ADVANCES IN THE UNDERSTANDING OF PHOSPHORUS SILICTE GLASS (PSG) FORMATION FOR ACCURATE PROCESS SIMULATION OF PHOSPHORUS DIFFUSION

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ABSTRACT: The diffusion of phosphorus mediated by phosphorus oxychloride (POCl$_3$) is extensively used in photovoltaics due to its enhanced diffusion speed and to the high controllability of the phosphorus at the wafer surface. However, the POCl$_3$ decomposition in the gas phase in phosphorus pentoxide (P$_2$O$_5$) as well as the subsequent oxidation reactions induced by P$_2$O$_5$ and O$_2$ at the silicon surface are not very well documented and increase the complexity of a realistic simulation of the POCl$_3$ diffusion. It is shown in this paper that the PSG growth model of Ghoshtagore [2] should apply correctly at least in a quantitative relative way to the PSG grown during a POCl$_3$ diffusion. This model allowed to show that the PSG contains a thin layer of 8.6 nm, presumably composed of SiO$_2$, which acts as a diffusion barrier with a subsequent impact on the phosphorus diffusion in silicon. In order to interpret ECV profiles of emitters obtained with various POCl$_3$ flows, a qualitative model based on the Ghoshtagore model is presented. This model emphasizes the role of O$_2$ at the silicon/PSG interface not only as a mediator of the PSG growth, but also as a generator of self-interstitials in silicon that will enhance the extension of the ECV profile tail. It also emphasizes the role of SiP precipitates in reducing the interstitial diffusion in silicon.
Keywords: Diffusion, Doping, Modeling

1 INTRODUCTION

While the POCl$_3$ diffusion process has the major advantage to accelerate the diffusion of dopants (because of the oxidation reaction at the surface) and to control the surface concentration by the solubility limit during the pre-deposition, it has the major disadvantage of not controlling accurately the amount of dopant introduced in silicon because of the anomalous diffusion of dopants at the silicon interface [1].

The kink of the phosphorus profile induced by this lack of controllability of the dopant flow is, on the one hand, beneficial for the contact formation, but on the other hand detrimental to the overall performance of the cell because of the higher recombination activity of the emitter.

The aforementioned oxidation reaction forms the so called phosphorus silicate glass (PSG) which can be considered usually, from the simulation point of view, as an infinite point-like source (the infinite source assumption). Providing that the phosphorus concentration in the PSG exceeds the solid solubility limit of P in Si the infinite source assumption can be made and the formation of the PSG can be discarded in the process simulation.

If, however, one aims at gaining controllability of the dopant flow to tailor the P profile at lower surface concentration (e.g not having the kink), then the concentration at the PSG/Si surface has to be below the solubility limit of P in Si and nor the formation nor the physical phenomenon in the PSG could be discarded in the physical simulation.

The literature is, however, rather poor about the PSG formation mechanism. One can notice the model proposed by Ghoshtagore [2] in 1976 to explain the PSG growth on SiO$_2$ which is a base of the qualitative model proposed in this paper.

In our former study [3] we studied the possibility of making a model of the POCl$_3$ diffusion that would still allow making the infinite source assumption.

While the parametrization of the integrated model of Bentzen [4] appears to hold at high POCl$_3$ flow, it was unsatisfactory at low POCl$_3$ flow because explicitly the assumption of infinite source does not hold true anymore.

From the diffusivity analysis of the low POCl$_3$ flow emitter profile we could draw the conclusion that the phosphorus diffusivity was higher at the beginning of the growth than later on. Based on this conclusion we set up an experiment in which the POCl$_3$ flow is maintained low at the beginning of the growth and is raised to a higher level for the remaining time of the diffusion.

This contribution aims therefore at studying the ECV electrochemical capacitance voltage (ECV) profiles of emitters obtained when the POCl$_3$ flow is varied during the diffusion at temperatures common in photovoltaics and interpreting it according to a qualitative model of PSG formation and evolution.

