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Role of Thermal SiO_2 on Passivation of Highly Doped Layer

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Abstract. In this paper we investigate the influence of thermal oxidation during and after $POCl_3$ diffusion. The main focus here is on the question of how far the presence of a thermally grown oxide layer has an influence on the emitter passivation. For this purpose, characterization methods such as electrochemical capacitance-voltage measurements and QSSPC are used. The novel finding of this paper is that in the case of a stack of passivation layers, the presence of the thermal oxide does not make a significant contribution to improved emitter passivation.

INTRODUCTION

The reduction of electrical losses in highly doped layers is part of many research projects (e.g., [1-4]). A thermal oxidation process plays an important role in the processing of low recombination emitters. The in-situ oxidation as a modification of a diffusion process has also been an important field of research in the last years [6]. It is still unclear to what extent the existence of a SiO_2 layer actually contributes to the passivation of a highly doped emitter. One may ask oneself whether the reduction of the surface concentration by thermal oxidation alone leads to the reduction of the emitter recombination.

EXPERIMENTAL

Sample Preparation

For the following investigations planar p-type Czochralski silicon (Cz-Si) wafers with a nominal bulk resistivity of 2 Ωcm and floating zone (FZ) Si wafers with a bulk resistivity of 200 Ωcm were used. All samples were prepared for the subsequent high temperature steps with a PIRANHA clean after saw damage etching.

<table>
<tr><td colspan="6" align="center">PIRANHA Clean</td></tr>
<tr><td colspan="2" align="center">POCl₃ Diffusion
Low P</td><td colspan="2" align="center">POCl₃ Diffusion
Mid P</td><td colspan="2" align="center">POCl₃ Diffusion
High P</td></tr>
<tr><td colspan="3" align="center">PSG removal</td><td colspan="3" align="center">No PSG removal</td></tr>
<tr><td colspan="6" align="center">Thermal Oxidation</td></tr>
<tr><td colspan="3" align="center">HF Etching</td><td colspan="3" align="center">No HF Etching</td></tr>
<tr><td colspan="6" align="center">PECVD a-SiN_x:H</td></tr>
</table>

FIGURE 1. Process sequence

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After cleaning, the samples were divided into 3 groups and diffused separately in a quartz tube $POCl_3$ diffusion furnace. The three $POCl_3$ diffusions differed in the setting of the $POCl_3/O_2$ gas flow which influences the phosphorus concentration of the emitter. As shown in a previous study [2], this has a strong influence on the concentration of the electrically active and inactive phosphorus at the emitter surface. Afterwards, the highly doped PSG layer was removed in diluted HF. This was followed by thermal oxidation in which all wafers were dry oxidized at a temperature of 900°C for 10 min. After the thermal processes, the thermal oxide layer was removed in diluted HF for half of the samples. This last group division is intended to show how far the existence of a thermal SiO_2 layer plays a role for dielectric emitter passivation.

Independent of the described first experiment, an in-situ oxidation was performed during $POCl_3$ diffusion which will be discussed in the last section of this work. The aim of this study is to show to what extent thermal oxidation can be replaced by in-situ oxidation. The in-situ oxidation, which takes place directly after the drive-in step of the $POCl_3$ diffusion, was carried out with the same process parameters as for the dry thermal oxidation.

For final emitter passivation, all samples were coated with a-SiN_x:H on both sides using plasma-enhanced chemical vapor deposition. The wafers were then fired under standard cofiring process conditions in a Centrotherm firing belt furnace at a set temperature of 840°C.

The electrically active phosphorus concentration was determined by means of the electrochemical capacitance-voltage (ECV) measurement, whereby a hydrophobic surface was secured by an HF dip before each measurement.

RESULTS

Doping Profiles before and after Thermal Oxidation

Let us first consider the change in P concentration due to thermal oxidation at 900°C depending on the emitter selected. For the emitter (High P) with the highest P concentration, the P concentration on the surface is reduced after oxidation from $4.87 \cdot 10^{20}$ cm^{-3} to $3.95 \cdot 10^{20}$ cm^{-3}, for the emitter with the mid P concentration from $4.56 \cdot 10^{20}$ cm^{-3} to $2.68 \cdot 10^{20}$ cm^{-3} and for the emitter with the lowest P concentration from $1.4 \cdot 10^{20}$ cm^{-3} to $2.8 \cdot 10^{19}$ cm^{-3}. It must be taken into account that thermal oxidation at 900°C causes both an additional activation of the electrically inactive phosphorus and an in-diffusion of the phosphorus, thus reducing the surface concentration.

