# SUITABILITY OF POCL<sub>3</sub> DIFFUSION PROCESSES WITH IN-SITU OXIDATION FOR FORMING LASER-DOPED SELECTIVE EMITTERS WITH LOW CARRIER RECOMBINATION

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ABSTRACT: Laser-doped selective emitters feature the advantage of more effective shielding of minority charge carriers from the metal contacts while allowing for low emitter saturation current density  $j_{0e}$  in the photoactive area. The formation of emitters by diffusion processes using phosphorus oxychloride (POCl<sub>3</sub>) with incorporated in-situ oxidation gains more and more attention as it allows for low  $j_{0e}$  below 90 fA/cm<sup>2</sup> on textured surface with silicon nitride passivation in industrial cycle times. Hence, the combination of both—POCl<sub>3</sub> diffusion with in-situ oxidation and laser doping—is very interesting. We examine four different POCl<sub>3</sub> diffusions with in-situ oxidation and one reference POCl<sub>3</sub> diffusion without in-situ oxidation in terms of their suitability for selective emitter laser doping. Detailed characterizations of the grown layers on the silicon surface are performed after diffusion with respect to the individual layer thicknesses of the phosphosilicate glass (PSG) and the intermediate silicon dioxide (SiO<sub>2</sub>) layer as well as the stacks' total phosphorus doses. The as-diffused depth-dependent charge carrier concentration profiles show that a second PSG deposition step attached after drive-in to the diffusion processes hardly impacts their course. We find that POCl<sub>3</sub> diffusions with in-situ oxidation—especially those with second deposition step—allow for effective laser doping. Thereby, the intermediate SiO<sub>2</sub> layer thickness plays a key role: the thicker the layer is the less phosphorus can be incorporated additionally from the PSG layer into the silicon.

Keywords: in-situ oxidation, POCl3 diffusion, selective emitter, laser doping, phosphosilicate glass

## 1 INTRODUCTION

Tube furnace diffusion processes using phosphorus oxychloride (POCl<sub>3</sub>) as liquid dopant precursor are the dominating emitter formation technology for p-type silicon solar cells [1]. Improving POCl<sub>3</sub> diffusion processes and the resulting emitter doping profiles is essential for further increasing the energy conversion efficiency of silicon solar cells. The reduction of emitter recombination, enabled by a fast progress in front contact screen printing paste properties, has been of major interest in the past few years.

An approach to realize less emitter recombination is the reduction of the surface doping concentration by implementing an in-situ oxidation into the POCl<sub>3</sub> diffusion process [2–9]. When applied to passivated emitter and rear solar cells (PERC) [10], energy conversion efficiencies beyond 21% are reported [6,11,12]. As the charge carrier recombination at the metal contacts is high for that kind of doping profiles with low surface doping concentration [13], one option for its decrease is the selective emitter approach.

Recently, selective emitters came back into focus for PERC solar cells targeting the 22% efficiency regime and above [6,11,12,14,15]. The selective emitter can be formed by, e.g., local laser doping out of the phosphosilicate glass (PSG) layer [16]. Correctly, POCl<sub>3</sub> diffusions form a stack layer consisting of a PSG layer and a silicon dioxide (SiO<sub>2</sub>) layer: the SiO<sub>2</sub> layer separates the PSG layer from the silicon surface [9,8,17,18]. Hereby, the SiO<sub>2</sub> layer features a much lower phosphorus concentration than the phosphorus-rich PSG layer.

For laser doping, sufficiently high phosphorus content within this PSG/SiO<sub>2</sub> stack layer is necessary. Hence, this paper investigates the combination of tube furnace POCl<sub>3</sub> diffusion with in-situ oxidation and the formation of selective emitters by laser doping out of the grown PSG/SiO<sub>2</sub> stack layer.

## 2 APPROACH

The approach pursued in this paper to ensure sufficient phosphorus content in the PSG/SiO<sub>2</sub> stack layer for effective laser doping is the implementation of a second deposition step with active nitrogen ( $N_2$ ) gas flow through the POCl<sub>3</sub> bubbler (i.e. active  $N_2$ -POCl<sub>3</sub> flow) at the end of the diffusion process.

