

**PHOSPHOROUS DOPING FROM APCVD DEPOSITED PSG**Felix Book<sup>1</sup>, Holger Knauss<sup>2</sup>, Carsten Demberger<sup>2</sup>, Florian Mutter<sup>1</sup>, Giso Hahn<sup>1</sup><sup>1</sup>University of Konstanz, Department of Physics, 78457 Konstanz, Germany<sup>2</sup>Gebr. Schmid GmbH, Robert-Bosch-Str. 32-36, 72250 Freudenstadt, Germany

Author for correspondence: felix.book@uni-konstanz.de, Tel.: +49 7531 88 3386

**ABSTRACT:** The phosphorous diffusion from atmospheric pressure chemical vapor deposition (APCVD) deposited phosphorus silicate glass (PSG) promises reduced process costs compared to the standard  $\text{POCl}_3$  diffusion process, since no  $\text{POCl}_3$  gas flow is necessary during the diffusion process. Therefore, much smaller or no spacing between the wafers is necessary and the throughput of the diffusion process can be significantly increased. Furthermore, it allows a structuring of the doping source prior to diffusion. We investigate the effect of basic process parameters concerning the deposition of the PSG and the capping layer on sheet resistance and uniformity. On standard aluminum back surface field (Al-BSF) solar cells, cell efficiencies of up to 19.6 % were achieved. In a high temperature co-diffusion process with reduced P content, the APCVD-PSG emitter passivated with fired PECVD- $\text{SiN}_x$  features low  $j_{0E}$  of 100  $\text{fA}/\text{cm}^2$  at 50  $\Omega/\text{sq}$ . This results in a high cell  $V_{oc}$  of 639 mV while leading to a  $j_{sc}$  loss due to increased Auger recombination in the deep emitter profile. This loss can partly be compensated by a selective emitter etch-back. It would not occur, when the doping profile is located at the rear side of a bifacial or back contact solar cell as a BSF.

**Keywords:** Diffusion, Doping, CVD Based Deposition

**1 INTRODUCTION**

The electrical quality of the n-type emitter plays a major role for the efficiency of today's industrial type solar cells. It is typically formed by a  $\text{POCl}_3$  diffusion process (see, e.g., [1]) which is well-established and optimized, however still a topic of current research. The PSG is grown during the high temperature diffusion from the  $\text{POCl}_3$  gas phase. It is therefore deposited on all sides of the wafer, and requires an edge isolation later in the process to prevent shunting by the rear side metallization.

The APCVD technology represents an alternative way to deposit the PSG as dopant source before the actual diffusion process [2,3]. This potentially also allows structuring the PSG for selective doping. The diffusion can be carried out either in an inline furnace [3] or, like in this work, in a tube furnace as used for  $\text{POCl}_3$  diffusion. Since no homogenous gas flow is required between the wafers, a smaller or no spacing between the wafers could be used. This can drastically increase the throughput and reduce the cost of the diffusion process. Another advantage is the one-sided deposition, which can make edge isolation obsolete, if the PSG wrap-around is removed by a single side HF clean before the diffusion.

A common application of P surface doping is a front or back surface field (FSF/BSF) for high efficiency n-type solar cells. Most of these cell concepts feature a B emitter, which can be formed in a co-diffusion process with P, but requires a higher diffusion temperature due to the lower diffusion constant of B compared to P. This results in a very low n-type sheet resistance, if an infinite P source is used. The sheet resistance therefore has to be controlled by the P content in the PSG or an additional diffusion barrier.

In this work we determine the main effects of relevant process parameters on the sheet resistance and uniformity. Furthermore, we investigate the possibility of controlling the sheet resistance of a high temperature diffusion (900 °C) by reducing the P content in the PSG. The electrical quality of the doping profiles is characterized in terms of emitter saturation current density  $j_{0E}$  and IV parameters of standard p-type Al-BSF solar cells.