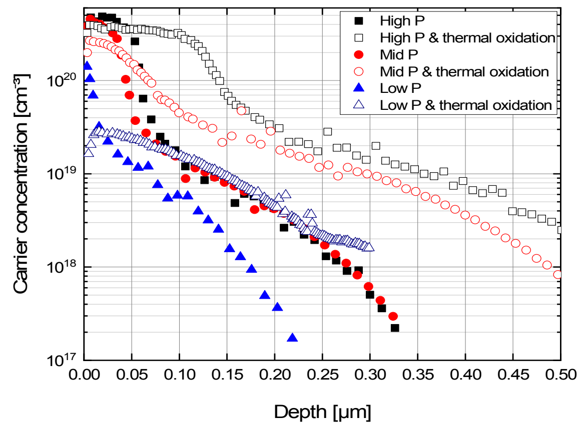

FIGURE 2. ECV measurements of phosphorus depth profiles of 3 $POCl_3$ diffusions with and without thermal oxidation. By increasing the $POCl_3/O_2$ gas flow during $POCl_3$ process, the P concentration at the emitter surface and in the emitter volume was increased.

Tab. 1 clearly shows that the reduction of the surface concentration is weakest in the case of the High P emitter, which contains a high amount of electrically inactive phosphorus. It can be assumed that the activation of electrically inactive phosphorus is associated with a dissolution of phosphorus precipitates. Due to the high concentration of these phosphorus precipitates in the emitter High P, the effect of P activation is relatively small. In contrast, emitters with reduced P precipitate density show that thermal oxidation causes a significant reduction of the maximum surface P concentration.

TABLE 1. Change in the maximum surface concentration before and after thermal oxidation as a function of 3 emitter types which differ in the concentration of electrically inactive phosphorus.

Emitter	Maximum P concentration after $POCl_3$ diffusion [10^{20} cm^{-3}]	Maximum P concentration after $POCl_3$ diffusion & thermal oxidation [10^{20} cm^{-3}]	Relative change of maximum P concentration due to thermal oxidation
High P	4.87	3.95	-19%
Mid P	4.56	2.68	-41%
Low P	1.41	0.28	-80%

Impact of Thermal Oxidation on Emitter Saturation Current Density

In the next part we consider the influence of the SiO_2 layer on the emitter saturation current density (j_{0E}) value [5] and thus on the emitter passivation.

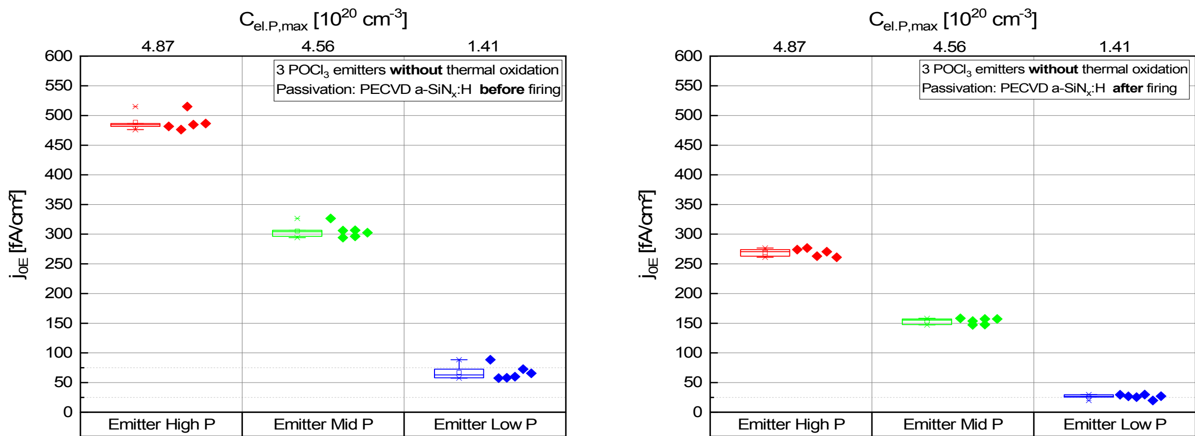

FIGURE 3. j_{0E} values of SiN_x or SiO_2/SiN_x passivated emitters before and after firing. All emitters were thermally oxidized at 900°C after removal of the PSG layer.

