently caused by very low phosphorus concentration in the pastes. It is mainly observed that an increase in R_{sh} is correlated to the value of σ . The significantly high value of σ from samples six and nine was presumably caused by visible dopant paste residues that remained even after PSG removal.

Afterwards these emitters were removed through a wet etch on both sides of all samples and a subsequent cleaning (Fig. 1). The silicon nitride (a-SiN_x:H) anti-reflection coating (ARC) was deposited on both sides of the wafers [15], followed by a thermal treatment as a co-firing step, which is necessary to allow hydrogen diffusion to defect passivation.

The surface passivation layers were processed identically with high passivation quality [15] to achieve low surface recombination velocities. Therefore, the measured effective minority carrier lifetime

Sample/source	R_{sh} [Ω/sq.]	σ [%]	$\tau_{eff\ bulk}$ [μs]
1/p-paste	51	9	12.6
2/p-paste	52	6	9.6
3/p-paste	54	5	11.6
4/p-paste	68	5	11.2
5/p-paste	74	5	11.9
6/p-paste	79	22	7.5
7/p-paste	95	7	8.5
8/p-paste	104	20	6.3
9/p-paste	119	36	6.9
10/p-paste	145	26	10.0
11/p-paste	711	19	3.2
12/POCl ₃ reference	59	5	8.5
13/Material control	—	—	1.9

Table 1. Comparison of sheet resistances (R_{sh}) and standard deviation (σ) in R_{sh} of screen-printed emitters and a POCl₃ reference emitter on mc-Si wafers as well as their effective lifetime ($\tau_{eff\ bulk}$) at $5 \times 10^{15} \text{cm}^{-3}$ averaged over a sample area of $\approx 13 \text{cm}^2$. Repeated measurements differ by $< 10\%$.

[16] (wafer analysis in Fig. 1) can be related directly to the bulk lifetime ($\tau_{eff\ bulk}$), listed in Table 1.

Compared to the material control sample 13 having a $\tau_{eff\ bulk}$ of 1.9μs in agreement with the material specification of $\tau_{eff\ bulk} \geq 2\mu\text{s}$, all other test samples – including reference samples – showed an increase in the effective bulk lifetimes, mainly because of gettering. The $\tau_{eff\ bulk}$ of samples one to five, and seven and 10 exhibit even more effective gettering and achieve $\tau_{eff\ bulk}$ equal to or higher than the

reference samples. However, samples six, eight, nine and 11 getter less effectively than the reference, due to a lower phosphorus concentration used during diffusion, as determined by R_{sh} . In general, the results in Table 1 demonstrate that screen-printed emitters can getter even more effectively than conventional POCl₃ emitters.

The gettering efficacy is displayed in Fig. 2, where the relative difference between $\tau_{eff\ bulk}$ of the non-gettered and gettered sample is plotted against the R_{sh} values.