**2 EXPERIMENTAL**

The solar cells presented in this work are processed on 2  $\Omega\text{cm}$  p-type Cz-Si according to the well-known process flow for industrial p-type Al-BSF solar cells:

- Alkaline texture
- PSG deposition (except  $\text{POCl}_3$  reference)
- Diffusion
- PSG removal / edge isolation
- $\text{SiN}_x\text{:H}$  deposition
- Screen printing
- Co-firing

The PSG was deposited at the University of Konstanz in a lab-type APCVD system (Schmid 5K6) with single lane ceramic roller wafer transport. The system features two chambers to deposit PSG and an undoped  $\text{SiO}_x$  capping layer in one process step. The first chamber can also be used to deposit undoped  $\text{SiO}_x$ , BSG or  $\text{AlO}_x$ . When process gas flows are varied, the total gas flow through the injector is kept constant by adapting the  $\text{N}_2$  dilution. The P weight percentage of the PSG layer (P [%wt.]) is calculated from the gas flows and can be set as an input process parameter.

The diffusion was carried out in an oxidation tube furnace or a  $\text{POCl}_3$  tube furnace. For solar cells with a selective emitter, an etch-back process was added after the diffusion, which consists of printing a mask, etch-back and mask removal [4].

An HF clean and, if applied, a single side etching of the rear side was carried out before  $\text{SiN}_x\text{:H}$  deposition. The metallization was performed by screen printing of industrially available Ag and Al paste with subsequent co-firing.

For some emitter profiles, symmetrical samples were processed to determine  $j_{0E}$  and the doping profile. These samples were processed on chemically polished 200  $\Omega\text{cm}$  p-type FZ-Si wafers. The effective lifetime was measured with a Sinton WCT-120 tester, the fit of  $j_{0E}$  was performed at  $\text{MCD} = 3 \cdot 10^{15} \text{ cm}^{-3}$ .

### 3 RESULTS

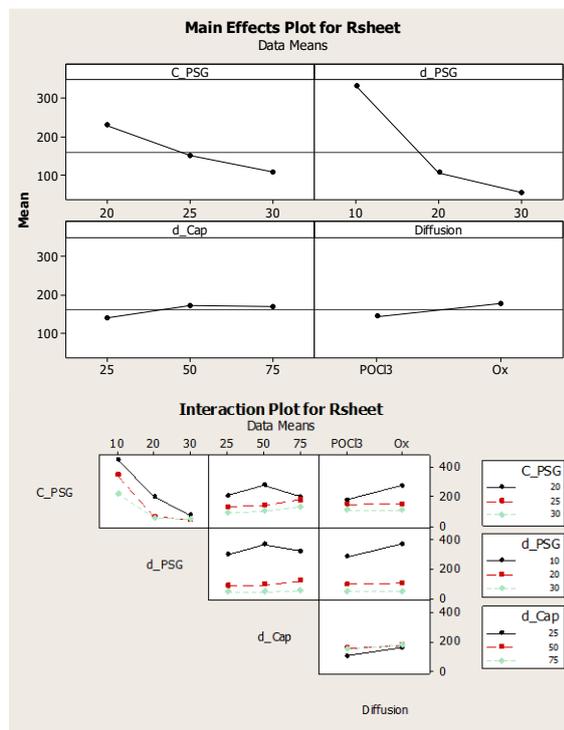
#### 3.1 Homogeneous emitter for p-type solar cells

If the APCVD-PSG is used instead of a  $\text{POCl}_3$  PSG for the formation of an emitter for standard Al-BSF or PERC solar cells, no additional boundary conditions concerning the diffusion process have to be considered. It was observed in previous experiments that for the APCVD-PSG a capping layer of undoped  $\text{SiO}_x$  is necessary to improve the process stability. As a starting point, the standard  $\text{POCl}_3$  diffusion program without  $\text{POCl}_3$  flow and a drive-in temperature of  $840^\circ\text{C}$  for 45 min was chosen. For a  $\text{POCl}_3$  emitter, this program typically results in a sheet resistance of  $50\text{--}55\ \Omega/\text{sq}$ .

