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Arsenic Diffusivity Study by Comparison of Post-Surface and Post-Implant Diffusion in Silicon with Local Density Diffusion (LDD-) Model Approximation

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Abstract

The LDD model was first applied to Arsenic concentration profiles determined in surface diffusion experiments by Yoshida and Arai [1]. The new method presented is based on a mathematical convolution with a delta-function-like concentration profile. By comparing the LDD approximation of post-surface diffusion with post-implant diffusion experiments, the same LDD model parameter *r* is found to hold for both experimental arrangements. This work found that post-implant diffusivity is concentration dependant and this might indicate an anomalous diffusion mechanism for Arsenic.

Keywords: Arsenic, Silicon, implant, diffusion, non-Gaussian diffusion model

Introduction

Arsenic is a key donor impurity for ultra shallow junction engineering in today's microelectronic technology. For high performance FET devices in the sub 100nm range it is critical to balance thermal dopant activation with the diffusion distance. The diffusion behavior of Arsenic was studied by surface diffusion experiments and described in terms of the dual pair diffusion model by Yoshida and Arai [1]. Arsenic implant and diffusion in Silicon is investigated by numerous teams and also part of the investigation in Ref. [2] for example. In many cases in the literature, numerical simulations are applied to model Arsenic diffusion by *ab initio* or kinetic Monte Carlo simulations [3]. With the LDD model the understanding of diffusion diverges by introducing both forward (towards the penetration direction) and backward (or reflected) diffusion current density. Since the LDD model was created and applied to Arsenic surface diffusion experimental results first time in Ref. [4], the model has been improved with focus on impurity post-implant and post-epitaxial diffusion profiles and clustering effects of Boron [5]. Based on the mathematical convolution

approach [6] the same diffusivity function holds under different experimental conditions. This work details LDD approximation results, obtained by SIMS profile approximations either post Arsenic implant or post-surface diffusion by the same convolution approach [6]. Surface diffusion is modeled by convoluting the LDD diffusivity function with a delta-function-like surface profile, as explained in the following section.

A. Convolution with delta function like surface profile

To describe Arsenic impurity diffusion post-surface and post-implant diffusion, both the initial impurity profile $c_0(x)$ and the diffusivity model $D(x)$ have to be considered. In this approach, the final concentration profile $c(x)$ is obtained by the mathematical convolution given in Equ. 1 ([6]).

$$c(x) = [c_0 * D](x) = \int_{-\infty}^{\infty} c_0(r)\, D(x-r)\, dr \tag{1}$$

In the case of impurity diffusion from a vapor atmosphere through the sample surface into the volume (positive x direction), the initial concentration slope $c_0(x)$ prior to diffusion is assumed to be a single surface concentration constant value c_0:

$$c_0(x) = \begin{cases} c_0 & x = 0 \\ 0 & else \end{cases} \tag{2}$$

Based on this assumption (see Equ. 2), the convolution integral of the initial concentration slope $c_0(x)$ and diffusivity model $D(x)$ as given in Equ. 1 is solved by partial integration in Equ. 3:

$$\int_{-\infty}^{\infty} c_0(r)\, D(x-r)\, dr = \int_{-\infty}^{\infty} c_0(r)\, D'(x-r) dr - \underbrace{\int_{-\infty}^{\infty} c_0{}'(r)\, D(x-r) dr}_{=0} \tag{3}$$

Considering Equ. 2, the integral in Equ. 3 simplifies further in Equ. 4 (ξ is an infinitesimal small environment around zero):

$$\int_{-\infty}^{\infty} c_0(r)\,D'(x-r)\,dr = \underbrace{\int_{-\infty}^{-\xi} c_0(r)\,D'(x-r)\,dr}_{=0} + \int_{-\xi}^{+\xi} c_0(r)\,D'(x-r)\,dr + \underbrace{\int_{+\xi}^{\infty} c_0(r)\,D'(x-r)\,dr}_{=0}$$