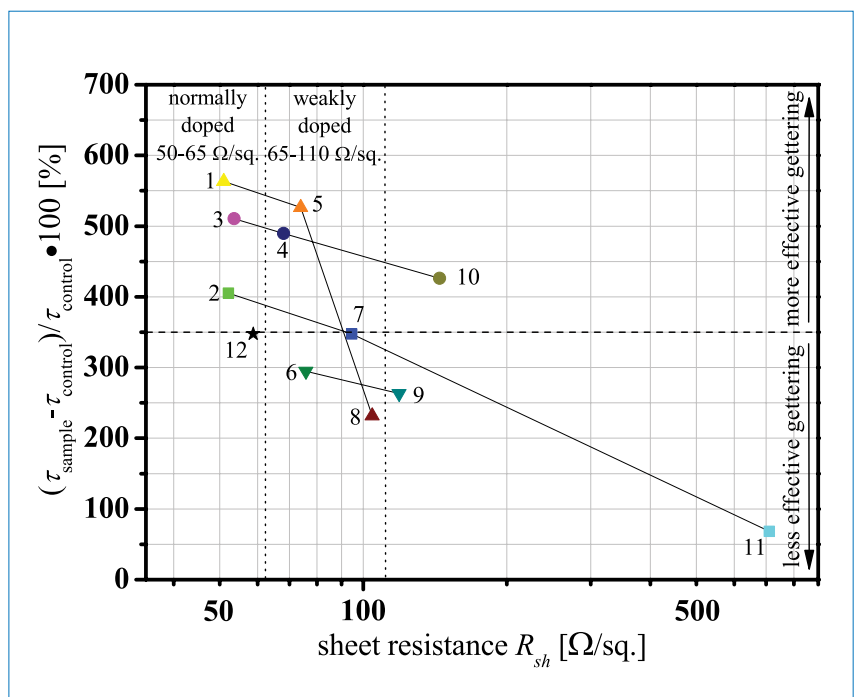


Figure 2. Gettering efficacy based on material control sample versus sheet resistance R_{sh} . A low R_{sh} allows a more effective gettering. Samples processed with dopant pastes from the same manufacturer are connected by a line as a guide to the eye.

A low R_{sh} associated with a high phosphorus concentration [11] yields higher gettering efficacy and vice versa. A similar correlation between gettering efficacy and the phosphorus concentration in $POCl_3$ emitters was found by Bätzner et al. [17]. High phosphorus concentration leads to better gettering by binding a higher number of impurities and enabling higher impurity solubilities, which decreases SRH recombination significantly [13].

“High phosphorus concentration leads to better gettering by binding a higher number of impurities and enabling higher impurity solubilities.”

Comparing a screen-printed and a $POCl_3$ emitter of similar R_{sh} , a higher peak and surface electrically active phosphorus concentration (C_p) is found for the $POCl_3$ emitter (Fig. 3). Whereas the overall phosphorus concentration is slightly higher (~10%), it is significantly higher if both sides of the $POCl_3$ emitter are accounted for. Yet the gettering efficacy of the dopant paste process is still better, as evidenced by the bulk lifetime measurements (Table 1). It is apparent that another process parameter changed, thus influencing

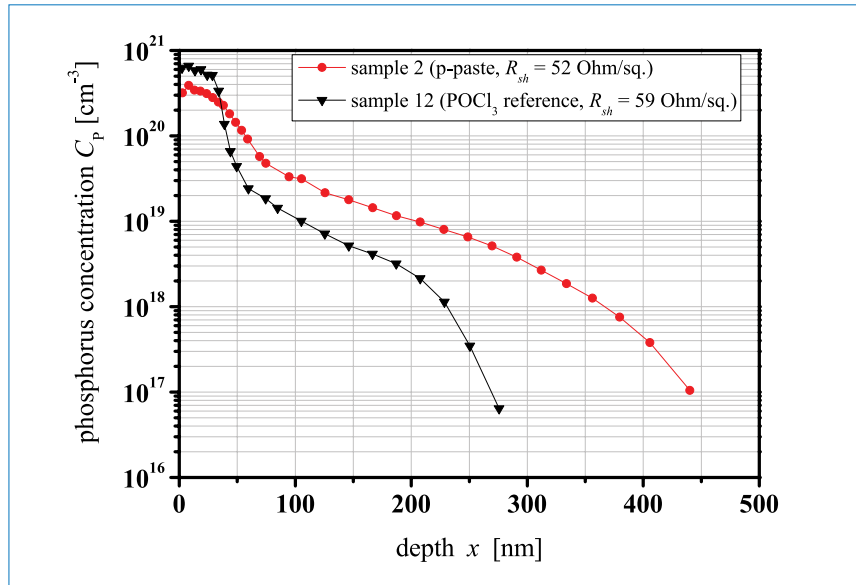


Figure 3. Typical electrically active phosphorus concentration C_p measured by the electrochemical capacitance voltage (ECV) method versus depth (x) in the silicon wafer. Included are a $POCl_3$ reference emitter (sample 12) and a screen-printed emitter (sample 2) with comparable R_{sh} . The $POCl_3$ emitter shows a higher phosphorus surface concentration than the screen-printed emitter, but otherwise the screen-printed emitter features a deeper phosphorus profile. R_{sh} values calculated from these profiles are identical to the values extracted from four-point-probe measurements (Table 1).

the gettering process more than the phosphorus concentration.

