

DIFFUSIVITY ANALYSIS OF POCl₃ EMITTER SIMS PROFILES FOR SEMI EMPIRICAL PARAMETRIZATION IN SENTAURUS PROCESS

G. Micard, A. Dastgheib-Shirazi, B. Raabe, G. Hahn

University of Konstanz, Department of Physics, Jacob-Burckhardt-Str. 29, 78464 Konstanz, Germany

Author for correspondence: gabriel.micard@uni-konstanz.de, Tel.: +49 7531 88 2060, Fax: +49 7531 88 3895

ABSTRACT: The diffusion of phosphorus mediated by phosphorus oxychloride (POCl₃) is extensively used in photovoltaics due to its higher controllability over phosphine. However, the POCl₃ decomposition in the gas phase as well as the subsequent oxidation reaction between silicon and the resulting phosphorus oxide are not very well documented and increase the complexity of a realistic simulation of the POCl₃ diffusion. This paper examines the possibility of modeling the POCl₃ diffusion only by modifying the diffusion constants of a standard phosphine mediated diffusion simulation implemented in Sentaurus process. To this aim, the Boltzmann-Mattano Analysis (BMA) is applied to experimental SIMS profiles in order to extract a concentration dependent effective phosphorus diffusivity. The fitting of diffusivity profiles is then performed to determine the specific diffusion constants of the diffusion mechanisms believed to be responsible for the phosphorus diffusion in silicon. Through the study of specific artifacts appearing in the diffusivity profile because of the non ideal conditions for application of the BMA, it is believed that at low POCl₃ flow, the surface concentration during the pre-deposition phase is low enough to induce an enhanced diffusivity at the early stage of the diffusion. Finally, the assumptions of this diffusivity fitting are reviewed and a model matching these assumptions is identified in Sentaurus Process for a direct implementation of the BMA results into Sentaurus Process.

Keywords: Diffusion, Doping, Modeling

1 INTRODUCTION

While the diffusion of phosphorus impurities in a silicon wafer is well known in microelectronics for several years, the diffusion process always involved phosphine (PH₃) as a dopant gas. To the contrary of phosphine, phosphorus oxychloride (POCl₃) decomposes itself in the gas phase into a phosphorus oxide which induces an oxidation of silicon additionally to the release of phosphorus.

From the simulation point of view there is a lack of reliable information about this particular oxidation reaction as well as about the diffusion of the phosphorus oxide into the phosphorus silicon glass (PSG). It is examined in this paper whether it is possible to perform a simulation of the emitter doping profile disregarding the growth of the PSG. With these considerations, the displacement of the PSG/silicon interface as well as the probable variation of the phosphorus concentration at this interface in time is assumed to modify the diffusivities of a standard model for phosphine mediated diffusion.

Assuming that the effective phosphorus diffusivity (D_{eff}) depends only on the phosphorus concentration (C), one can extract this dependence from a SIMS profile making use of the Boltzmann-Mattano Analysis (BMA).

Because the BMA involves the calculation of the numerical derivative of the profile, the resulting $D_{\text{eff}}(C)$ curve is in general very noisy. We propose here to use the Savitsky-Golay Filter (S-G Filter) to extract the smoothed value of the profile derivative and of the profile resulting in a less noisy $D_{\text{eff}}(C)$ curve, particularly at low C values.

It was shown in [1] that the dependence of the effective diffusivity on the concentration could be modeled in terms of the diffusivities associated with various diffusing species: Si-interstitial/P pairs, vacancy/P pairs, and P-interstitials.

It is shown in this paper that this modeling is consistent with the parameters of the pair diffusion model in Sentaurus process allowing the results of this method to be used in a semi empirical parameterization of Sentaurus process.

SIMS profiles were measured for samples at the same temperature, same pre-deposition and drive-in time, same oxygen flow only varying the nitrogen flow in the POCl₃ bubbler.

A decrease of the effective diffusivity of Si-interstitials as well as vacancy-P pairs is observed for increased POCl₃ flow.