2 THEORY

2.1 PSG growth model

Starting from a thick SiO$_2$ layer in which P$_2$O$_5$ is diffused Eldridge and Balk [5] developed a semi-empirical growth law of the form

$$x_{PSG} \propto \sqrt{c_p t} \exp\left(-E_a / kT\right) \qquad (1)$$

in which x_{PSG} is the PSG thickness, c_p is the P$_2$O$_5$ concentration in the gas phase, t the diffusion time, E_a the activation energy, k the Boltzmann constant and T the diffusion temperature.

The P$_2$O$_5$ concentration could be strictly proportional to the POCl$_3$ concentration assuming that the decomposition of POCl$_3$ in an excess of O$_2$ goes to completion [5].

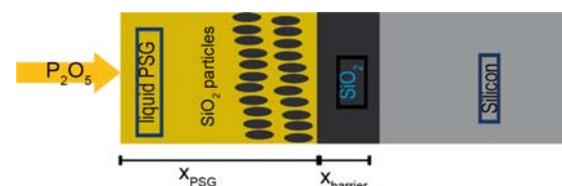Based on the work of Eldridge and Balk, Ghoshtagore [2] proposed a model sketched in Fig. 1.

Figure 1: Ghoshtagore model of PSG growth on SiO$_2$

The first layer of the PSG is a SiO_2/P_2O_5 mixture that is liquid at diffusion temperature because of a high P_2O_5 content. When the P_2O_5 concentration decreases close to the solid solubility of P_2O_5 in SiO_2, silicon dioxide crystallites begin to appear in the liquid. Further on, when the P_2O_5 concentration equals the solid solubility of P_2O_5 in SiO_2, a very thin layer of SiO_2 forms before reaching pure SiO_2. The thickness of this layer is, however, so low that it can be neglected [2].

2.2 Oxidation and interstitial flow in Si

An important aspect of the $POCl_3$ diffusion in silicon is the oxidation reaction at the Si surface. It has been measured and investigated theoretically [6] that such an oxidation increases the amount of self-interstitials at the silicon surface. At very high oxidation rate the concentration of interstitials could be multiplied by a factor close to 100 [6].
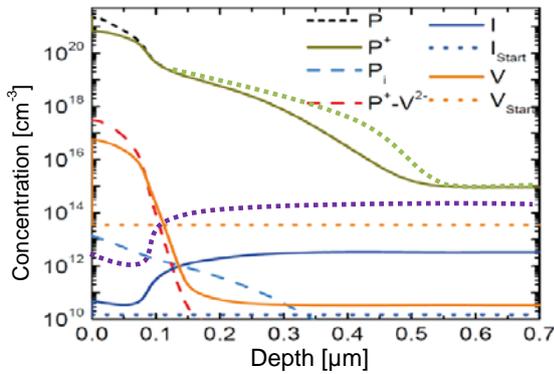

Figure 2: Synopsis Sentaurus simulation of a phosphorus diffusion including the concentration of phosphorus (P), electrically active phosphorus (P^+), Phosphorus-interstitial pairs (P_i) Phosphorus-vacancy pairs (P^+-V^{2-}) , silicon self-interstitials (I) with initial concentration (I_{start}) and vacancies (V) with initial concentration (V_{start}) (taken from [7]). The dashed violet line sketches an increase of interstitial concentration induced by an oxidation reaction at the Si surface and the dashed green line sketches its influence on the phosphorus profile tail shape.

Fig. 2 shows a synopsis SENTAURUS simulation of a phosphorus diffusion showing that the diffusivity in the high concentration range (the kink) is mediated by phosphorus-vacancy pairs and thus depends on the vacancy concentration. In the low concentration range (the tail), interstitials are more numerous than vacancies and the phosphorus diffusion occurs by phosphorus-interstitial pairs.

One can see in Fig. 2 that even if the concentration of interstitials is multiplied by 100 (violet dashed line), their number would be in any case much lower than the vacancy concentration in the kink. This means that the kink will not be modified by the increased number on interstitials, but only the tail will increase (green dashed line).