The most likely candidate is the effective gettering time, which had been kept constant in the previous studies, where the correlation between gettering

and phosphorus concentration has been investigated [17]. Here, however, the emitters are processed in fundamentally different ways. In the case of the screen-printed emitters a dopant paste layer of several μm in thickness is deposited

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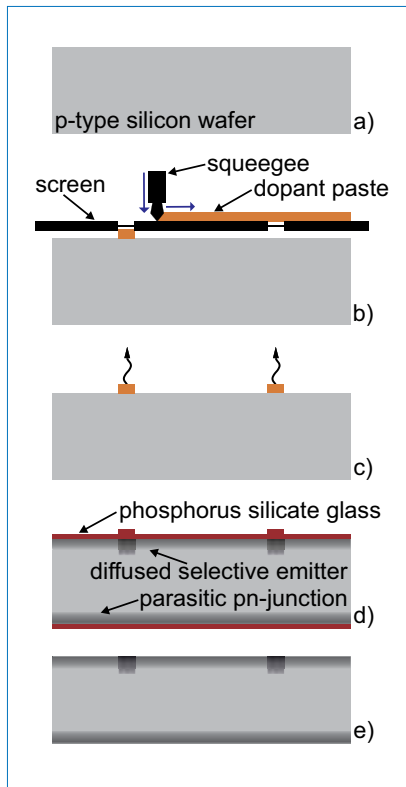


Figure 4. Process sequence for the selective emitter fabrication: a) wet chemical texturing and cleaning; b) screen-printing of phosphorus dopant paste; c) dopant paste drying; d) single-step diffusion of highly- and lowly-doped areas of the selective emitter; e) PSG removal.

onto the wafers. This represents a finite doping source, which is available during the entire high temperature process, including furnace stabilization time. Diffusion and gettering start immediately upon reaching the necessary temperature. In the case of POCl_3 emitters, a PSG layer of a typical thickness of 10nm has to form after the high temperature is stabilized and the POCl_3 gas flow has been activated. Phosphorus diffusion into the silicon, and hence gettering, cannot start without a PSG layer. During diffusion the phosphorus supply in the PSG is refilled from the gas phase, creating an infinite doping source and leading to a higher surface and peak phosphorus concentration (Fig. 3).

Consequently, the overall time during which gettering was possible, i.e. the effective gettering time, was about 42 minutes for the POCl_3 process, minus the time for PSG layer formation. For the screen-printed emitters, the effective gettering time, including temperature stabilization, was about 61 minutes – almost 50% longer. This difference in gettering and diffusion times is responsible for the increased gettering efficacy (Table 1) and deeper emitter profiles of the screen-printed emitters (Fig. 3). It should be noted that this increased effective gettering

