

A STUDY OF VARIOUS METHODS FOR THE ANALYSIS OF THE PHOSPHOSILICATE GLASS LAYER

M. Steyer¹, A. Dastgheib-Shirazi¹, H. Wagner², G. Micard¹, P.P. Altermatt², G. Hahn¹

¹Dep. of Physics, University of Konstanz, Jacob-Burckhardt-Str. 29, 78457 Konstanz, Germany

²Dep. Solar Energy, Inst. Solid-State Physics, Leibniz University of Hannover, 30167 Hannover, Germany

Author for correspondence: michael.steyer@uni-konstanz.de Tel.: +49 7531 882080, Fax: +49 7531 883895

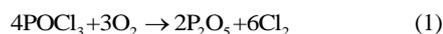
ABSTRACT: The understanding and therefore the optimization of n⁺-emitter formation in crystalline silicon using POCl₃-diffusion requires a more detailed knowledge of the dopant source: the PhosphoSilicate Glass (PSG) layer. The growth of PSG during the phosphorus diffusion process depends on several process parameters, such as temperature, duration, POCl₃-N₂ and O₂ gas flows. In this work, we compare the uncertainties in various methods for PSG thickness measurements: by an Atomic Force Microscope (AFM), a profilometer, a Scanning Electron Microscope (SEM) and a spectroscopic ellipsometer. We then quantify how the PSG thickness is influenced by the process parameters. We also measure the total amount of phosphorus (P-dose) in the PSG layer using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and quantify the P dose in dependence of the process parameters as well. Finally, by combining both the measured PSG thickness and the dose, we successfully determine a lower limit for the phosphorus concentration in the PSG layer. It is, depending on the process parameters, between 7×10²¹ cm⁻³ and 1.2×10²² cm⁻³, which is a remarkably narrow range. These results will help to improve the phosphorus diffusion model by considering both the PSG growth behavior and PSG composition, and so will facilitate the development of a predictive model for the POCl₃ diffusions process.

Keywords: Diffusion, Emitter, POCl₃, PSG

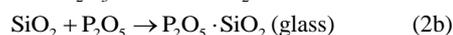
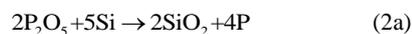
1 INTRODUCTION

The POCl₃-diffusion is the most common method of n⁺-emitter formation in c-Si solar cells. The optimum emitter for a screen printed solar cell is a compromise of low emitter saturation current, high collection probability for minority carriers, low contact resistance and good lateral conductivity. Therefore an extended adjustment of diffusion parameters is needed. A possibility to find optimized diffusion parameters is simulation. However, the simulation of POCl₃ emitter formation is still in discrepancy to experimental results. Common phosphorus diffusion models [1-2] do not include the dopant source (PSG) as boundary condition and the PSG growth behavior. Attempts to include the PSG layer in the diffusion model were made in Refs. [3] and [4]. Our primary aim has been a more realistic model [4-5] by including these PSG properties. Therefore, a quantitative analysis of the PSG in dependence of diffusion parameters is necessary. In this work we focus on methods for the analysis of the PSG thickness and its total amount of phosphorus.

The POCl₃-diffusion process at a temperature between 800°C and 900°C is usually divided into two main steps: pre-deposition and drive-in. In the pre-deposition, the wafers are exposed to a gas-flow of POCl₃-N₂, O₂ and N₂ such that mainly [6] P₂O₅ glass is formed. The following reaction is commonly cited [7]:



The P₂O₅ is reduced by Si to form SiO₂. At the same time, the atomic phosphorus at the Si interface diffuses into the Si bulk (where it forms the n⁺-emitter) and glass is formed:



Hence, the PSG layer is assumed to be partially a glass composed of P₂O₅ and SiO₂, but its composition is only sparsely known. In a following drive-in step, the POCl₃-N₂ flow is turned off and the phosphorus in the Si wafer is further driven in.

In this study, we focus on the pre-deposition, in which the highly doped PSG is formed. Varying the diffusion parameters thereby strongly influences the PSG growth.