3 STUDY OF PSG THICKNESS

The model of Ghoshtagore explained in Sec. 2.1 does not describe a priori the PSG growth for the $POCl_3$ diffusion in Si, because there is no thick SiO_2 layer in this case.

However, O_2 molecules diffusing through the PSG will oxidize silicon and form SiO_2 as a layer or at least a dense network of SiO_2 crystallites.

It is known that the diffusion coefficients of P_2O_5, O_2 and P in silicon dioxide are low, and thus a SiO_2 layer would act as a strong diffusion barrier for these species influencing further P diffusion in Si.

It can only be inferred in this study (details in Sec. 5) that the P_2O_5 and O_2 flow reaching the Si interface could be reduced significantly between the beginning and the end of the diffusion which is consistent with the formation of a diffusion barrier.

Because of the likely presence of this barrier and its composition close to SiO_2, we will assume that the liquid phase 'sees' always a 'SiO_2 like' layer and that the model of Ghoshtagore for the thickness of the PSG (Eq. 1) is correct at least in a quantitative relative way.

It is important to mention that what is usually called PSG in the photovoltaic community is the layer that forms on silicon during the $POCl_3$ diffusion and could be removed using an HF dip. Therefore, in contrast to Ghoshtagore's definition of the PSG, it additionally includes the SiO_2 barrier. The total layer thickness is the thickness estimated by profilometer or Atomic Force Microscopy (AFM) but also the one estimated by ellipsometry, because the whole layer has optical constants close to silicon dioxide.

Considering that only the $POCl_3$ flow is varied for different samples (oxygen flow, temperature and diffusion time set to constant values standard in photovoltaics) one can express the thickness of the full PSG layer with the help of Eq. 1 as:

$$x_{fullPSG} = x_{barrier}\left(\Phi_{POCl3}\right) + A \cdot \sqrt{\Phi_{POCl3}}$$
(2)

with A being an arbitrary constant.

If one now assumes that $x_{barrier}$ is independent of the $POCl_3$ flow for these process conditions and that the $POCl_3$ flow is normalized to an arbitrary flow Φ_0, one gets the following relationship

$$x_{fullPSG} = x_{barrier} + B \cdot \sqrt{\Phi_{POCl3}/\Phi_0}$$
(3)

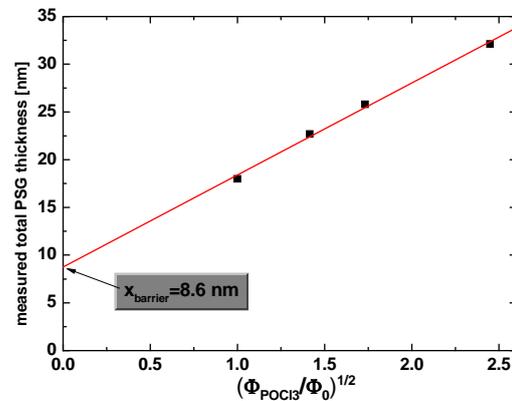with B being an arbitrary constant.

Figure 3: PSG thickness measurement represented as a function of the square root of the normalized $POCl_3$ flow

Consistently with Eq. 3, Fig. 3 shows the thickness of the PSG measured by ellipsometry as a function of the

square root of the normalized POCl$_3$ flow for emitters diffused using POCl$_3$ flows between Φ_0 and 6 Φ_0.

One can observe that the fitting according to Eq. 3 shows an almost perfect linearity. Therefore the assumption of $x_{barrier}$ being independent of the POCl$_3$ flow seems to be fulfilled and $x_{barrier}$=8.6 nm for these diffusion conditions and time. This value seems reasonable considering that a smaller value would not affect significantly the supply of P to the silicon wafer and a higher value should reduce it to a negligible value.