A full factorial design of experiment (DoE) was performed to investigate the effect of the following factors on the emitter sheet resistance and uniformity:

- PSG P concentration ( $C_{\text{PSG}} = 20/25/30\ \%\text{wt.}$ )
- PSG thickness ( $d_{\text{PSG}} = 10/20/30\ \text{nm}$ )
- Capping thickness ( $d_{\text{Cap}} = 25/50/75\ \text{nm}$ )
- Diffusion in  $\text{POCl}_3$  or oxidation tube furnace (effect of P from the tube wall)

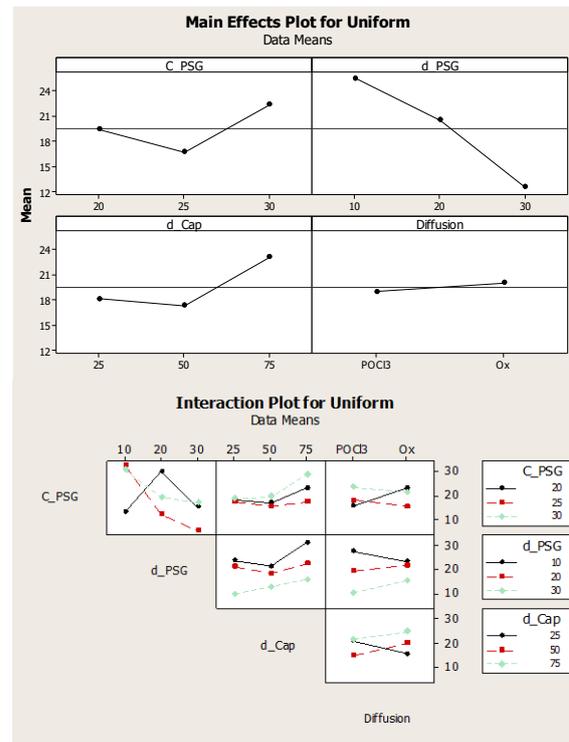
The main effects and interaction of the factors on  $R_{\text{sheet}}$  and uniformity are presented in Fig. 1 and 2. The different PSG and capping layers result in a wide range of  $R_{\text{sheet}}$  ( $41\text{--}650\ \Omega/\text{sq}$ ) and a uniformity of  $3\text{--}64\ \%$ . Each data point represents the mean value of all samples with the indicated factor combination.



**Figure 1:** Main effects and interactions of the investigated factors on  $R_{\text{sheet}}$  of the P diffusion from APCVD-PSG.

A strong effect of  $C_{\text{PSG}}$  can be observed, especially for the thin PSG layers.  $R_{\text{sheet}}$  values below  $80\ \Omega/\text{sq}$  could only be achieved with  $d_{\text{PSG}}$  of at least  $20\ \text{nm}$ . On these samples, the uniformity improves with increasing  $d_{\text{PSG}}$ . A thicker capping layer leads to an increase of  $R_{\text{sheet}}$ , which

can be attributed to a diffusion of P in the capping layer. In terms of  $R_{\text{sheet}}$  uniformity, a thick PSG layer with a thin to medium capping layer seems desirable. This combination leads to an  $R_{\text{sheet}}$  of  $70\ \Omega/\text{sq}$  for the lowest  $C_{\text{PSG}}$  of  $20\ \%\text{wt.}$ . Higher  $C_{\text{PSG}}$  result in  $R_{\text{sheet}}$  below the typical range of Al-BSF solar cell emitters. The diffusion of P from the  $\text{POCl}_3$  furnace tube wall shows a small effect, which only becomes relevant for thin  $d_{\text{PSG}}$  and  $d_{\text{Cap}}$ .



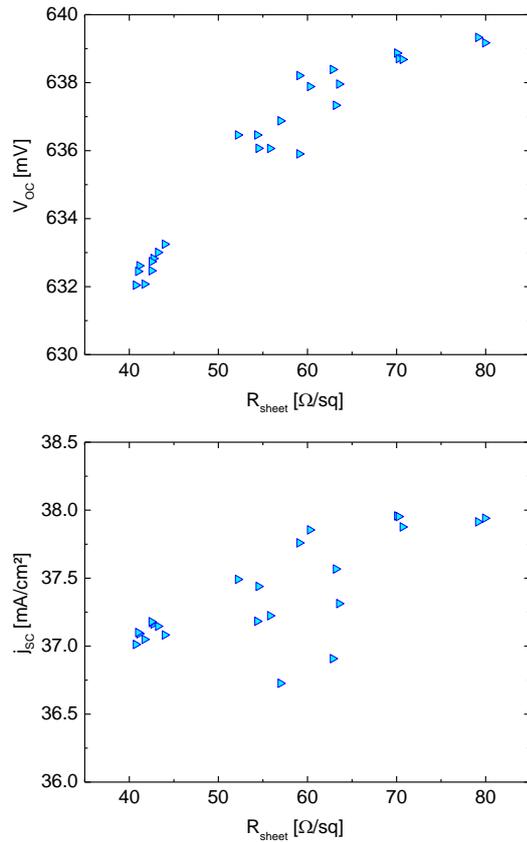
**Figure 2:** Main effects and interactions of the investigated factors on  $R_{\text{sheet}}$  uniformity of the P diffusion from APCVD-PSG.