In the first part, the PSG thickness is investigated by different analysis methods in dependence of diffusion parameters. In the second part we determine the total amount of phosphorus. Information about PSG thickness and dose allow us to determine the phosphorus concentration in the PSG, which will be discussed in the last part of this work. This is in contrast to methods such as Secondary Ion Mass Spectrometer (SIMS), which have proved difficult so far because calibrated standards are needed and have been difficult to obtain, and there are also charging effects during the measurements.

2 ANALYSIS OF PSG THICKNESS

In this section, we compare the measurement uncertainty of four different methods for determining the PSG thickness: ellipsometry, profilometry, AFM and SEM.

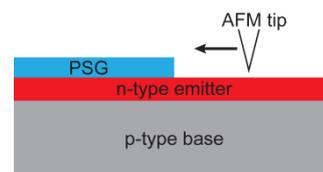


Figure 1: The PSG step for AFM and profilometer measurements (schematic).

The basic material for the experiment was p-type, <100> orientated, FZ (FloatZone) Si wafers with a bulk

resistivity of 2 Ωcm and a surface area of 5 x 5 cm^2 . For the AFM and profilometer measurements, we found it necessary to use mechanically polished wafers with a roughness below 1 nm in order to detect thin PSG thicknesses in a range of 10 to 80 nm.

After cleaning the wafers, we performed a POCl_3 diffusion process whereby we only focused on the pre-deposition. The reference diffusion parameters are a pre-deposition duration of 20 min, a temperature of 840°C, a $\text{POCl}_3\text{-N}_2$ flow of Φ_0 and a constant O_2 flow. In process A, only the $\text{POCl}_3\text{-N}_2$ flow was varied. In process B, we repeated this but with a temperature of 880°C, and in process C we used a longer pre-deposition duration of 40 min. To determine the PSG thickness with an AFM or profilometer, it is necessary to remove the PSG locally to create a step. Therefore, a mask was printed on a part of the sample. Then the unprotected PSG was etched off with HydroFluoric acid (HF). After this, the mask was removed by a wet chemical procedure. Finally, the PSG thickness was measured using the step height between the etched and unetched areas (see Figure 1).

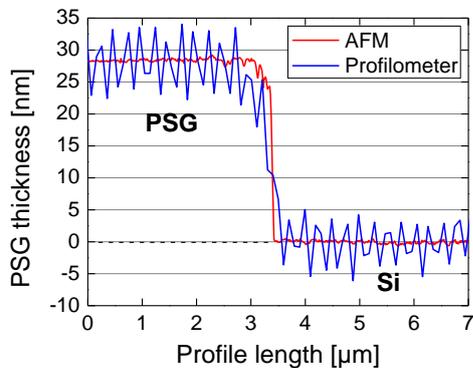


Figure 2: Measured step height of the same sample with AFM and profilometer; both yield the same PSG thickness of 28 nm but with different uncertainties.

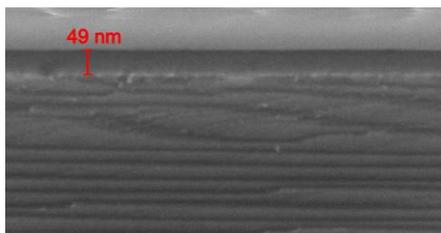


Figure 3: SEM image of the cleaved edge for the sample of process B with a $3\Phi_0$ $\text{POCl}_3\text{-N}_2$ flow. The determined PSG thickness is 49 nm.

An example of the AFM and the profilometer step measurement is shown in Figure 2. The measured surface shows a much stronger fluctuation with the profilometer, so that we average the height for 1 μm profile length. With the AFM we measured a surface area of 12 μm x 1.2 μm using the tapping mode. In addition we took 12 μm long line profiles with a mechanical profilometer. For both methods, three line profiles were averaged each time. The homogeneity of the PSG thickness on the total wafer was examined and showed a maximum discrepancy of only 1 nm for an average step height of 28 nm with the AFM, while we determined a maximum discrepancy of 4 nm for an average step height

of 30 nm with the profilometer. So as expected, the AFM shows a lower uncertainty than the profilometer.

The PSG thickness was also determined with a spectroscopic ellipsometer. Thereby, the sample can be measured immediately after the diffusion process with the full PSG layer. In Figure 4 to 6 all three methods are compared for the diffusion process A, B, and C. With the ellipsometer we usually measured the greatest thickness with a deviance below 4 nm in comparison to the AFM measurements.