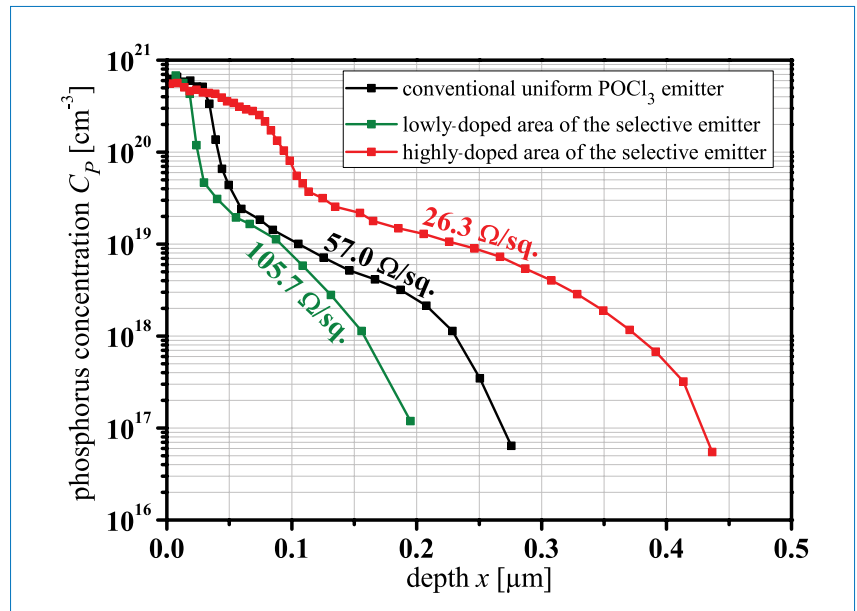


Figure 5. Electrically active phosphorus concentration C_p versus emitter depth (x). C_p was determined by ECV measurements. The selective emitter shows highly- and lowly-doped areas in contrast to the conventional uniform POCl_3 emitter.

time does not change the overall process duration, but is rather a consequence of the earlier availability of phosphorus.

Analysis of selective emitters

The samples for selective emitter characterization and subsequent solar cell analysis were processed on similar material as before, but with a thickness of 190 μm after texturing. The samples for the selective emitter analysis were prepared by a wet chemical acid texturing and a subsequent cleaning (Fig. 4a), which were followed by the emitter formation steps: screen-printing of a phosphorus dopant paste for the highly-doped area of the selective emitter on the wafer front side (Fig. 4b), drying of the dopant paste (Fig. 4c) followed by a uniform POCl_3 diffusion to form the lowly-doped area of the selective emitter and to drive the phosphorus from the paste into the wafer

(Fig. 4d). Additional reference emitters were processed with only the conventional batch POCl_3 diffusion on both wafer sides. After emitter diffusion, the PSG was removed (Fig. 4e) and the emitter was characterized by four-point-probe measurements to determine R_{sh} .

ECV measurements [18] were conducted to determine the spatially resolved phosphorus doping profiles of the selective emitters. In addition, R_{sh} values were also calculated using the corresponding doping profiles and results were compared with the values from the four-point-probe measurements.

The analysis of selective emitter structures revealed two well distinguished areas with respect to different doping, which was observed by four-point-probe and ECV measurements. The ECV measurements of C_p (Fig. 5) and the extracted values of R_{sh} certify the uniform POCl_3 reference emitter with a typical R_{sh} of 57.0 Ω/sq . For

Emitter type	V_{oc} [mV]	J_{sc} [mA/cm^2]	FF	η [%]
Selective	615.6 \pm 1.2	34.0 \pm 0.1	0.73 \pm 0.01	15.3 \pm 0.2
POCl_3	613.7 \pm 1.5	33.3 \pm 0.0	0.75 \pm 0.01	15.1 \pm 0.1

Table 2. Parameters of the I - V measurements on mc-Si solar cells with screen-printed selective emitters and uniform POCl_3 emitters as reference. Values listed are averaged over five cells and errors given are σ .

Emitter type	J_{01} [pA/cm^2]	J_{02} [nA/cm^2]	R_s [Ωcm^2]	R_p [$\text{k}\Omega\text{cm}^2$]
Selective	0.7 \pm 0.0	87.6 \pm 8.2	0.53 \pm 0.08	1.4 \pm 0.1
POCl_3	0.9 \pm 0.0	78.2 \pm 6.8	0.56 \pm 0.10	1.1 \pm 0.3

Table 3. Parameters of the I - V data fit by the two-diode-model of mc-Si solar cells with screen-printed selective emitters and uniform POCl_3 emitters as reference. Values listed are averaged over five cells and errors given are σ .

the selective emitter R_{sh} the highly-doped area is around $26.3\Omega/\text{sq.}$ and for the lowly-doped area around $105.7\Omega/\text{sq.}$ These measurements demonstrate the existence of the selective emitter structure, which is also visible in the different C_p profiles (Fig. 5). This claim is further supported by the four-point measurements of R_{sh} , where very similar values were measured.