Fig. 3 shows the measured j_{0E} values for the reference diffusions without thermal or in-situ oxidation before and after firing. The reduction of the surface concentration was achieved by adjusting the gas flows during the $POCl_3$ diffusion process. The improved passivation quality of the emitter with reduced surface concentration is clearly visible. After firing, emitters with a maximum carrier concentration of $1.41 \cdot 10^{20}$ cm^{-3} show j_{0e} values of 25 fA/cm².

In Fig. 4 the results of the samples with thermal oxidation after removal of the PSG layer are displayed. The left picture clearly shows that the existence of the SiO_2 layer before firing leads to a reduced j_{0E} value for all emitter types. If the SiO_2 layer is removed before a-SiN_x:H deposition, this always leads to a deteriorated emitter passivation. The lower the P concentration of the emitter, the stronger this effect becomes. The emitter surface, which is less disturbed due to the lack of inactive phosphorus, can be well passivated with SiO_2 even before firing. However, this strong trend is no longer dominant if the samples are fired. In this case, the existence of the thermally grown SiO_2 layer has no significant influence on emitter passivation. The j_{0E} values of both two groups with and without SiO_2 layer reach j_{0E} values between 13 and 25 fA/cm². It must be considered that the oxidation process causes a strong reduction of the surface concentration, but at the same time also an increase of the plateau width. In summary, it is shown here that after the firing process the existence of the SiO_2 layer leads to a weak reduction of the j_{0E}.

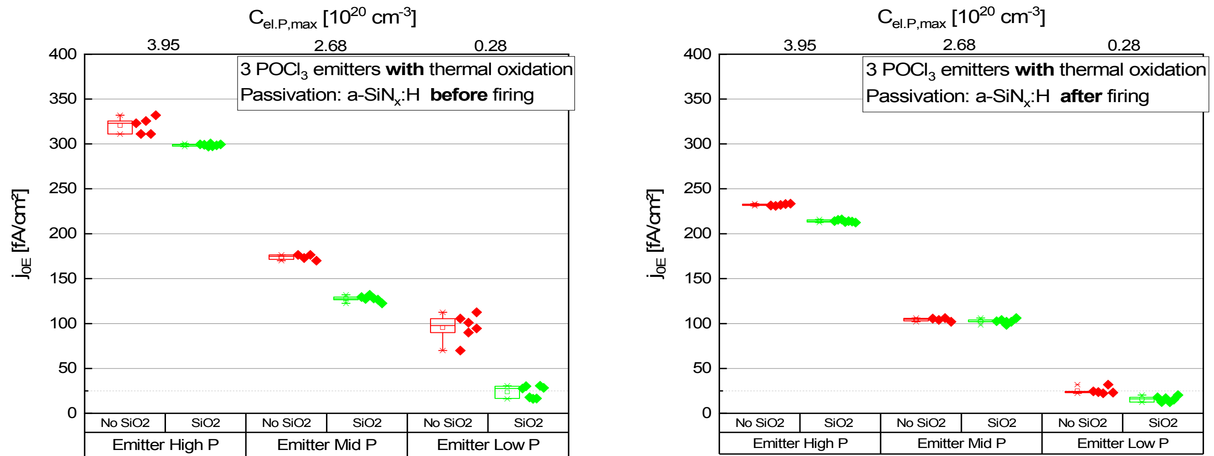

FIGURE 4. j_{0E} values of SiN_x or SiO_2/SiN_x passivated emitters before and after firing. All emitters were thermally oxidized at 900°C after removal of the PSG layer.