2 THEORY AND IMPLEMENTATION

2.1 Boltzmann-Mattano method

The concentration of phosphorus (C) in silicon is described by the second Fick's law expressed in one dimension in equation (1).

$$\frac{d}{dx} \left(D_{\text{eff}}(C) \frac{dC}{dx} \right) = \frac{dC}{dt} \quad (1)$$

Assuming that the effective diffusivity D_{eff} depends only on the concentration, Boltzmann [2] showed that, using the following transformation

$$\xi = \frac{x - x_M}{2\sqrt{t}} \quad (2)$$

in which x_M is the location of the Mattano interface (see later in the text), the second Fick's law that is a partial differential equation, could be expressed as

$$\frac{d}{d\xi} \left(D_{\text{eff}}(C) \frac{dC}{d\xi} \right) = -2\xi \frac{dC}{d\xi} \quad (3)$$

that is a non linear ordinary differential equation. Eq. (3) can be re-written to get $D_{\text{eff}}(C)$ which, coming back to the original variable, reads:

$$D_{\text{eff}}(C^*) = -\frac{1}{2t} \left(\frac{dx}{dC} \right)_{C^*} \int_{C_0}^{C^*} (x - x_M) dC \quad (4)$$

Where C_0 is the concentration obtained when the concentration does not change any more with depth and t is the diffusion time assuming no change in the diffusion conditions (same gas flows and same temperature). For practical reasons C_0 is taken to be the lowest value of the experimental profile.

Concerning the Mattano interface, it is the location where, at the end of the experiment, the dose of phosphorus found at its right side equals the total dose that arrived from the left side by diffusion [3]. However, considering that the surface concentration at the silicon/PSG interface is above the solubility limit of P in Si, one can consider the source to be infinite and thus consider that the Mattano interface is at 0 (the surface cannot be depleted and thus all the phosphorus dose in silicon originates from the surface). This assumption will, however, fail if the surface concentration becomes lower than the solid solubility which can happen at low POCl_3 flow.

The BMA involves the evaluation of the integral and of the derivative of the inverse profile ($x(C)$ instead of $C(x)$). Because of these features, two issues arise in the computation of the BMA:

- The numerical evaluation of the derivative can be very noisy if performed straightforwardly.
- Because of the noise a deeper consecutive point could have a slightly higher value than the considered point while the physical background implies that the concentration profile is a monotonically decreasing function of the depth. This will
 - reverse the sign of the derivative which implies a negative diffusivity and
 - make the inverse profile ambiguous (two values of x are possible for the same C).

We deal with these issues by means of the Satvisky-Golay Filter.

2.2 Satvisky-Golay Filter

This filter performs the least square (L-S) fitting of a window (with odd numbers of points) of the measured signal and replaces the central point of the window by the evaluation of the L-S polynomial at this abscissa. The window is then swept and the procedure repeated over the whole signal length.

Satvisky and Golay [4] observed that if the measured points are equally spaced, this procedure reduces to a classical digital filtering [5] and thus to a convolution by a suitable vector that depends on the order of the mentioned L-S polynomial and on the width of the window.

Thus, by taking a low order polynomial (order 3 to 5) and a large window (more than 11 points), one obtains a smoothing of the signal that preserves the global shape while removing the noise efficiently.

A very interesting point for the present case is that one can derive easily from the coefficient of the L-S polynomial the coefficients of its derivative. One can thus obtain a smoothed version of the derivative by the same procedure as for smoothing the signal just by changing the coefficients of the filtering vector.

The profile is divided in three different parts, the plateau, the kink, and the tail that are filtered independently because of different properties of noise and global shape of these different parts. Indeed, the stronger the noise, the larger the window and the more complicated the variation of the global shape is, the higher the degree of the polynomial. At the junction of two regions, one then must take care of not having a too high discrepancy between profile value and derivative estimated from both sides in order to reduce an unavoidable artifact in the BMA (see Fig. 3).

One can see in Fig. 1 that the evaluation of the derivative by the S-G filter improves drastically the

smoothness of the extracted derivative in comparison to the direct extraction from the profile or even from the S-G smoothed profile (see Fig. 2).