Performance of selective emitter solar cells

All solar cells presented in this work were processed in a conventional industrial process line with wet chemical acid texturing, emitter formation, an $\text{SiN}_x\text{:H}$ deposition for the ARC [15] and metallization by screen-printing, which also creates an aluminium back-surface field (BSF). Solar cells with selective emitters were processed with the combination of screen-printing and POCl_3 diffusion as described earlier (Fig. 4). The reference solar cells were processed with uniform emitters using the conventional POCl_3 diffusion. Consequently, the solar cells were characterized by I - V , suns V_{oc} [19], spectral response (SR) and reflection measurements. The I - V data were fitted by the two-diode-model and the IQE was calculated from the SR and reflection data [20].

The I - V measurements (Table 2) certify the selective emitter solar cells with the highest average solar cell efficiencies (η), with values of up to 15.3%. The η gain of up to 0.2% absolute is realized with lower fill factors (FF) than the reference solar cells with uniform POCl_3 emitters. The slightly lower FF of the selective emitter solar cells are presumably caused by the solar cell process, which was not optimized for this emitter type. Nevertheless, values of the open circuit voltage (V_{oc}) and short circuit current density (J_{sc}) are also increased and show the highest values for the selective emitter solar cells.

In the following section the differences in the I - V curves are discussed using the two-diode-model parameters [21] (Table 3) and further solar cell characterization. From the I - V data, the parameters' diffusion current density (J_{01}), recombination current density (J_{02}), series resistance (R_s) and parallel resistance (R_p) are derived according to the two-diode-model and listed in Table 3. The R_p of all solar cells is sufficiently high to exclude shunting losses, which would result in a low FF. The solar cells with selective emitters have slightly lower R_s values due to the lower contact resistance using selective emitter structures as well as differences in individual co-firing parameters.

J_{02} is traditionally considered a measure for recombination in the space charge region and can be related to the density of recombination centres in solar cells. A more effective gettering should reduce the

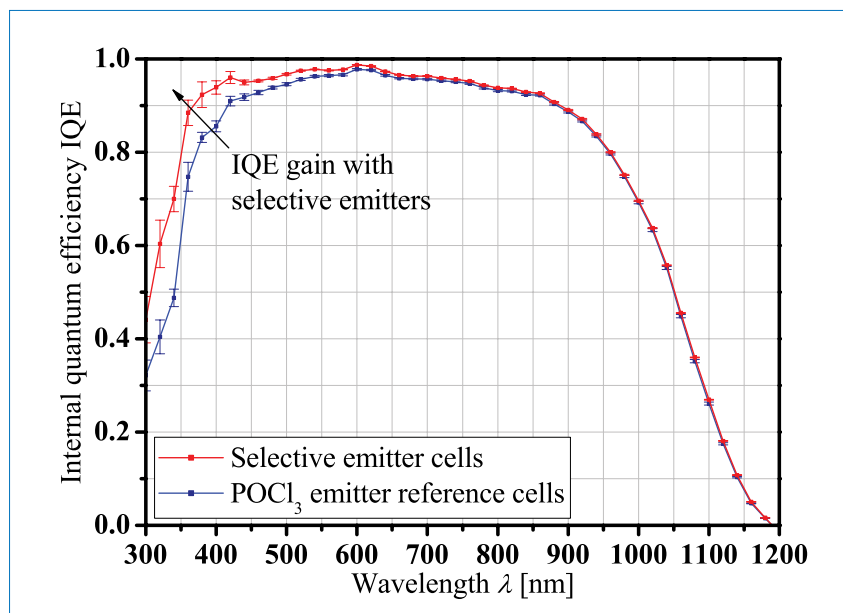


Figure 6. Internal quantum efficiencies (IQE) versus wavelength λ for selective emitter solar cells (red curve) and reference cells with uniform POCl_3 emitters (blue curve). All IQE data are averaged over five solar cells, error bars indicate σ .