We investigate two pairs of POCl<sub>3</sub> diffusion processes that feature an in-situ oxidation and that are performed with and without a second deposition step, respectively. POCl<sub>3</sub> diffusion without in-situ oxidation but second deposition step serves as reference. Table I summarizes the examined POCl<sub>3</sub> diffusion processes. Process details and the labeling of the processes are discussed in detail in section 2.1.

The schematic experiment plan in Fig. 1 depicts the three groups of test samples fabricated and the different characterization approaches applied in this work. Full-square p-type Czochralski-grown silicon (Cz-Si) wafers with an edge length of 156 mm serve as starting material. After either saw damage etching or alkaline texturing, the five different tube furnace POCl<sub>3</sub> diffusion processes form the emitter and the PSG/SiO<sub>2</sub> stack layer.

The different POCl<sub>3</sub> diffusion processes, the applied

**Table I:** Summary of the five investigated POCl<sub>3</sub> diffusion processes. The emitter dark saturation current densities  $j_{0e}$ , determined on alkaline textured surface after passivation by a conventional SiN<sub>x</sub> layer and firing, are taken from Refs. [4,11,13]. (n.d.: not determined)

POCl <sub>3</sub>	1 <sup>st</sup> dep.	drive-in	2 <sup>nd</sup> dep.	j0e
process	$(N_2 POCl_3)$	$(O_2 \text{ share})$		(fA/
				cm <sup>2</sup> )
Ref 2 <sup>nd</sup> dep	med	< 4%	yes	42
in-situ thin	low	100%	-	73
in-situ thin 2 <sup>nd</sup> dep	low	100%	yes	n.d.
in-situ thick	high	100%	-	85
in-situ thick 2nd dep	high	100%	yes	n.d.

Group 1	Group 2	Group 3		
p-Typ Cz-Si, 156 mm edge length				
Saw damage etch	Alkaline texturing			
POCl <sub>3</sub> diffusion variation				
Wafer cutting	PSG/SiO <sub>2</sub> etch	Reflection meas.		
Ellipsometry	ICP-OES	Laser doping		
Selective etching	Four point probe measurements			
Ellipsometry	ECV	)		

**Figure 1:** Experiment plan for investigating laser doping out of the SiO<sub>2</sub>/PSG stack layer formed by different POCl<sub>3</sub> diffusion processes. (ECV: electrochemical capacitance-voltage measurements; ICP-OES: inductively coupled plasma optical emission spectrometry).

further process steps, and the utilized characterization methods are being discussed in the following sections.

## 2.1 POCl<sub>3</sub> diffusion processes

We target at low content of inactive phosphorus at the surface in the as-diffused emitter and thus, low charge carrier recombination in the homogeneously-doped area. For this purpose, we select the five POCl<sub>3</sub> diffusion processes summarized in Table I. For three of the five processes, we previously characterized their emitter dark saturation current density  $j_{0e}$  in Refs. [4,11,13]. The  $j_{0e}$  values on alkaline textured surface passivated by a conventional silicon nitride (SiN<sub>x</sub>) passivation layer that is formed by plasma-enhanced chemical vapor deposition are found to be between 42 fA/cm<sup>2</sup>  $\leq j_{0e} \leq 85$  fA/cm<sup>2</sup> after simulated contact firing (see also Table I, rightmost column).

Table I also contains characteristic process parameters for the examined POCl3 diffusion processes. We label the processes with respect to the used in-situ oxidation and the thickness of the resulting total PSG/SiO<sub>2</sub> stack layer. The reference process "Ref 2nd dep" has no in-situ oxidation as the oxygen (O2) share in the gas atmosphere during drive-in is below 4% but features a second PSG deposition with active N2-POCl3 flow after the drive-in. For the other four processes, the drive-in with 100% O2 share is similar. Corresponding to the name convention, the processes "in-situ thin" and "in-situ thick" feature either a thin or a thick PSG/SiO2 stack layer after diffusion, respectively (see section 3.1). The N<sub>2</sub>-POCl<sub>3</sub> and O<sub>2</sub> gas flows during the first deposition are a factor two to three lower for the process "in-situ thin" than for the process "in-situ thick". The suffix "2<sup>nd</sup> dep" indicates that a second PSG deposition step with active N<sub>2</sub>-POCl<sub>3</sub> flow follows the drive-in step. The two process variations with the same second deposition step as used for the reference process are accordingly named "in-situ thin 2<sup>nd</sup> dep" and "in-situ thick 2<sup>nd</sup> dep".