Applying the BMA (Eq. (4)) using the S-G filtered profile and derivative leads to the $D_{\text{eff}}(C)$ profile presented in Fig. 3.

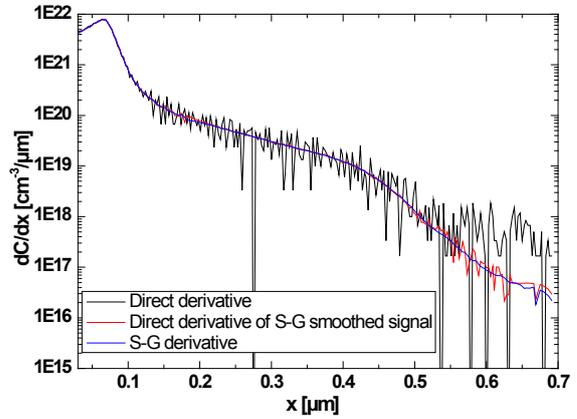


Figure 1: Example of a profile derivative obtained directly from the profile (black), from the Satvisky-Golay (S-G) filtered profile (red), and obtained by the estimation of the derivative of the S-G filter (blue).

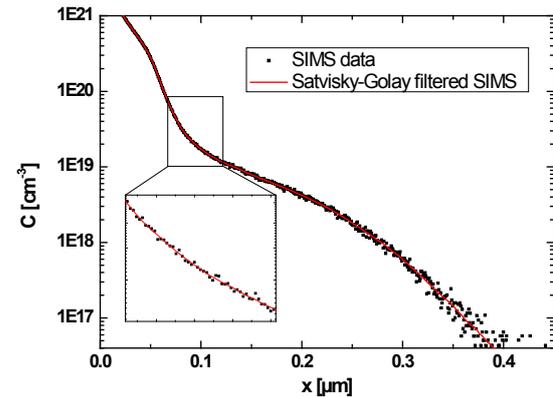


Figure 2: Example of an S-G filtered profile.

2.3 Effective diffusivity profile fitting.

It is described in [1] that four diffusion mechanisms need to be considered to understand a full range phosphorus profile in silicon.

- At low concentration range ($C < 5 \cdot 10^{18} \text{ cm}^{-3}$) the phosphorus diffusion occurs through the replacement of a lattice silicon atom by a neighbouring interstitial phosphorus atom (Pi diffusion). The lattice silicon atom is kicked out to an interstitial position thus the name of “kick out” for this phenomenon.
- At higher concentration ($5 \cdot 10^{18} < C < 10^{20} \text{ cm}^{-3}$) this diffusion mechanism becomes limited by the increasing amount of silicon atoms in interstitial position (self interstitial). One should then consider the diffusion of self interstitial (i diffusion) as a limiting mechanism.
- At even higher concentration ($10^{20} < C < 5 \cdot 10^{20} \text{ cm}^{-3}$), phosphorus diffuses via vacancies which are present in large enough quantities (Pv diffusion).
- Finally, when the concentration reaches the solubility limit of P in Si at room temperature ($C > 5 \cdot 10^{20} \text{ cm}^{-3}$),

formation of precipitates induce an apparent reduction of the effective diffusivity.

Discarding the last mentioned phenomenon, all the others bear their own diffusion equation and thus their own diffusivities with a specific Arrhenius dependence to the temperature and specific power law dependence to the electron concentration:

$$D_{P_i, P_v} = D_{0P_i, P_v} \left(\frac{n}{n_i} \right)^{k, l, m} \cdot h \quad (5)$$

In which h is the so called field enhancement factor which expression is:

$$h = 1 + \frac{C}{2n_i} \left(\left(\frac{C}{2n_i} \right)^2 + 1 \right)^{-1/2} \quad (6)$$