The samples with a sheet resistance below  $80\ \Omega/\text{sq}$  were used to process Al-BSF solar cells without edge isolation. This results in a shunt resistance of  $200\text{--}1400\ \Omega/\text{sq}$  and shows, that despite the one-sided deposition, at least a single side HF-Dip after the PSG and capping deposition is necessary. However, it has almost no effect on  $V_{\text{oc}}$  and  $j_{\text{sc}}$ , which are shown in Figure 3. The expected increase in both values with increasing  $R_{\text{sheet}}$  can be observed. In the  $50\text{--}65\ \Omega/\text{sq}$  range, some solar cells show a reduced  $j_{\text{sc}}$ . These cells also exhibit a poor  $R_{\text{sheet}}$  uniformity and can be assigned to the PSG combination  $C_{\text{PSG}} = 30\ \%\text{wt.}$  and  $d_{\text{PSG}} = 20\ \text{nm}$ .

On selected solar cells, an additional edge isolation with a dicing saw was carried out. This results in an efficiency of  $19.6\ \%$  for the best cell of which the IV data is shown in Tab. I.

**Table I:** IV data of the best Al-BSF solar cell from the APCVD-PSG and  $\text{POCl}_3$  emitter group.

PSG	$V_{\text{oc}}$ [mV]	$j_{\text{sc}}$ [ $\text{mA}/\text{cm}^2$ ]	FF [%]	$\text{Eta}$ [%]
APCVD	640	38.1	80.4	19.6
$\text{POCl}_3$	639	38.3	79.7	19.5



**Figure 3:**  $V_{OC}$  and  $j_{SC}$  vs.  $R_{sheet}$  of 6" standard p-type solar cells with an emitter diffused from various APCVD layers of the DoE shown in Figure 1.

The high fillfactor of this cell with an  $R_{sheet}$  of 79  $\Omega/sq$  demonstrates, that the APCVD-PSG emitter can be well contacted with conventional screen printing paste. The reference solar cells with a 65  $\Omega/sq$   $POCl_3$  emitter were processed equally but with edge isolation by single side etching after the diffusion. The high and similar cell efficiency compared to the well optimized  $POCl_3$  emitter proves, that the APCVD-PSG allows for at least equally high emitter quality. Since only one cell per parameter set was processed, this experiment cannot be regarded as an optimization in terms of solar cell efficiency. This will be performed in an upcoming experiment with selected deposition parameter sets, that have resulted in good  $R_{sheet}$  uniformity.

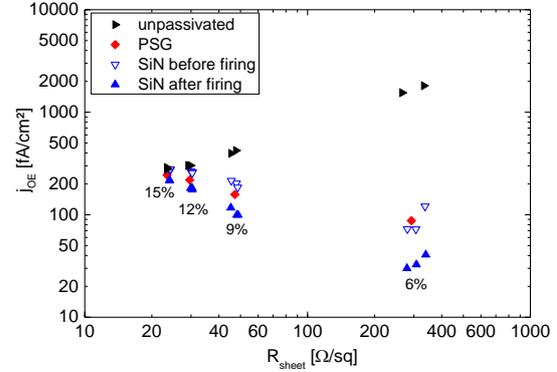
### 3.2 High temperature diffusion

For this study, a 900 °C diffusion with high temperature plateau of 45 min was chosen. This temperature profile is sufficient to obtain an  $R_{sheet}$  below 100  $\Omega/sq$  for a B diffusion from APCVD BSG. In order to achieve sufficiently high  $R_{sheet}$ , the P content in the PSG was reduced and varied between 6-15 %wt. in a 50 nm PSG layer capped with 50 nm of undoped  $SiO_x$ , that was deposited in the second APCVD chamber.