2.2 Determination of layer thicknesses by means of selective etching

In order to extract the individual thicknesses of the PSG and SiO<sub>2</sub> layers formed during the five POCl<sub>3</sub> diffusions, the wafers with saw damage etched surface of group 1 in Fig. 1 are cut into 36 pieces each after diffusion. Ellipsometry measurements are performed before and after stepwise etching the stack layers in 0.1 wt% hydrofluoric acid (HF) solution [9]. As the etching rate is dependent on the phosphorus concentration within the respective layer [8,9], the thickness of each layer can be extracted. The detailed procedure is described in Ref. [9].

Applying this procedure, we examine the individual thicknesses of the PSG and  $SiO_2$  layers of the five diffusion processes and the impact of a second deposition step on these layer thicknesses for diffusion processes with insitu oxidation.

2.3 Determination of phosphorus doses and charge carrier concentration profiles

We use the inductively coupled plasma optical emission spectrometry (ICP-OES) [19] to determine the phosphorus dose within the total  $PSG/SiO_2$  stack layer on alkaline textured surfaces. Therefore, the stack layers of the wafers of group 2 in Fig. 1 are etched in diluted HF and the solution is analyzed with respect to its phosphorus concentration.

After the PSG/SiO<sub>2</sub> stack layer has been removed, the samples are further characterized with respect to their doping properties. Electrochemical capacitance-voltage measurements (ECV) [20] yield the charge carrier concentration profiles. The profiles are scaled to match the sheet resistances  $R_{\rm sh}$  [13,21], which are locally determined by four point probe (4pp) measurements around the ECV spots.

## 2.4 Suitability for laser doping

To examine the suitability of the POCl<sub>3</sub> diffusion processes with respect to laser doping, we use a pulsed ultraviolet (UV) ns-laser with a wavelength  $\lambda_{\text{laser}} = 355 \text{ nm}$  [22].

Subsequent to reflection measurements of the PSG/SiO<sub>2</sub> stack layer on textured surface for the wafers of group 3 in Fig. 1, we prepare 2 x 2 cm<sup>2</sup>-large test fields as shown in Fig. 2 applying four different pulse energies  $E_{p,set} = \{62 \ \mu J; 74 \ \mu J; 90 \ \mu J; 120 \ \mu J\}$  at constant pulse-to-pulse and line-to-line distances  $d_{pulse} = 15 \ \mu m$  and  $d_{line} = 25 \ \mu m$ , respectively. Then, the evolution of  $R_{sh}$  for the applied laser processes for the different POCl<sub>3</sub> diffusions is determined by 4pp measurements.

## 3 RESULTS

3.1 PSG/SiO<sub>2</sub> layer thicknesses after POCl<sub>3</sub> diffusion

Fig. 3 shows the individual thicknesses of the PSG and SiO<sub>2</sub> layers  $d_{PSG}$  and  $d_{SiO_2}$ , respectively, for the five diffusion processes investigated in this work.

For the reference process "Ref 2<sup>nd</sup> dep", the PSG layer with  $d_{PSG} = (24 \pm 2)$  nm is about four times thicker than the SiO<sub>2</sub> layer with  $d_{SiO2} = (6 \pm 1)$  nm. Chen et al. [18] reported a nearly constant SiO<sub>2</sub> layer thickness  $d_{SiO2} \approx$ 6 nm for different deposition times and POCl<sub>3</sub> flow rates for common diffusion processes without in-situ oxidation, while they found the total stack layer thicknesses *d* 



**Figure 2:** Image scan of an alkaline textured Cz-Si wafer with  $PSG/SiO_2$  stack layer after laser doping. The visible square fields with a size of 2 x 2 cm<sup>2</sup> were processed with different laser parameters.



**Figure 3:** Individual layer thicknesses  $d_{PSG}$  and  $d_{SiO2}$  of the PSG and the SiO<sub>2</sub> layer, respectively, formed on the silicon surface during the five POCl<sub>3</sub> tube furnace diffusions from Table I. The individual thicknesses are extracted by the selective etching procedure described in Ref. [9].

to be between 10 nm < d < 40 nm. Hence, the layer thicknesses found for our reference process without in-situ oxidation "Ref 2<sup>nd</sup> dep" are in accordance with those found by Chen et al., although Chen et al. investigated processes without second PSG deposition.