Considering that the self interstitial diffusion limits the interstitial phosphorus pair diffusion and that the vacancy phosphorus diffusion is an independent phenomenon, the effective diffusivity can be expressed as:

$$D_{eff} = D_{P_v} + \frac{D_i D_{P_i}}{D_{P_i} + D_i} \quad (7)$$

The electron concentration is computed at low concentration under equilibrium condition by the law of mass action under the requirement of charge neutrality:

$$n = \frac{1}{2} \left(C + \sqrt{C^2 + 4n_i^2} \right) \quad (8)$$

However, for concentrations above 10^{20} cm^{-3} , one should take into account that a part of the phosphorus is not activated and thus does not contribute to the concentration of electrons. Because in this range the intrinsic carrier concentration is much lower than the free electron concentration that could be assumed equal to the density of activated phosphorus, one could use the following empirical relationship [1]:

$$C = n + \frac{2(1.6 \cdot 10^{-41}) \cdot n^3}{1 - 1.6 \cdot 10^{-41} \cdot n^2} \quad (9)$$

which needs to be inverted numerically for getting the n value although an analytical expression exists but is very tedious.

The intrinsic concentration is calculated according to:

$$n_i = 1.8 \cdot 10^{21} \exp\left(-\frac{0.66}{kT}\right) \quad (10)$$

According to this model, an example of fitting is shown in Fig. 3.

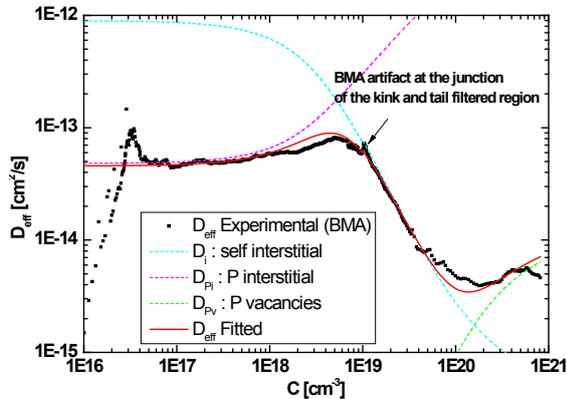


Figure 3: Example of phosphorus effective diffusivity as function of the concentration extracted from the S-G filtered profile of Fig. 2 with the fitting curve taking into account the mechanisms of self interstitial diffusion, interstitial phosphorus diffusion and BMA and vacancy diffusion.

3 EXPERIMENTS AND CONDITIONS OF APPLICATION

The BMA has been performed on emitter SIMS profiles obtained by POCl_3 diffusion at various high POCl_3 flows on Cz-Si. The known flow is the nitrogen flow that goes through the POCl_3 bubbler. The temperature is maintained constant at a standard value for industrial solar cells.

The first observation comes from the fact that the time to be used in the BMA equation (Eq. (4)) should be the total time of the diffusion assuming no change in the gas flows and the temperatures. In our case the gas flow changes between the pre-deposition and the drive-in phase. Therefore, strictly speaking the BMA cannot be applied. However, one has to remark in Eq. (4) that the diffusion time t is just a scaling factor and thus does not influence the shape of the curve. At high POCl_3 flow, the diffusivity curves extracted are qualitatively very similar to the ones found by Bentzen et al. for spray-on diffusion [1] except for a scaling factor.

Assuming that the diffusivity at low concentration (thus far from the surface) is the least subjected to variations between spray on and POCl_3 diffusion and that in both case a clear plateau value can be observed (see for $C < 10^{18} \text{ cm}^{-3}$ in Fig. 3), we defined an effective diffusion time for the whole process allowing us to superpose this plateau part in our diffusivity curve to the one of Bentzen et al. at the same temperature.

It is thus assumed that different diffusion conditions at the surface do not affect the diffusion mechanism happening deep in the wafer at low concentration.

4 RESULTS AND DISCUSSIONS

The effective time found to be used in the BMA was of the order of the total diffusion time used in the experiment (pre-deposition plus drive-in time) to 10% accuracy. One can therefore conclude that the phosphorus concentration at the PSG silicon interface remained above the solubility limit of P in Si during the whole process time allowing us to make the assumption of an infinite source for the whole diffusion time.

This assumption that appears to be valid for the four considered POCl_3 flows is probably not valid for lower flows and/or higher ratio $t_{\text{drive-in}}/t_{\text{pre-dep}}$.