$j_{OE}$  was measured after diffusion with the PSG as a passivation, after removing the PSG (unpassivated) and with a 75 nm  $SiN_x$  passivation before and after firing (see Figure 4).

The unpassivated samples show an increase in  $j_{OE}$  for high  $R_{sheet}$  emitters due to a reduced field effect passivation. The PSG passivated samples feature  $j_{OE}$  values below the  $SiN_x$  passivated ones before firing. However,

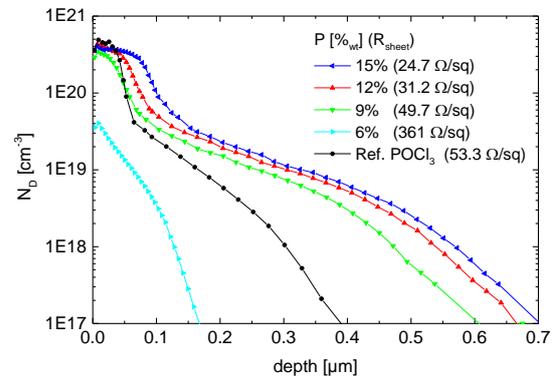
the PSG is hygroscopic and dissolves to phosphoric acid in air, which impedes its application for solar cell passivation. If the time between deposition and diffusion exceeds several hours, the wafers therefore should be stored in a dry cabinet.



**Figure 4:**  $j_{OE}$  of emitters diffused from APCVD-PSG with varied P content. Data shown for unpassivated surfaces and passivation with the PSG or  $SiN_x$  before and after firing.

The APCVD-PSG emitter passivated with a fired  $SiN_x$  shows the lowest  $j_{OE}$  values. For 9 %wt. PSG, 100 fA/cm<sup>2</sup> are achieved at an  $R_{sheet}$  of 50  $\Omega/sq$ . At the same  $R_{sheet}$ , a  $POCl_3$  emitter typically features a value of approx. 220 fA/cm<sup>2</sup> [5].

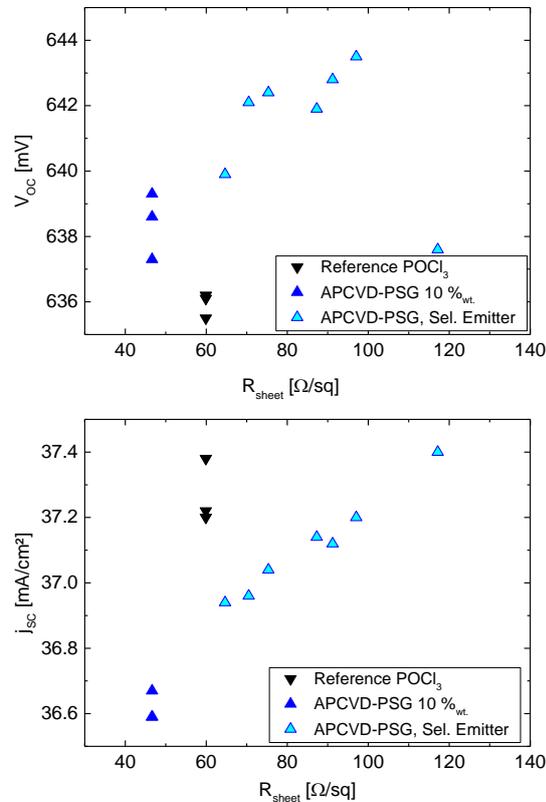
Doping profiles measured by ECV are shown in Figure 5. The high temperature diffusion leads to a very deep profile. For a reduced P content in the PSG, the profile is "shifted" towards the surface, leading to a shallow kink with very similar surface P concentration for  $P > 9$  %wt.. At 6 %wt. the kink disappears and surface concentration drops, resulting in a drastic increase in  $R_{sheet}$ . In direct comparison of the 50 Ohm/sq emitter with a reference  $POCl_3$  emitter profile of similar sheet resistance, a deeper profile with lower doping concentration (below the solubility limit) within the kink is observed for the APCVD-PSG, resulting in reduced recombination losses and  $j_{OE}$ .