In contrast,  $d_{SiO2}$  for the process "in-situ thin" in Fig. 3 is significantly larger with  $d_{SiO2} = (19 \pm 2)$  nm. This thicker intermediate SiO<sub>2</sub> layer is formed by the insitu oxidation [9]. During in-situ oxidation, the oxygen from the atmosphere diffuses through the PSG and SiO<sub>2</sub> layers and reacts with the silicon at the surface to form SiO<sub>2</sub>.

Attaching a second PSG deposition for process "insitu thin 2<sup>nd</sup> dep", the second deposition clearly leads to an increase in  $d_{PSG}$  to  $d_{PSG} = (23 \pm 1)$  nm, while  $d_{SiO2}$  is reduced to  $d_{SiO2} = (12 \pm 2)$  nm. This result (i.e. the increase in  $d_{PSG}$  while  $d_{SiO2}$  is decreased) is in accordance with results we found in Ref. [9], where we investigated the influence of a second PSG deposition step on the PSG/SiO<sub>2</sub> stack layer for a diffusion process without insitu oxidation. We propose that the reduction in  $d_{SiO2}$ results from the diffusion of phosphorus from the PSG layer to the PSG/SiO<sub>2</sub> interface, where they react with SiO<sub>2</sub> to form additional PSG [18]. The PSG layer thickness for process "in-situ thin 2<sup>nd</sup> dep" is comparable to that of the reference process.

Processes "in-situ thick" and "in-situ thick 2<sup>nd</sup> dep" feature significantly higher total layer thicknesses *d* than the other processes as the N<sub>2</sub>-POCl<sub>3</sub> and O<sub>2</sub> gas flows during first PSG deposition are two to three times higher; see Table I. The strong first PSG deposition for "in-situ thick" results in a total thickness of  $d \approx 70$  nm, while the weak first PSG deposition for the reference process and both "in-situ thin"-processes results in  $d \approx 30$  nm. For diffusion "in-situ thick",  $d_{SiO2} = (50 \pm 2)$  nm is more than twice as large as  $d_{PSG} = (23 \pm 2)$  nm. The attached second PSG deposition for process "in-situ thick 2<sup>nd</sup> dep" hardly affects these layer thicknesses:  $d_{SiO2} = (50 \pm 2)$  nm and  $d_{PSG} =$  $(27 \pm 2)$  nm. Only  $d_{PSG}$  is about 3 nm larger.

In contrast to the process "in-situ thin  $2^{nd}$  dep",  $d_{SiO2}$  is not decreased for process "in-situ thick  $2^{nd}$  dep" by adding the second PSG deposition step. As the intermediate SiO<sub>2</sub> layer is more than twice as thick for "in-situ



**Figure 4:** Total phosphorus dose within the PSG/SiO<sub>2</sub> stack layer for POCl<sub>3</sub> diffusion processes with and without second deposition step, determined by ICP-OES.

thick", it seems that there is either a critical  $SiO_2$  layer thickness, which represses the increase of  $d_{PSG}$  by a second deposition step, or a critical PSG layer thickness, from which point the PSG layer growth occurs slower.

Also remarkable is the fact that for all processes that feature the (same) second deposition step, similar  $d_{PSG}$  values between 23 nm  $\leq d_{PSG} < 27$  nm are found, irrespective on the gas flows used during first deposition and drive-in. On the other hand,  $d_{SiO2}$  varies significantly between 6 nm  $\leq d_{SiO2} < 50$  nm.

# 3.2 Phosphorus dose of the PSG/SiO2 stack layers

The phosphorus dose within the total PSG/SiO<sub>2</sub> stack layers on textured surface is determined by ICP-OES. The ICP-OES measurement gives the phosphorus weight within the examined solution in  $\mu$ g/l. This quantity is converted to the amount of phosphorus atoms and then divided by the sample area. As the diffusion occurs on both wafer surfaces, that value is further divided by two to obtain the phosphorus dose  $D_{\text{Phos}}$  for one wafer side.