The fact that $x_{barrier}$ seems independent of the POCl$_3$ flow suggests that an equilibrium has been reached after 20 min of these diffusion condition.

4   STUDY OF ECV PROFILES

The samples of the first experiment were p-type Cz-Si wafers diffused for 20 min at various POCl$_3$ flows while keeping the O$_2$ flow and the temperature constant to standard values.
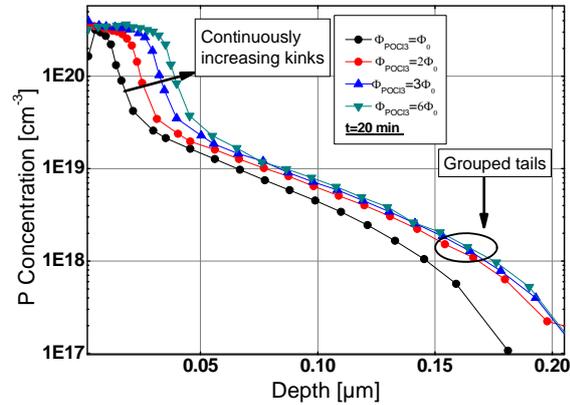

Figure 4: ECV profiles of emitters grown using Φ_{POCl3}=Φ_0, 2 Φ_0, 3 Φ_0 and 6 Φ_0 for t=20 min

In can be observed in Fig. 4 that while the kinks increase continuously with Φ_{POCl3}, the tail of the profile for Φ_{POCl3}=Φ_0 is lower than the tails of the three other profiles which are grouped together.

In a second experiment the Cz wafers were diffused for at first 10 min at Φ_{POCl3}=Φ_0 and the following 10 min at Φ_{POCl3}= Φ_0, 2Φ_0, 3Φ_0, 6Φ_0 (Fig. 5).

One can observe in Fig. 5 that while the kinks are slightly increasing with increasing POCl$_3$ flow during the second diffusion phase, the tail shows the inverse behavior except when the flow remains at Φ_0 for the following 10 min.

5 PSG FORMATION INTERPRETATION

Based on the Ghoshtagore model, an interpretation sketched in Fig. 6 is proposed.

Because the upper part of the PSG is liquid, the diffusion of P$_2$O$_5$ and O$_2$ is enhanced and therefore does not limit their transport.

The high P$_2$O$_5$ content of liquid PSG triggers the melting of the SiO$_2$ barrier. A significant flow of O$_2$ (red arrow) and P$_2$O$_5$ (light green arrow) through the barrier is expected to occur only when the barrier is thin. These flows would therefore be very strongly thickness
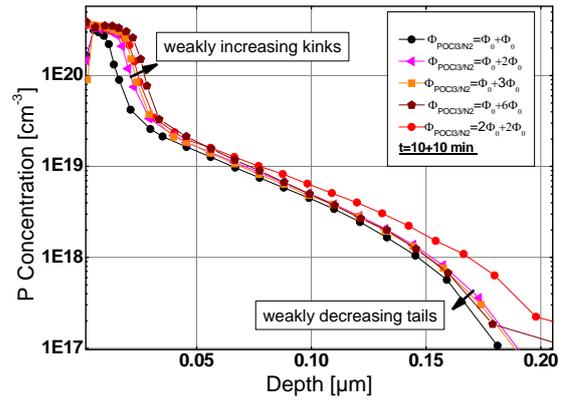

Figure 5: ECV profiles of emitters grown using Φ_{POCl3}=Φ_0 for the first 10 min of diffusion and Φ_{POCl3}=Φ_0, 2 Φ_0, 3 Φ_0 and 6 Φ_0 for the following 10 min
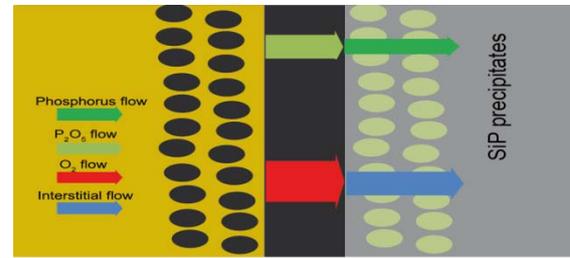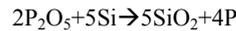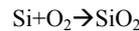