**Figure 5:** Doping profiles from ECV measurements of emitter samples shown in Figure 4.

The emitter from the high temperature diffusion was further investigated by processing Al-BSF solar cells from 2  $\Omega cm$  6" p-type Cz-Si. The optimal P content that allows a good contact with screen printed Ag paste was determined in an experiment not shown here to 10 %wt.. On some solar cells with an APCVD-PSG emitter, an

additional selective emitter etch-back with a variation of the etch depth was applied. All solar cells were processed in parallel,  $V_{oc}$  and  $j_{sc}$  are shown in Figure 6.



**Figure 6:**  $V_{oc}$  and  $j_{sc}$  of 6" standard p-type solar cells with a reference  $POCl_3$  emitter and emitter diffused from APCVD PSG and selectively etched back to various  $R_{sheet}$ .

In good agreement with the  $j_{0E}$  results, the homogeneous APCVD-PSG emitter features higher  $V_{oc}$  than the reference  $POCl_3$  emitter, even with a lower  $R_{sheet}$ . However, a significant loss in  $j_{sc}$  is observed. In combination with the higher contact resistance of the APCVD-PSG emitter solar cells, this leads to an average loss in cell efficiency of 0.4 % and a highest cell efficiency of 18.7 % vs. 19.1 % for the reference cells. The generally lower level compared the solar cells presented in section 3.1. is due to a higher area fraction of the front side metallization.

The selective etch-back of the APCVD-PSG emitter leads to an increase in  $V_{oc}$  and  $j_{sc}$ . The latter rises to the level of the reference cells for an etch-back to approx. 100-120  $\Omega/sq$ . The increase in  $R_{sheet}$  reduces the fillfactor (not shown here) of the selective emitter solar cells. The highest cell efficiency of 18.9 % was achieved at 75  $\Omega/sq$ .

The  $R_{sheet}$  at which the kink is completely removed can be calculated from ECV profiles to approx. 80  $\Omega/sq$ . At an etch-back to this value, the losses resulting from the reduced blue response are still higher than for the reference cells. This indicates, that a large contribution of the emitter recombination arises from the deep tail of the profile. In contrast, the low surface P concentration leads to comparably small losses in the kink. The efficiency gain, that can be achieved by selectively etching the emitter surface, is therefore smaller than for typical  $POCl_3$  emitters with high surface P concentration.

#### 4 SUMMARY

The similarly high cell efficiency of 19.6/19.5 % indicates, that the electrical quality of the APCVD-PSG emitter can compete with the well-established  $POCl_3$  emitter while promising low process costs, improved process control and compatibility to advanced cell concepts.

If  $R_{sheet}$  of the high temperature co-diffusion process is controlled by the P content in the PSG, the deep doping profile leads to significant  $j_{sc}$  loss when located at the illuminated side of the cell. However, this is not relevant for the application as a BSF on n-type solar cells, which is therefore the preferred cell structure for co-diffusion from APCVD deposited doping sources on both sides of the solar cell. By applying an additional selective etch-back, the  $j_{sc}$  loss could be reduced, but the loss in efficiency compared to the reference  $POCl_3$  emitter solar cells was not fully compensated.

#### 6 ACKNOWLEDGEMENTS

Part of this work was funded by the German BMWi (0325632, 0325581). The content is the responsibility of the authors.

#### 7 REFERENCES

- [1] G.S. May, S.M. Sze, Fundamentals of Semiconductor Fabrication (Wiley-VCH, 2004).
- [2] A. Slaoui, B. Hartiti, J.C. Muller, R. Stuck, M. Lohmarti, P. Siffert, in 22nd IEEE Photovolt. Spec. Conf. (Las Vegas, USA, 1991) 445-449.
- [3] K.O. Davis, K. Jiang, C. Demberger, H. Zunft, H. Haverkamp, D. Habermann, W.V. Schoenfeld, Phys. Stat. Sol. RRL **7** (2013) 319.
- [4] H. Haverkamp, A. Dastgheib-Shirazi, B. Raabe, F. Book, G. Hahn, in 33rd IEEE Photovolt. Spec. Conf. (San Diego, 2008), 430-433.
- [5] F. Book, Hocheffiziente Industriesolarzellen mit selektiver Oberflächendotierung, Dissertation, University of Konstanz, 2014.