Fig. 4 shows the obtained phosphorus doses  $D_{Phos}$  for the five diffusion processes. It is evident that the second PSG deposition step leads to significantly higher  $D_{Phos}$ that ranges between  $(2.3 \pm 0.3) \cdot 10^{15} \text{ cm}^{-2} \le D_{Phos} \le$  $(2.8 \pm 0.4) \cdot 10^{15} \text{ cm}^{-2}$ . For process "in-situ thin", the second deposition leads to an increase in  $D_{Phos}$  from  $D_{Phos} \approx$  $(0.61 \pm 0.09) \cdot 10^{15} \text{ cm}^{-2}$  to  $D_{Phos} \approx (2.3 \pm 0.3) \cdot 10^{15} \text{ cm}^{-2}$ , which corresponds to a factor of four. Process "in-situ thick" with very thick intermediate SiO<sub>2</sub> layer, see Fig. 3, shows a slighter increase in  $D_{Phos}$  due to the second deposition step. This is consistent with the assumption that the majority of the phosphorus is located in the PSG layer [9,18] and hence a slight increase in  $d_{PSG}$  correlates with a slightly higher  $D_{Phos}$ .

## 3.3 Phosphorus doping profiles after POCl<sub>3</sub> diffusion

Fig. 5(a) shows the as-diffused charge carrier concentration profiles of the reference process and the two diffusion processes "in-situ thin" and "in-situ thin 2<sup>nd</sup> dep", determined by ECV measurements on textured surface. The profile depth  $d_{prof}$  at a dopant concentration  $N = 10^{17}$  cm<sup>-3</sup> is between 320 nm  $< d_{prof} < 400$  nm. It is clear that the surface charge carrier concentration  $N_{surf} = (6.5 \pm 0.7) \cdot 10^{19}$  cm<sup>-3</sup> for the reference process "Ref 2<sup>nd</sup> dep" is lower than for the "in-situ thin"-process with  $N_{surf} = (2.1 \pm 0.2) \cdot 10^{20}$  cm<sup>-3</sup>. On the other hand, the course of the profiles for processes



**Figure 5:** Charge carrier concentration profiles obtained by the ECV technique after PSG etching on textured surface for the five diffusion processes stated in (a) and (b). The emitter sheet resistances  $R_{\rm sh}$  as well as the integrated total charge carrier dose  $Q_{\rm ECV}$  are stated.

"in-situ thin" and "in-situ thin  $2^{nd}$  dep" is very similar. Hence, the performed second deposition step hardly affects the resulting doping profile. This is confirmed by the integrated total charge carrier dose  $Q_{ECV}$  given in Fig. 5(a), which is similar for both processes within the measurement uncertainty.

Although the PSG/SiO<sub>2</sub> layer thicknesses are very similar for the processes "Ref  $2^{nd}$  dep" and "in-situ thin  $2^{nd}$  dep" (Fig. 3), the courses of the profiles are different.

Fig. 5(b) shows the charge carrier concentration profiles of, the reference process and the two diffusion processes "in-situ thick" and "in-situ thick 2<sup>nd</sup> dep". Here,  $d_{\text{prof}}$ is very similar for all processes with  $d_{\text{prof}} \approx 400$  nm. Both "in-situ thick"-processes with  $N_{\text{surf}} = (1.8 \pm 0.2) \cdot 10^{20}$  cm<sup>-3</sup> result in very similar charge carrier concentration profiles as obtained for the two "in-situ thin"-processes. Again, it is clear that the performed second deposition step hardly affects the resulting doping profile: the charge carrier concentrations are very similar either without or with second deposition. This is also confirmed by the integrated total charge carrier dose  $Q_{\text{ECV}}$  given in Fig. 5(b), which is similar for both processes.



**Figure 6:** Reflection measurements on textured surface with the PSG/SiO<sub>2</sub> stack layers from the indicated POCl<sub>3</sub> diffusion processes.

3.4 Impact of laser doping on sheet resistance

As the laser doping process is at least partly dependent on the coupling of the laser radiation into the silicon material, the absorption A of the samples is of interest. In order to obtain A, we measure the reflection R which is dependent on the surface morphology and the total layer thickness of the PSG/SiO<sub>2</sub> stack. Commonly, lasers with wavelengths between 355 nm  $\leq \lambda_{laser} \leq 1030$  nm are used for laser doping approaches [23]. Within this work, we use a UV ns-laser at  $\lambda_{laser} = 355$  nm.