In-situ Oxidation

In the last part of this study the influence of in-situ oxidation on emitter passivation is investigated. As already shown in the last section, the existence of the SiO_2 layer does not play a significant role for the emitter passivation. It could be shown that in the case of lowly doped emitter structures j_{0E} values below 25 fA/cm² could be achieved even without the existence of the SiO_2 layer. Thus, the improved emitter passivation was caused by the strong reduction of the surface concentration during thermal oxidation. Such an increased reduction of the surface concentration can also be achieved by in-situ oxidation during $POCl_3$ diffusion. After termination of the $POCl_3$ process an in-situ oxidation was performed at an elevated temperature of 900°C and under conditions of high oxygen gas flow.

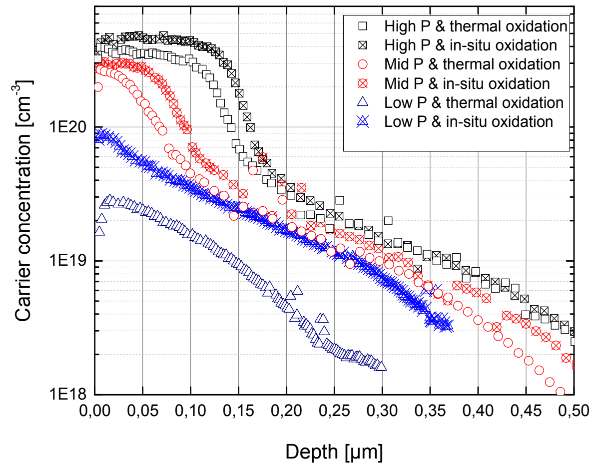

FIGURE 5. Comparison of carrier concentrations measured by ECV for 3 different $POCl_3$ emitters with in-situ oxidation and with thermal oxidation.

A comparison of the ECV profiles of emitters with thermal oxidation and those with in-situ oxidation can be seen in Fig. 5. This shows that the in-situ oxidation leads to an increased surface concentration, most probably because the PSG layer is still present as a dopant source during the process. In order to compensate this effect, a reduced surface concentration can be achieved by adjusting the gas flows during the $POCl_3$ process prior to in-situ oxidation.

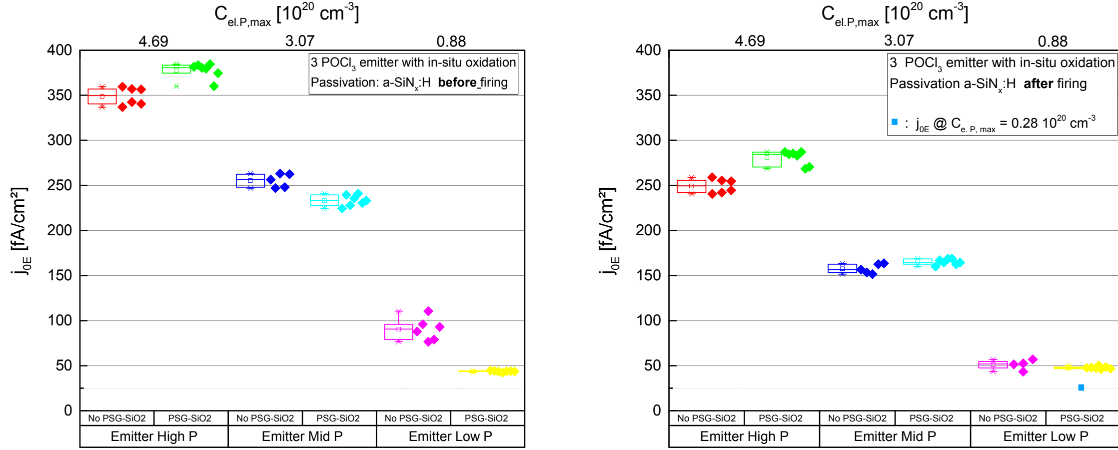

FIGURE 6. j_{0E} values of SiN_x or $PSG\text{-}SiO_2/SiN_x$ passivated emitters before and after firing. All emitters were thermally oxidized via in-situ oxidation at 900°C during $POCl_3$ diffusion process.