$$= c_0 \int_{-\xi}^{+\xi} D'(x-r)\,dr = c_0\left[D(x-r)\right]_{-\xi}^{+\xi} \qquad (4)$$

$$\begin{array}{ll} \textit{with } \xi \to +0 & D(x-\xi) = D(x) \\ \textit{and } \xi \to -0 & D(x+\xi) = 0 \end{array}$$

$$= \underline{\underline{c_0 D(x)}}$$

Because the diffusivity model *D(x)* is always defined independently from the absolute concentration level as given in Equ. 5, the scaling factor c_0 in Equ. 4 represents the integral value of the post diffusion impurity slope, as shown in Equ. 6.

$$\int_{-\infty}^{+\infty} D(x)\,dx = 1 \qquad (5)$$

$$\int_{-\infty}^{\infty} c(x)\,dx = c_0 \int_{-\infty}^{\infty} D(x)\,dx \;\rightarrow\; \underline{\underline{c_0 = \int_{-\infty}^{\infty} c(x)\,dx}} \qquad (6)$$

Equ. 6 proves that c_0 is equal to the integral of the LDD approximation post-surface diffusion. Fig. 1 illustrates Equ. 6 schematically, by convoluting a diffusivity function *D(x)* with delta-function-like surface concentration profile $c_0(x)$. If we set parameter $c_0=1$ (see Fig. 1a) or to a value according to Equ. 6 (see Fig. 1b) it can be seen in Fig. 1, that the convolution result *c(x)* in Fig. 1b is perfect aligned with *D(x)*. This is expected from calculus mathematics point of view also.

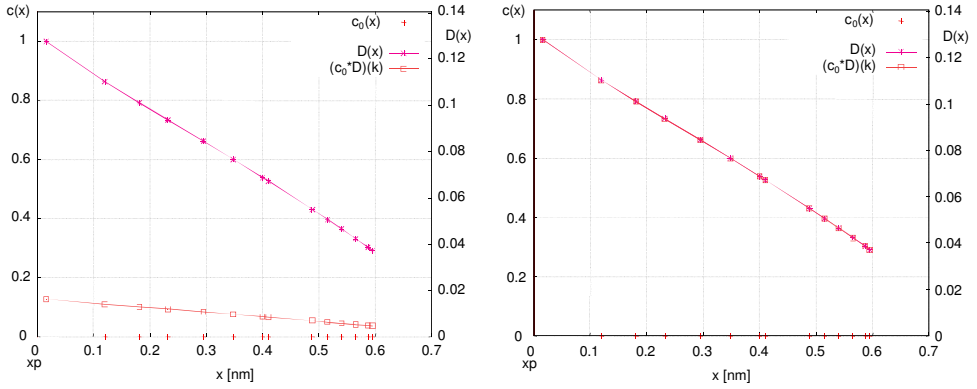


Figure 1: Mathematical convolution result of delta function like $c_0(x)$ profile according to Equ. 2 with diffusivity function $D(x)$ (Equ. 6) of LDD model for a) $c_0=1$ and b) c_0 =5.45 according to Equ. 6 ($D(0)$ =0.1835, see Equ. 4).

B. LDD model

As introduced earlier [5], the Local Density Diffusion (LDD-) model, given in Equ. 7 for delta-function-like profile $c_0(x)=c_0$ (e.g. $c_0*D(x) \Rightarrow c_0 \times D(x)$), is based on Equ. 8 in a one dimensional frame. Equ. 7 consist of a quadratic term for forward and a logarithmic term for backward diffusivity, as well as the zero diffusion term ZD. Zero diffusion (ZD) is used for Boron diffusion in Silicon and Silicon-Germanium alloys [5], but is not seen for Arsenic diffusion in Silicon so far and is therefore not considered in this work.