Fig. 6 shows *R* as a function of wavelength  $\lambda$ . *R* is significantly lower at  $\lambda_{laser} = 355$  nm for both "in-situ thick" diffusion processes compared to the other processes as they feature a thicker PSG/SiO<sub>2</sub> stack layer. As the transmission is zero for  $\lambda_{laser}$ , the absorption is A = 1 - R. For the results plotted in Fig. 7, we multiplied the applied pulse energy  $E_{P,set}$  with the corresponding *A*, in order to account for the differences in reflection. However, note that the reflectance changes dramatically during the application of each laser pulse due to local heating and melting of the wafer surface.

Fig. 7 summarizes the obtained sheet resistances  $R_{\rm sh,4pp}$ , determined by 4pp measurements after laser doping. All three images (a) to (c) have in common that  $R_{\rm sh,4pp}$  decreases continuously with increasing  $E_{\rm P}$ . For the reference POCl<sub>3</sub> diffusion process with second deposition "Ref 2<sup>nd</sup>" (no in-situ oxidation) in Fig. 7(a),  $R_{\rm sh,4pp}$  is reduced from  $R_{\rm sh,4pp} \approx 100 \,\Omega/\text{sq}$  to  $R_{\rm sh,4pp} \approx 20 \,\Omega/\text{sq}$  if  $E_{\rm P}$  is increased to  $E_{\rm P} \approx 100 \,\mu$ J. For both diffusion processes with in-situ oxidation and second deposition in Fig. 7(a), also a significant reduction in  $R_{\rm sh,4pp} \approx 25 \,\Omega/\text{sq}$  and  $R_{\rm sh,4pp} \approx 30 \,\Omega/\text{sq}$  is seen for the processes "in-situ thin 2<sup>nd</sup> dep" and "in-situ-thick 2<sup>nd</sup> dep", respectively. However, the reductions in  $R_{\rm sh,4pp}$  are somewhat weaker pronounced than for the reference.

Referring to Figs. 3 and 4, it is clear that the different thicknesses of the intermediate SiO<sub>2</sub> layer is the dominating property which causes the differences in the obtained  $R_{sh,4pp}$  values after laser doping in Fig. 7(a), as all three POCl<sub>3</sub> diffusion processes feature comparable  $d_{PSG}$  and  $D_{Phos}$ . The thicker the intermediate SiO<sub>2</sub> layer is, the less is the achievable reduction in  $R_{sh,4pp}$ . The presence of a thick intermediate SiO<sub>2</sub> layer ( $d_{SiO2} \approx 50$  nm) thus retards the in-corporation of phosphorus from the PSG layer into the silicon surface considerably compared to the thinner SiO<sub>2</sub> layer ( $d_{SiO2} \approx 12$  nm) present for the "in-situ thin



**Figure 7:** Emitter sheet resistances  $R_{sh,4pp}$  after laser doping for the pulse energies  $E_P$ —which correspond to the applied pulse energies  $E_{P,set}$  times the absorption A—of the respectively indicated diffusion processes in (a) to (c). The pulse-to-pulse as well as the line-to-line distance is constant for all  $E_P$ . One hundred 4pp measurements are performed for all diffusion processes without laser doping (-), while ten 4pp measurements are performed per  $E_P$  and per diffusion process.

 $2^{nd}$  dep" diffusion process. The even thinner intermediate SiO<sub>2</sub> layer ( $d_{SiO2} \approx 6 \text{ nm}$ ) of the reference process allows for an even stronger laser doping.

Fig. 7(b) shows the impact of the second deposition step during POCl<sub>3</sub> diffusion for the "in-situ thin" processes. Obviously, the second deposition and thus, the higher  $D_{Phos}$  as shown in Fig. 4, allows for significantly higher doping resulting in lower  $R_{sh,4pp}$  values. Remember that the second deposition step not only increases  $D_{Phos}$  but also leads to the decrease in the intermediate SiO<sub>2</sub> layer thickness; see Fig. 3. A thinner SiO<sub>2</sub> layer also allows for higher laser doping, compare Fig. 7(a).