We nevertheless observe in Fig. 4 that it is not possible to fit the phosphorus vacancy pair diffusion mechanism for the lowest POCl_3 flow, which is an indication of a beginning breakdown of the aforementioned assumption.

We observe in Fig. 4 a local increase of the diffusivity at low concentration that increases as the POCl_3 flow decreases. This phenomenon may be correlated with the changing of flow between the pre-deposition and the drive-in phase of the diffusion.

Indeed considering that during the pre-deposition the POCl_3 flow was low, the phosphorus concentration was low at the surface at the beginning of the diffusion, possibly in the range in which the highest diffusivity of phosphorus is observed (around $C = 5 \cdot 10^{18} \text{ cm}^{-3}$). During this period phosphorus at the surface diffused fast and deep until the density at the surface reached a higher value and becomes limited by the diffusivity of self interstitials. Therefore, the phosphorus diffused at this early period of diffusion penetrated deeper in the wafer

Table I: Fitting parameters for the $D_{\text{eff}}(C)$ curve according to parameters defined by Eq. (5).

Parameters at $T=T_{\text{diff}}$	D_{0Pi} (cm ² /s)	k	D_{0i} (cm ² /s)	l	D_{0Pv} (cm ² /s)	m
A. Bentzen [1] Spray-on Diffusion	1.394E-14	0.5	3.83E-13	-1.8	1.99E-19	2
$\Phi_{\text{POCl}_3/\text{N}_2}=3 \Phi_0$	1.394E-14	0.62	3.69E-13	-1.8	1.23E-19	2
$\Phi_{\text{POCl}_3/\text{N}_2}=1.5 \Phi_0$	1.394E-14	0.7	4.92E-13	-1.8	1.56E-19	2
$\Phi_{\text{POCl}_3/\text{N}_2}=\Phi_0$	1.394E-14	0.75	5.23E-13	-1.8	1.96E-19	2
$\Phi_{\text{POCl}_3/\text{N}_2}=0.75 \Phi_0$	1.394E-14	0.8	5.97E-13	-1.8	2.39E-19	2

than the phosphorus diffused afterwards. This higher amount of phosphorus found deeper in the wafer is translated into an increase of the low concentration diffusivity by virtue of the principle of the BMA (diffusivity evaluated from the integral of the concentration starting at $C=C_{\text{min}}$).

We can therefore deduce that the higher and the broader the increase of diffusivity, the longer the phosphorus concentration at the surface stays at a value close to $C=5 \cdot 10^{18} \text{ cm}^{-3}$.

The fitting of the diffusivity curves for the different POCl_3 flows was performed while discarding the aforementioned local increase of diffusivity and scaling the is the low C plateau diffusivity (D_{0Pi} value) equals the one found by Bentzen et al. (justification in the preceding chapter). For consistency reasons each power (k,l,m) was set at the same optimum value between samples of various POCl_3 flows, and when possible to the value found by Bentzen et al. The final set of extracted parameters is presented in Tab. I.

It is observed that the optimum k is always higher than the ones of Bentzen et al. [1] and is increasing for the decreasing of POCl_3 flow.

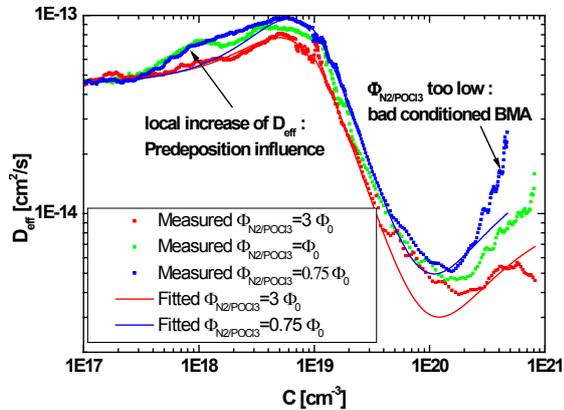


Figure 4: Comparison of diffusivity profiles extracted for three different values of the POCl_3 flow with some fittings. The effect of artifacts due to bad conditioning of the BMA at high concentration and non identical conditions during the diffusion (pre-deposition and drive-in) are indicated by arrows.