$$c_0 \times D(x) = c_0 \left[2 - \frac{1}{4}\left(\frac{x}{x_i} + r \right)^2 - \frac{1}{2}\log\left(\frac{x}{x_i} + r \right) \right] + ZD(\ldots) \tag{7}$$

$$\Delta c + \frac{1}{x}\nabla c + c_0 = 0 \tag{8}$$

Equ. 8 originates from Fick's 2nd law given in Equ. 9 by replacing the total diffusion current density j from Equ 10. Equ. 8 is further extended by adding the concentration constant c_0 in agreement with former work (see Ref. [5]):

$$k\Delta c - \dot{c} = 0 \tag{9}$$

$$j = \frac{1}{A}\dot{n} = \frac{1}{A} V \ \dot{c} = x \ \dot{c} \tag{10}$$

Considering Fick's 1st law in Equ. 11, Equ. 8 is derived under the assumption of a constant volume over time.

$$j = -k\nabla c \tag{11}$$

Experiments

Six samples of mono crystalline silicon with <100> surface orientation are used for Arsenic implantation at 20keV and 5×10^{15} or 5×10^{14} cm^{-2} dose. This is followed by either a spike or soak anneal, or no anneal for reference (see Table. 1). Following sample preparation, SIMS spectra were measured on a CAMECA tool as shown in Fig. 2 and discussed in next section.

Table 1: Sample preparation overview for Arsenic implant and anneal experiments in this work.

(1)	(2)	(3)	(4)	(5)
Sample No.	Arsenic, 20keV, $5\times10^{15}cm^{-2}$, tild=7deg		Arsenic, 20keV, 5×10^{14} cm^{-2}, tild=7deg	
	Spike Anneal (75K/s, 1070°C)	Soak Anneal 1050°C, 5s, N_2	Spike Anneal (75K/s, 1070°C)	Soak Anneal 1050°C, 5s, N_2
#34	Reference			
#33	x			
#32		x		
#31			Reference	
#30			x	
#29				x

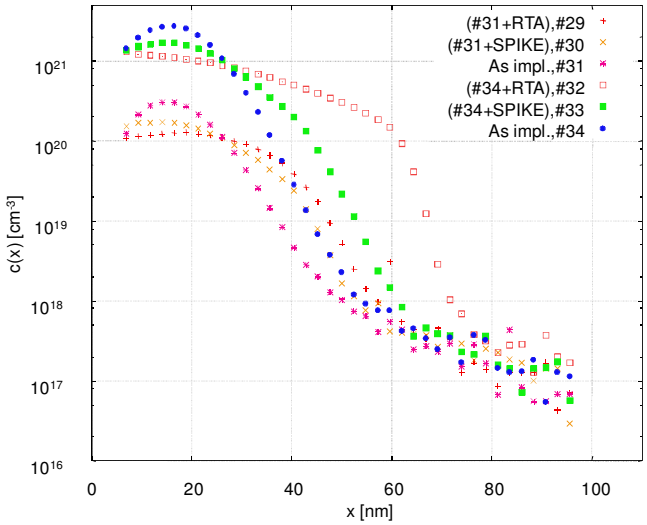


Figure 2: Arsenic SIMS profiles obtained from samples processed as listed in Tab. 1.

Discussion

A. Arsenic Surface Diffusion

In order to compare the concentration profile from this work with post-surface-diffusion experiments, a sequence of Arsenic SIMS spectra at 850°C, 900°, 950°C and 100°C anneals is taken from Ref. [1]. These Arsenic profiles [1], labeled #As1-#As4 are shown in Fig. 3. The plots in Fig. 3 are scaled by a penetration depth parameter $x/\sqrt{t}$, as provided in Ref. [1]. All post diffusion SIMS spectra labeled "(*c0*D*)(*k*)" in Fig. 3 are obtained by the convolution approach given in Equ. 1. Fig 3 also shows the diffusivity function *D(x)* (Equ. 7) and the delta-function-like surface concentration profile c_0 (see Equ. 2). The applied LDD model parameters in Fig. 3 are summarized in Tab. 2. The approximation parameter *r* given in Tab. 1 is adjusted

compared to the former reference value of 0.43 (Ref. [4]) down to r=0.33 for two reasons:

(i) A LDD model adjustment with unified x- coordinates was introduced, as can be seen by comparing Equ. 7 with Equ. 6 in Ref [4]. This affects the LDD model parameter r. The penetration depth parameter x_i is also shifted with this model change.