For the "in-situ thick" processes in Fig. 7(c),  $R_{sh,4pp}$  decreases with increasing  $E_P$ , but only slightly lower values are seen for the POCl<sub>3</sub> diffusion process with second deposition at each  $E_P$ . This can be explained by the only slight increase of the phosphorous dose due to the second deposition (see Fig. 4). The thick intermediate SiO<sub>2</sub> layer (see Fig. 3) seems to prevent the in-diffusion of phosphorus atoms from the PSG into the silicon for both "in-situ thick" processes, although slightly more phosphorus is provided within the PSG/SiO<sub>2</sub> stack layer for "in-situ thick 2<sup>nd</sup> dep" (see Fig. 4).

#### 5 SUMMARY AND CONCLUSION

Five different diffusion processes utilizing phosphorus oxychloride (POCl<sub>3</sub>) as liquid dopant precursor are examined with respect to their as-diffused properties and their suitability with laser doping from phosphosilicate glass (PSG) to form a selective emitter structure. Therefore, variations in deposition parameters, in-situ oxidation (e.g. high oxygen flow during drive-in), and the influence of a second PSG deposition step (e.g. active N<sub>2</sub> flow through the POCl<sub>3</sub> bubbler after drive-in) are investigated.

The POCl<sub>3</sub> diffusions with in-situ oxidation result in grown stack layers consisting of silicon dioxide (SiO<sub>2</sub>) and PSG, whose intermediate SiO<sub>2</sub> layers with a thickness  $d_{SiO2} = (19 \pm 2)$  nm or  $d_{SiO2} = (50 \pm 2)$  nm are twice as thick as the PSG layers with thicknesses  $d_{PSG} = (10 \pm 1)$  nm and  $d_{PSG} = (23 \pm 1)$  nm, respectively. The total PSG/SiO<sub>2</sub> stack layer thickness depends on the cho-

sen gas flows during deposition. The higher POCl<sub>3</sub> and  $O_2$  gas flows result in thicker stack layers.

The implementation of a second PSG deposition step for the diffusion process with in-situ oxidation results in increased PSG layer thicknesses, while the charge carrier concentration profiles hardly change. The SiO<sub>2</sub> layer thickness decreases if the intermediate SiO<sub>2</sub> layer before second deposition does not exceed a critical thickness. Or, there is a critical PSG layer thickness from which the PSG layer growth occurs slower. The reference POCl<sub>3</sub> diffusion without in-situ oxidation but with second deposition features a thin SiO<sub>2</sub> with  $d_{SiO2} = (6 \pm 2)$  nm, while the PSG layer is about four times thicker.

We find that the POCl<sub>3</sub> diffusion processes with second PSG deposition feature a higher total phosphorus dose  $D_{Phos}$  within the PSG/SiO<sub>2</sub> stack layers.  $D_{Phos}$  ranges between  $(2.3 \pm 0.3) \cdot 10^{15}$  cm<sup>-2</sup>  $\leq D_{Phos} \leq (2.8 \pm 0.4) \cdot 10^{15}$  cm<sup>-2</sup> for all processes with second deposition.

Laser doping applied to the PSG/SiO2 stack layers reduces the emitter sheet resistance  $R_{\rm sh}$  with increasing laser pulse energy. It is found that for the POCl<sub>3</sub> diffusion processes with second PSG deposition, Rsh can be significantly more reduced compared with the POCl<sub>3</sub> diffusion processes without second deposition as long as the intermediate SiO<sub>2</sub> layer thickness is a few 10 nm or less. From  $R_{\rm sh} \approx 90 \,\Omega/{\rm sq}$  after diffusion,  $R_{\rm sh}$  can be reduced to 15  $\Omega/sq < R_{sh} < 35 \Omega/sq$  by laser doping. This result suggests that the additionally provided phosphorus from the second deposition step is advantageous for laser doping. For POCl<sub>3</sub> diffusion processes with in-situ oxidation, the reduction in  $R_{\rm sh}$  by the laser process is weaker for thicker intermediate SiO<sub>2</sub> layers. For SiO<sub>2</sub> layer thicknesses above about 50 nm, laser doping results in similar  $R_{\rm sh}$ values measured on samples either diffused with or without second PSG deposition step.

In summary, our results show that POCl<sub>3</sub> diffusion processes with in-situ oxidation are suitable for the formation of selective emitters by laser doping.

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