Emitter type	Pseudo FF	Pseudo η [%]
Selective	0.80 ± 0.01	16.3 ± 0.2
POCl_3	0.79 ± 0.01	15.8 ± 0.2

Table 4. Parameters of the Suns V_{oc} measurements of mc-Si solar cells with screen-printed selective emitters and uniform POCl_3 emitters as reference. Values listed are averaged over five cells and errors given are σ .

SRH recombination, yielding to a low J_{02} . The lowest J_{02} values of $78.2\text{nA}/\text{cm}^2$ are observed by the reference solar cells due to stronger gettering caused by the higher doping of the reference POCl_3 emitter with R_{sh} of around $59\Omega/\text{sq.}$, compared to the selective emitters with R_{sh} of around $103\Omega/\text{sq.}$ for $\sim 92\%$ of the emitter area.

J_{01} mainly provides information about the recombination in the emitter and at the surface. The lower doping in the illuminated area of the selective emitter structure results in lower J_{01} values of $0.7\text{pA}/\text{cm}^2$ for these solar cells compared to the reference solar cells with J_{01} values of $0.9\text{pA}/\text{cm}^2$. The difference in J_{01} is directly responsible for the difference in V_{oc} , as confirmed by a simulation using the two-diode-model.

The differences in J_{01} are also monitored in the IQE curves (Fig. 6). The selective emitter solar cells feature a higher IQE than the uniform POCl_3 reference solar cells in the wavelength range from 300 to 600nm. This IQE gain is caused by reduced recombination in the selective emitter structure due to the lower emitter doping. Furthermore, the demonstrated IQE gain of the selective emitter solar cells increases the J_{sc} of these cells (Table 2). The IQE spectra of both solar cell types are nearly identical above 600nm.

Finally, the processed solar cells were characterized by Suns V_{oc} measurements

[19] to evaluate the potential of the developed selective emitter cells. These measurements neglect the influence of R_s in the solar cells and allow the calculation of a pseudo FF and pseudo η . The values determined are listed in Table 4. The pseudo FF of selective emitter solar cells shows a gain of 0.01% absolute over the reference solar cells. Considering the higher real FF (Table 2) of the reference solar cells, it is obvious that selective emitter solar cells can benefit greatly from further optimizations. The pseudo η of selective emitter solar cells show a gain of 0.5% absolute over the reference solar cells. Taking into account that R_s is neglected in this measurement, the largest optimization potential is in the geometrical design of the selective emitter grid lines and in the individually adjusted metallization using modified silver pastes.

Conclusion

The developed selective emitter concept allows an η gain of 0.2% absolute in processed mc-Si solar cells on an industrial scale and shows a possible η gain of 0.5% absolute. The gain originates from the front surface, as evidenced by the IQE gain in the UV region. J_{sc} and V_{oc} are also seen to increase.

ECV and four-point-probe measurements

prove the existence of selective emitter structures consisting of highly- and low-doped areas, which were processed in a single diffusion step by combining screen-printing of phosphorus dopant pastes and POCl_3 diffusion.

Most of the employed phosphorus dopant pastes are suitable for emitter formation and allow a high gettering efficacy. This is shown with single-sided uniform screen-printed emitters, which can getter mc-Si wafers more effectively than the reference double-sided uniform POCl_3 emitter.

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About the Author



Tobias Markus Pletzer is a postdoctoral research fellow and project manager in the photovoltaic group of the Institute of Semiconductor Electronics at RWTH Aachen University, Germany. He received his Ph.D. in 2010 in the Faculty of Electrical Engineering and Information Technology at the RWTH Aachen University and completed his study in computer engineering successfully with a diploma degree as a graduate engineer in 2004 at the University of Siegen, Germany. In his scientific work, he focuses on solar cell technologies, especially on new concepts and characterization techniques.

Enquiries

RWTH Aachen University
Sommerfeldstraße 24, D 52074 Aachen, Germany
Tel: +49 241 80 27892
Email: pletzer@iht.rwth-aachen.de