Figure 6: Sketch of the PSG transport phenomena based on the Ghoshtagore model (the legend is the same as in Fig. 1).

dependent. Then P$_2$O$_5$ reaching Si reacts to form P and SiO$_2$ according to

$$2P_2O_5+5Si \rightarrow 5SiO_2+4P$$

and O$_2$ reacts to form SiO$_2$ according to

$$Si+O_2 \rightarrow SiO_2$$

Because of the much higher content of O$_2$ than of P$_2$O$_5$ in the diffusion furnace, the second reaction is expected to be the main contributor to the formation of SiO$_2$ at the Si interface.

This oxidation reaction is also known to increase the amount of interstitials at the silicon surface (see Sec. 2.2) and thus increases the flow of interstitials (blue arrow) into the silicon.

The first reaction creates a large amount of phosphorus at the Si surface, and its concentration can exceed the solid solubility of P in Si. In such a case silicon phosphide (SiP) precipitates are formed in the silicon, reducing the phosphorus diffusion in silicon (green arrow). We make the assumption that they also reduce the diffusion of interstitials.

The sketches of Fig. 7 are a representation of the various flows crossing the PSG and silicon at an arbitrary time (but the same for all sketches) before the end of diffusion for various POCl$_3$ flows in the gas phase. At the end of the diffusion it is likely that the barrier layers have the same thickness (or at least similar) as explained in Sec. 3.
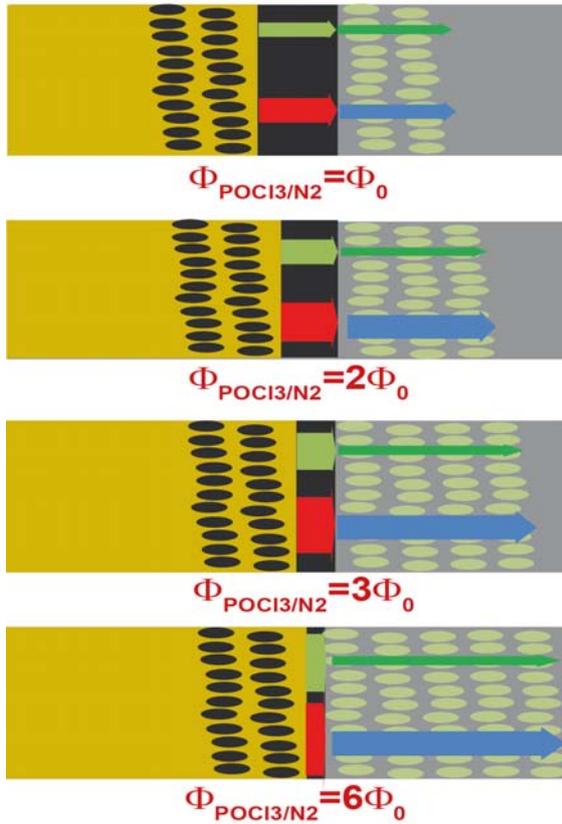
Figure 7: Sketch of the transport phenomena in the PSG before the end of the diffusion for various Φ_{POCl3} values (the legend is the same as in Fig. 1 and Fig. 6)

At low POCl$_3$ flow, because of the low P$_2$O$_5$ content of the PSG, the barrier melting is low and thus the barrier is thick. The flow of P$_2$O$_5$ and O$_2$ through the barrier is therefore low and so is the creation of P and interstitials at the Si surface. A low P content at the Si surface induces a low creation of SiP precipitates and therefore SiP does not present a large barrier to phosphorus and to the interstitials. However, the low density of interstitials has the direct consequence to induce a low tail while the low SiP content induces a low kink.