(ii) An LDD approximation of Arsenic diffusion post implant is found to be more sensitive to model parameter adjustments and an r value of 0.33 is found to be more appropriate. This point is discussed later in this section.

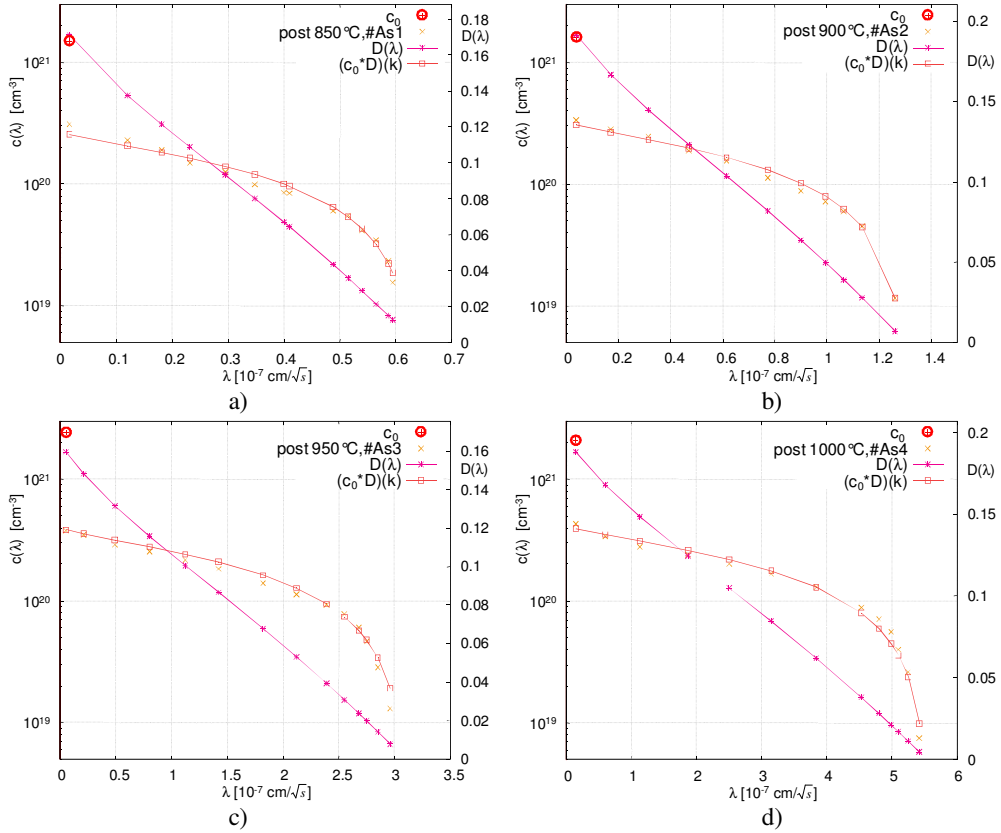


Figure 3: Arsenic SIMS profiles after surface diffusion experiments as published in Ref. [1] and LDD model approximation ("(*c0*D)(k)", Equ. 7) by convolution approach as given in Equ. 1. Sample data and approximation parameters are listed in Tab. 2

Table 2: LDD model parameters (Equ. 7) for Arsenic SIMS spectra shown in Fig. 3 after convoluting (Equ. 1) with initial delta function like surface concentration profile $c_0(\lambda)=c_0$ (Equ. 2).