In addition we also determined the PSG thickness for samples of process B by SEM (Figure 3 and 5). However, we found the detection of PSG thicknesses below 25 nm hardly possible. Also the uncertainty is high due to tilting and defining the exact interface.

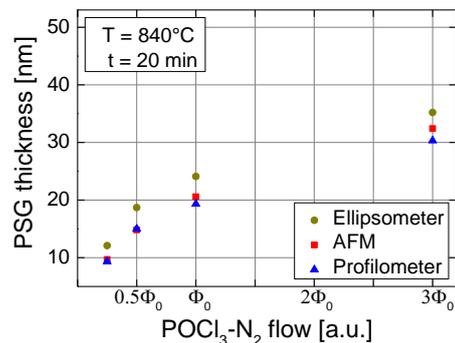


Figure 4: Process A: PSG thickness as a function of the $\text{POCl}_3\text{-N}_2$ flow (relative to our standard flow Φ_0), determined using the AFM, a profilometer or an ellipsometer.

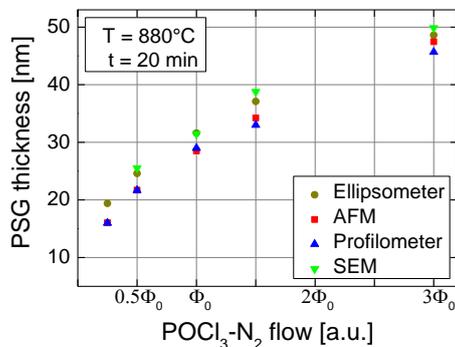


Figure 5: Process B: PSG thickness as a function of the $\text{POCl}_3\text{-N}_2$ flow as in Fig. 4 but with an increased temperature of 40°C.

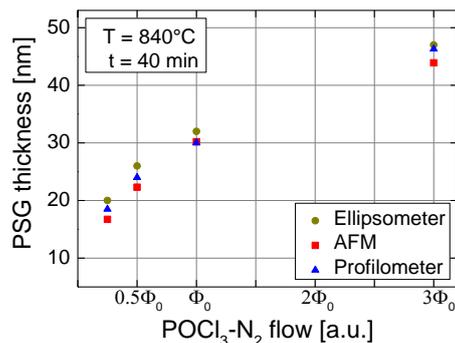


Figure 6: Process C: PSG thickness as a function of the $\text{POCl}_3\text{-N}_2$ flow as in Fig. 4 but with an increased duration of 20 min.

The measurements show that increasing the temperature by 40°C (process B) has nearly the same effect on the thickness as doubling the duration to 40 min (process C). For a very high POCl₃-N₂ flow, the PSG growth shows a saturation effect, which can be explained with the lower O₂ flow compared to the overall flow. As shown in equation (1), both POCl₃ and O₂ are necessary to form P₂O₅. However, in these experiments only the total PSG thickness can be detected. Analysis methods on different layers within the PSG are still in the development phase.

In addition, we also investigated the PSG thickness at constant temperature, POCl₃-N₂ and O₂ flow, but with varying the pre-deposition time. The results are shown in Figure 7. As expected [7], The PSG thickness d_{PSG} grows approximately parabolic with the pre-deposition time t and can be described with the following function:

$$d_{PSG} = c\sqrt{t} \quad (3)$$

Based on the three measurement methods, we determined the proportionality constant c for our standard POCl₃-N₂ flow Φ_0 (see Table I). The constant for a low POCl₃-N₂ flow of $0.5\Phi_0$ is about 3.8-4.2 nm min^{-1/2} (based on ellipsometer measurements for 10, 20, 30 and 40 min), while a high POCl₃-N₂ flow of $3\Phi_0$ results in 6.1-6.6 nm min^{-1/2} (based on ellipsometer measurements for 10 and 30 min). A refined growth model was recently published in [8]

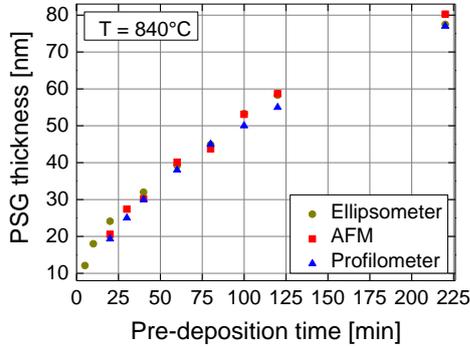


Figure 7: PSG thickness as a function of pre-deposition time.