In order to investigate the influence of the PSG-SiO_2 layer on the emitter passivation, for part of the samples the PSG-SiO_2 layer was wet-chemically removed after in-situ oxidation. Subsequently, all samples were symmetrically passivated with PECVD SiN_x:H and fired. The focus is to show to what extent a PSG-SiO_2 layer can be used as a passivation layer after in-situ oxidation.

Fig. 6 shows the measured j_{0E} values for the two cases before and after firing. Similar to the thermal oxidation discussed above, the existence of the PSG-SiO_2 layer seems to have a positive influence on the emitter passivation (emitter Mid-P & Low-P). This, however, applies here mainly to the case before firing. After firing, the influence of the PSG-SiO_2 layer on the emitter passivation is compensated by the H-passivation of the a-SiN_x:H. For the emitter with the highest P concentration (High-P) the removal of the PSG-SiO_2 layer before the SiN_x deposition results in a reduction of the j_{0E} values. It should be noted here that the High-P emitter has a high concentration of electrically inactive P in the PSG-SiO_2 layer and the silicon interface. The removal of the PSG-SiO_2 layer in the case of the High-P emitter permits improved H passivation of the emitter surface by the released hydrogen of the SiN_x:H layer after firing. A comparison of the modified Mid-P emitter with the reference diffusion shows that both have a comparable j_{0E} value of 150 fA/cm², but this value is already reached with the modified in-situ oxidation emitter at a higher carrier concentration. In the case of a $C_{el.\ P,\ max}$ of $0.88 \cdot 10^{20}$ cm^{-3}, an average j_{0E} values of 50 fA/cm² can be achieved without additional thermal oxidation. The existence of the PSG-SiO_2 layer does not play a decisive role when considering emitter structures with reduced surface carrier concentration. However, it can also be seen that a PSG-SiO_2/SiN_x stack already reaches the minimum j_{0E} value before firing. Thus, this stack can be used as a passivation layer for low temperature processes as firing does not lead to any further improvement of the passivation quality.

A comparison with Fig. 4 (thermal oxidation) shows that the j_{0E} values for samples after in-situ oxidation show a slight increase compared to samples after thermal oxidation. This is due to the fact that the surface concentration of the emitters is increased due to the existence of the PSG layer during the in-situ oxidation. By adjusting gas flows during diffusion, a j_{0E} value of 25 fA/cm² was achieved with in-situ oxidation at a surface concentration of $0.28 \cdot 10^{20}$ cm^{-3}. With regard to the homogeneity on a wafer it must be mentioned that the used wafers have a size of 25 cm^2. In this case a uniformity of about 3% was measured on the wafer during both ex-situ and in-situ oxidation.

TABLE 2. Comparison of j_{0E} values of emitters with in-situ oxidation and reduced surface concentration of $0.28 \cdot 10^{20}$ cm^{-3}.

	With PSG-SiO₂		**Without PSG-SiO₂**	
	Before firing	After firing	Before firing	After firing
j_{0E} [fA/cm^2]	24	25	45	26

Thus, it could be shown that in-situ oxidation during the $POCl_3$ process can replace a separate thermal oxidation. As for the results shown in Fig. 3, the presence of the PSG-SiO_2 layer at carrier concentrations below $3 \cdot 10^{20}$ cm^{-3} does not lead to a significant improvement of the emitter passivation after firing. In the case of the adapted emitter with the reduced surface concentration of $0.28 \cdot 10^{20}$ cm^{-3}, the contribution of PSG-SiO2 to emitter passivation after firing is only 1 fA/cm^2.

SUMMARY

In this paper we discussed the influence of thermal oxidation and in-situ oxidation on emitter profiles and on the passivation quality of $POCl_3$ emitters. It has been showed that the decrease of the emitter saturation current density is primary related to the change of the emitter profile and in particular to the change of the surface concentration. In the case of a passivation stack with SiO_2-SiN_x the presence of SiO_2 does not significantly decrease the emitter current density after firing. The reduction of the surface concentration and at the same time the reduction of j_{0E} is also demonstrated using in-situ oxidation during the $POCl_3$ process. In both cases, ex-situ thermal oxidation and in-situ oxidation, j_{0E} values down to 25 fA/cm^2 has been demonstrated.

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