At medium and increasing POCl$_3$ flow the melting rate of the barrier is increased more and more because of the increased P$_2$O$_5$ content in the PSG. The barrier then becomes more and more permeable to O$_2$ and P$_2$O$_5$ which induces a higher formation of SiP precipitates and a higher density of interstitials in Si. The higher the density of SiP precipitates, the broader the kink.

On the other hand, the broader the SiP region, the higher the reduction of diffusivity for the interstitials which could compensate the gain in density at the surface. Therefore, the flow of interstitials is almost the same for all medium and high POCl$_3$ flow cases, even slightly decreasing with increasing POCl$_3$ flow. However, the influence of a higher concentration in the kink with increasing POCl$_3$ flow tends to increase the global level of the profiles, therefore the tails are slightly increasing with POCl$_3$ flow.

One has to mention that the interstitial flow was in any of these cases higher than that for the lowest POCl$_3$ flow sample, and therefore the tails for medium and high

POCl$_3$ flow profiles are all larger than the one at low POCl$_3$ flow.

Concerning the second experiment, the model remains valid, but we have to consider that the barrier was initially thicker (except for the case $\Phi_{POCl3}=\Phi_0$ that is common to both experiments). Therefore, more time is needed during the higher Φ_{POCl3} phase to melt the barrier enough to have a significant P$_2$O$_5$ and O$_2$ flow through it. The direct consequence is a delay of the diffusion process. Because for this experiment the kinks are reduced to almost the same magnitude (while weakly increasing with the POCl$_3$ flow), the effect of a higher concentration to increase the global level of the profile is weaker than in the first experiment.

The tails that should weakly reduce with increasing POCl$_3$ are far less compensated by this effect and they appear as weakly reducing with the POCl$_3$ flow.

We observed in our former study [3] that the diffusivity was increasing while reducing the POCl$_3$ flow at the beginning of the diffusion. This is consistent with the present study except for the low POCl$_3$ flow case that was not investigated in our former study.

6 FUTURE WORK

It was shown in our former study that the adaptation of Bentzen's parametrization [4], that discards the PSG formation, to model profiles obtained at low POCl$_3$ flow would be very dependant of the process conditions and not very physical. It is therefore proposed to include the PSG as a two-layer entity, and its growth should be calibrated with respect to thickness and phosphorus dose.

As P$_2$O$_5$ is supposed to react only at the silicon surface and P$_2$O$_5$ should have a very different diffusion behavior in the PSG than P in Si, we suggest including P$_2$O$_5$ in the model as a diffusing species through the PSG that reacts at the PSG/Si surface to form P.

Because the oxidation reaction at the silicon surface (dependant on the O$_2$ concentration) has a significant impact on the phosphorus diffusion in Si through the creation of interstitials, it is proposed to include O$_2$ as a diffusing species through the PSG that not only is taken into account for the PSG growth, but also for the interstitial injection in Si.

It is finally to be taken into account that SiP precipitates can reduce the diffusion of interstitials in Si.

The proposed model is presently under development.

7 CONCLUSION

Based on the model of Ghoshtagore for PSG growth on SiO$_2$, an exploitation of PSG thickness data obtained for POCl$_3$ diffusion at various POCl$_3$ flow has revealed the presence of a thin diffusion barrier. Its thickness could be estimated to be $x_{barrier}$=8.6 nm in the present diffusion conditions and diffusion time.

The fact that $x_{barrier}$ seems to be independent of the POCl$_3$ flow suggests that an equilibrium has been reached after 20 min under these diffusion condition.

The interpretation of ECV profiles of various emitters was performed according to a qualitative model of the PSG formation that is based on the Ghoshtagore model. Several aspects like the role of O$_2$ in increasing the interstitial density in Si as well as the role of SiP in reducing the interstitial diffusion were introduced in this

model and are likely to be of high importance for the quantitative model to be developed further.

8 ACKNOWLEDGEMENT

9 REFERENCES

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