Table I: Proportionality constant c in Eq. (3) for the parabolic PSG growth based on measurements shown in Figure 7.

Method	c [nm min ^{-1/2}]
Ellipsometer	5.3 ± 0.3
AFM	5.0 ± 0.3
Profilometer	4.8 ± 0.3

In conclusion, the AFM seems to be the most precise method to determine the total PSG thickness. However, using an ellipsometer without any sample preparation is a sufficient alternative, too.

3 ANALYSIS OF P-DOSE IN PSG

In this part, we determine the phosphorus dose in the PSG layer using Inductively Coupled Plasma Optical

Emission Spectrometry (ICP-OES). The measured phosphorus dose for diffusion processes A and B is shown in Figure 8, using p-type FZ wafers with a bulk resistivity of 2 Ωcm. The diagram shows a nearly linear relation between the variation of POCl₃-N₂ flow and the dose. This is in contrast to Figure 3 and 4, where a high POCl₃-N₂ flow of $3\Phi_0$ shows saturation in PSG thickness. In Figure 9 the P-dose in the PSG is shown as a function of pre-deposition time for both FZ and Cz wafers. The Cz wafers are p-type as well with a bulk resistivity of 2 Ωcm. There is no clear trend relating the differences between FZ and Cz. To estimate the uncertainty, we examine all four measurements at 100 min pre-deposition time. The maximum difference of the average PSG dose is about 11%.

The P-dose shows, similarly to the thickness of the PSG layer, a parabolic behavior with time. Based on all measurements shown in Figure 9 we determine a proportionality constant of $(4.5 \pm 0.6) \times 10^{15}$ cm⁻² min^{-1/2}.

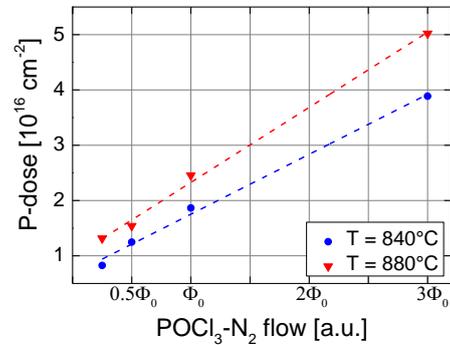


Figure 8: P-dose in the PSG, determined with ICP-OES, as a function of the POCl₃-N₂ flow at temperatures of 840°C and 880°C, respectively, using FZ wafers. The dashed lines represent a linear fit.

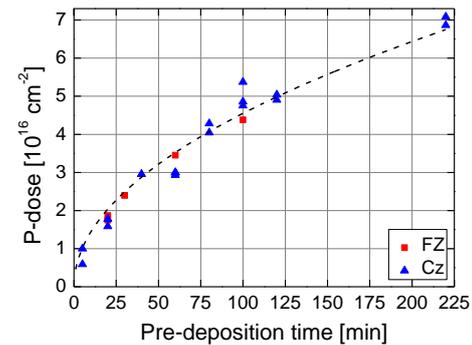


Figure 9: P-dose in the PSG, determined with ICP-OES, as a function of pre-deposition time at a constant POCl₃-N₂ flow of Φ_0 and 840°C, for both FZ and Cz wafers. The dashed line represents a parabolic fit.

4 P-CONCENTRATION IN PSG

Under the assumption that the concentration of phosphorus is rather independent of depth in the PSG layer, the average P-concentration in the PSG can be determined by dividing the P-dose by the measured PSG thickness. But assuming this, it should be kept in mind that next to the PSG-Si interface, a SiO₂ layer is formed where the P-concentration may be reduced. Thus, the computed value of the phosphorus concentration in the

PSG is only a lower limit. Only a separate analysis of the SiO₂ and P₂O₅ layer would allow the determination of an effectively doped PSG layer.