As Bentzen et al. attributed this value below one to a strong supersaturation of interstitial phosphorus, we conclude that these interstitials are less supersaturated than he described for spray-on diffusion. Spray-on diffusion implies from the start a very high phosphorus concentration at the surface which is the case here only for the highest POCl_3 flow, for which the value of k is the closest from the one he found. This observation is then in agreement with his result.

Reasonable agreement between BMA profile and fitting were found considering l and m to be at the same value Bentzen et al. found.

An increase of D_{0Pv} is then observed with decreasing POCl_3 flow. This correlated phenomenon is consistent with a higher saturation of the vacancies at high POCl_3 flow by oxygen that reduces the amount of free vacancies and then the ability of phosphorus to diffuse by a vacancies assisted mechanism.

An increase of D_{0i} is also observed with decreasing POCl_3 flow. This correlated phenomenon is viewed as a consequence of the aforementioned lower supersaturation.

4 INTEGRATION OF THESE RESULTS IN SENTAURUS PROCESS

The present analysis uses a computation of the carrier density based only on the local phosphorus concentration. Therefore, a model computing self consistently the Poisson equation (the model labeled ‘Charged’ in Sentaurus) and thus taking into account all the sources of charge is discarded to use the result of the present analysis.

As shown previously, self interstitial diffusion explains the decrease of diffusivity in the mid range concentration by limiting the supply of self interstitials necessary to mediate the interstitial phosphorus pair diffusion mechanism. A model discarding the diffusion of self interstitials is therefore inconsistent with the present analysis result and its subsequent use in implementation. However, the present analysis assumes also that the pair creation or dissociation reactions are in equilibrium.

With the two above considerations, the Sentaurus process model that seems to be best suited for the implementation of the results of this analysis is the ‘Pair’ model.

Clustering issues are only dealt with by a very simple model based only on the solid solubility of P in Si, and therefore the model ‘Solid’, that is based only on the solid solubility, seems to be the most suitable.

5 FUTURE WORK

It is planned to investigate the role of oxygen in the reduction of diffusivity of phosphorus by making the same kind of investigation varying the oxygen flow.

The influence of diffusion during pre-deposition resulting in a local increase of apparent diffusivity at low concentrations will be further investigated by varying the pre-deposition conditions.

The integration of the BMA analysis results will be integrated in Sentaurus process.

6 CONCLUSION

It has been shown that the use of the Savitsky-Golay (S-G) filter can enhance the accuracy of the Boltzmann-Mattano Analysis (BMA) providing an adaptation of the filter parameters with respect to the noise amplitude and the global shape of the profile.

The study of artifacts like the local increase of apparent diffusivity due to a lower concentration at the surface during pre-deposition gives some information about the conditions during pre-depositions.

Therefore, despite the fact that the BMA is used in ill-conditions, the interpretation of the specific artifacts induced by the non ideal conditions of application gives some information about the pre-deposition condition.

The fitting of the BMA by the Bentzen model [1] are in general pretty accurate within the limit of application of the BMA. Therefore, providing a tuning of the pair model in Sentaurus process it seems reasonable to obtain a good match between the experimental and simulated profile.

However, because several phenomena are discarded in the present analysis one should retune the parameters for all flows and temperature until a model taking into account the aforementioned phenomena is developed.

7 ACKNOWLEDGEMENT

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

8 REFERENCES

- [1] A. Bentzen. et al., J. Appl. Phys. 99 (2006) 064502.
- [2] L. Boltzmann, Wiedemanns Ann. Phys. 53 (1894) 959.
- [3] H. Mehrer, "Diffusion in solids" Springer-Verlag Berlin Heidelberg (2007).
- [4] A. Savitzky, M.J.E. Golay, Anal. Chem. 36(8) (1964) 1627-1639.
- [5] R.W. Hamming, "Numerical Methods for Scientists and Engineers", 2nd ed., Dover Publications, New York, (1986).