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

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ABSTRACT: The diffusion of phosphorus mediated by phosphorus oxychloride (POCl₃) 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 POCl₃ decomposition in the gas phase in phosphorus pentoxide (P₂O₅) as well as the subsequent oxidation reactions induced by P₂O₅ and O₂ at the silicon surface are not very well documented and increase the complexity of a realistic simulation of the POCl₃ 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 POCl₃ diffusion. This model allowed to show that the PSG contains a thin layer of 8.6 nm, presumably composed of SiO₂, 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 POCl₃ flows, a qualitative model based on the Ghoshtagore model is presented. This model emphasizes the role of O₂ 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 POCl₃ 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). Provided that the phosphorus concentration in the PSG exceeds the solid solubility limit of P in Si and nor the formation nor the concentration at the PSG/Si surface has to be below the solubility (e.g. not having the kink), then the dopant flow to tailor the P profile at lower surface concentration (e.g. to have the kink) 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 Ghoshthagore [2] in 1976 to explain the PSG growth on SiO₂ 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 POCl₃ 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 POCl₃ flow, it was unsatisfactory at low POCl₃ flow because explicitly the assumption of infinite source does not hold true anymore.

From the diffusivity analysis of the low POCl₃ 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 POCl₃ 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 POCl₃ 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 SiO₂ layer in which P₂O₅ is diffused Eldridge and Balk [5] developed a semi-empirical growth law of the form

\[ x_{PSG} \propto \sqrt{c_p \cdot \exp(-E_a/kT)} \]  

(1)

in which \( x_{PSG} \) is the PSG thickness, \( c_p \) is the P₂O₅ concentration in the gas phase, \( t \) the diffusion time, \( E_a \) the activation energy, \( k \) the Boltzmann constant and \( T \) the diffusion temperature.

The P₂O₅ concentration could be strictly proportional to the POCl₃ concentration assuming that the decomposition of POCl₃ in an excess of O₂ goes to completion [5].

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

![Figure 1: Ghoshthagore model of PSG growth on SiO₂](image-url)
The first layer of the PSG is a SiO2/P2O5 mixture that is liquid at diffusion temperature because of a high P2O5 content. When the P2O5 concentration decreases close to the solid solubility of P2O5 in SiO2, silicon dioxide crystallites begin to appear in the liquid. Further on, when the P2O5 concentration equals the solid solubility of P2O5 in SiO2, a very thin layer of SiO2 forms before reaching pure SiO2. 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 POCl3 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].

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 POCl3 diffusion in Si, because there is no thick SiO2 layer in this case. However, O2 molecules diffusing through the PSG will oxidize silicon and form SiO2 as a layer or at least a dense network of SiO2 crystallites.

It is known that the diffusion coefficients of P2O5, O2 and P in silicon dioxide are low, and thus a SiO2 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 P2O5 and O2 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 SiO2, we will assume that the liquid phase ‘sees’ always a ‘SiO2 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 POCl3 diffusion and could be removed using an HF dip. Therefore, in contrast to Ghoshtagore’s definition of the PSG, it additionally includes the SiO2 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.

Figure 3: PSG thickness measurement represented as a function of the square root of the normalized POCl3 flow Consistently with Eq. 3, Fig. 3 shows the thickness of the PSG measured by ellipsometry as a function of the

\[ x_{\text{PSG}} = x_{\text{Naive}} \left( \frac{\Phi_{\text{POCl3}}}{\Phi_0} \right)^{1/2} + A \frac{\sqrt{\Phi_{\text{POCl3}}}}{\Phi_0} \]

with A being an arbitrary constant.

If one now assumes that \( x_{\text{Naive}} \) is independent of the POCl3 flow for these process conditions and that the POCl3 flow is normalized to an arbitrary flow \( \Phi_0 \), one gets the following relationship

\[ x_{\text{PSG}} = x_{\text{Naive}} + B \frac{\sqrt{\Phi_{\text{POCl3}}}}{\Phi_0} \]

with B being an arbitrary constant.
square root of the normalized POCl₃ flow for emitters diffused using POCl₃ flows between Φ₀ and 6 Φ₀.

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 POCl₃ 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 POCl₃ flow suggests that an equilibrium has been reached after 20 min of these diffusion conditions.

4 STUDY OF ECV PROFILES

The samples of the first experiment were p-type Cz-Si wafers diffused for 20 min at various POCl₃ flows while keeping the O₂ flow and the temperature constant to standard values.

In can be observed in Fig. 4 that while the kinks increase continuously with ΦPOCl₃, the tail of the profile for ΦPOCl₃ = Φ₀ 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 ΦPOCl₃ = Φ₀ and the following 10 min at ΦPOCl₃ = Φ₀, 2Φ₀, 3Φ₀, 6Φ₀ (Fig. 5).

One can observe in Fig. 5 that while the kinks are slightly increasing with increasing POCl₃ flow during the second diffusion phase, the tail shows the inverse behavior except when the flow remains at Φ₀ 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 P₂O₅ and O₂ is enhanced and therefore does not limit their transport.

The high P₂O₅ content of the liquid PSG triggers the melting of the SiO₂ barrier. A significant flow of O₂ (red arrow) and P₂O₅ (light green arrow) through the barrier is expected to occur only when the barrier is thin. These flows would therefore be very strongly thickness dependent. Then P₂O₅ reaching Si reacts to form P and SiO₂ according to

\[ 2P₂O₅ + 5Si \rightarrow 5SiO₂ + 4P \]

and O₂ reacts to form SiO₂ according to

\[ Si + O₂ \rightarrow SiO₂ \]

Because of the much higher content of O₂ than of P₂O₅ in the diffusion furnace, the second reaction is expected to be the main contributor to the formation of SiO₂ 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 POCl₃ 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.
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.

At high POCl$_3$ flow, because of the high P$_2$O$_5$ content of the PSG, the barrier melting is high and thus the barrier is thin. The flow of P$_2$O$_5$ and O$_2$ through the barrier is therefore high and so is the creation of P and interstitials at the Si surface. A high P content at the Si surface induces a high creation of SiP precipitates and therefore SiP presents a large barrier to phosphorus and to the interstitials. However, the high density of interstitials has the direct consequence to induce a large tail while the high SiP content induces a large kink.

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.

Concentrating 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 $\Phi_{POCl3}$ 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 parameterization [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 (dependent 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 conditions.

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

The authors wish to express many thanks to L. Mahlstaedt for the help during the cells processing.

9 REFERENCES