Figure 10 shows the measured P-dose divided by the measured PSG thickness (as determined by AFM) for a variation of POCl₃-N₂ flows. For our standard diffusion (process A with a POCl₃-N₂ flow of Φ_0), we determine a value of about $9 \times 10^{21} \text{ cm}^{-3}$. If we compute the concentration for the POCl₃-N₂ flow variation with a higher temperature of 880°C, a lower concentration is observed, as the diffusivity is strongly temperature dependent.

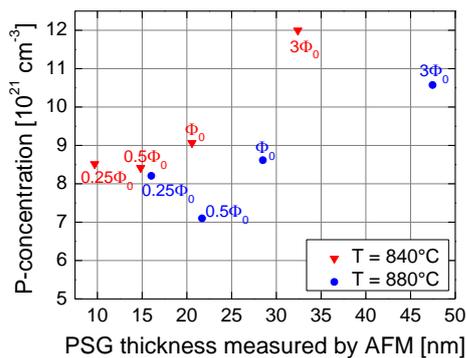


Figure 10: Lower limit of the P-concentration in the PSG layer, derived from dividing the measured P-dose by the AFM measured PSG thickness. The variation of POCl₃-N₂ flow is given relative to our standard flow Φ_0 . The red symbols represent our standard temperature of 840°C (process A); the blue symbols a higher temperature of 880°C (process B).

5 CONCLUSIONS AND OUTLOOK

The PSG thickness can be analyzed with an AFM or profilometer by masking followed by local etching to form a step in the PSG layer. These methods have been compared to ellipsometer measurements to verify the fitting model. Using the AFM seems to be the most reliable method, but the sample preparation is more elaborate. On the other hand the ellipsometry measurement is a fast and non-destructive method.

In the second experiment the total amount of phosphorus in the PSG (dose) was measured with the ICP-OES analysis tool. For the investigated PSG samples we determined a value for the P-dose in a range of $1 \cdot 10^{16} \text{ cm}^{-2}$ to $7 \cdot 10^{16} \text{ cm}^{-2}$, depending on the process parameters.

With the knowledge of the measured PSG thickness and dose, we were able to calculate the lower limit of the phosphorus concentration in the PSG. The lower limit assumption is due to the fact that the phosphorus concentration in the PSG may be reduced next to the PSG-Si interface. For that reason still a quantitative analysis of the PSG composition is required to determine the effective P-concentration in the PSG.

The various studies of the PSG layer properties are useful for the general understanding of emitter formation and the improvement of phosphorus diffusion models including the PSG layer as a dopant source for simulation procedures.

6 ACKNOWLEDGEMENTS

The basic project for parts of this report was financially supported by our industry partners centrotherm photovoltaics AG and SolarWorld Innovations. The financial support from the BMU project FKZ 0325079 is gratefully acknowledged in particular for the characterization equipment.

7 REFERENCES

- [1] S.T. Dunham, J. Electrochem. Soc. 139 (1992) 2628.
- [2] H. Bracht, H.H. Silvestri, I.D. Sharp, E.E. Haller, Phys. Rev. B 75 (2007) 035211.
- [3] J. Schön, W. Warta, Proc. 23rd European PV Solar Energy Conf. Valencia (2008) 1851.
- [4] H. Wagner, A. Dastgheib-Shirazi, R. Chen, S.T. Dunham, M. Kessler and P.P. Altermatt, Proc. 37th IEEE PV Specialists Conf., Seattle (2011), in print.
- [5] A. Dastgheib-Shirazi, M. Steyer, G. Micard, H. Wagner, P.P. Altermatt, G. Hahn, Proc. 38th IEEE PV Specialists Conf. Austin, (2012), in press,
- [6] D.C. Douglass, T.M. Duncan, K.L. Walker, R. Csencsits, J. Appl. Phys. 58 (1985) 197.
- [7] J. Dathe, W. Müller, L. Grasser Z. für angew. Physik 30 (1970) 272.
- [8] R. Chen, H. Wagner, A. Dastgheib-Shirazi, M. Kessler, Z. Zhu, P.P. Altermatt, S.T. Dunham, Proc. 38th IEEE PV Specialists Conf. Austin, (2012), in press,