(1)	(2)	(3)	(4)
Sample	Anneal Temp. [°C] (see [1])	LDD model approximation (r=0.33) c_0 (cumulative)	λ_i
#As1	850	1.5×10^{21}	0.46
#As2	900	1.6×10^{21}	0.96
#As3	950	2.4×10^{21}	2.22
#As4	1000	2.1×10^{21}	4.10

B. Arsenic post Implant and Diffusion

Arsenic SIMS profiles post implant and anneal, shown in Fig. 2, are used for LDD model approximation by the identical global model parameter r=0.33 as before in this work. The Arsenic profiles pre- and post-anneal ($c_0(x)$ and $c(x)$), as well as the LDD model approximation profile "$(c_0*D)(k)$" and the related diffusivity function $D(x)$ are shown in Fig. 4, for the samples listed in Tab. 1. Neither impurity surface- reflection nor surface-out-diffusion was taken into account for this simulation, because there was no clear evidence for such effects in the measurement. Fig. 4a,b shows results post high Arsenic dose implantation of 5×10^{15}cm^{-2} , while Fig. 4c,d shows profiles with ten times lower Arsenic implant dose (5×10^{14}cm^{-2}). The projected Arsenic penetration depth x_p is matched at 16 nm for all samples, because of the same applied implant acceleration voltage as given Tab. 1. After Spike anneal treatment of samples #33 and #30, the Arsenic LDD model penetration depth parameter x_i was found to be matched at 21 nm in Fig. 4a,c and to be independent of implant dose.

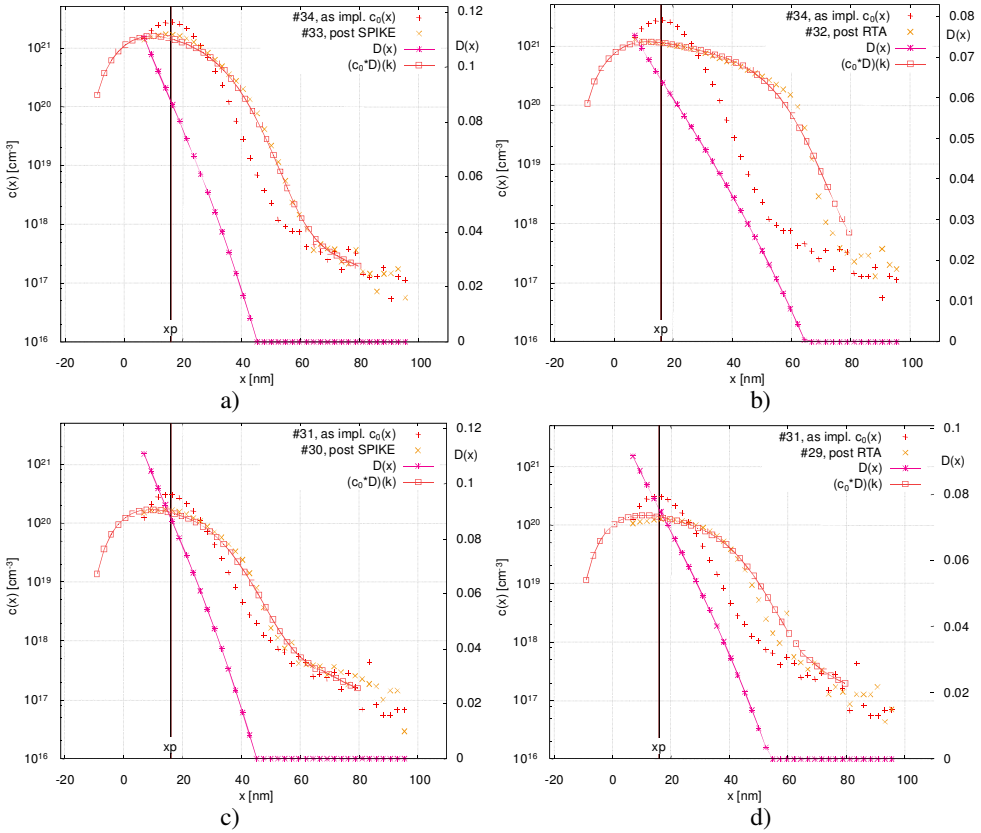
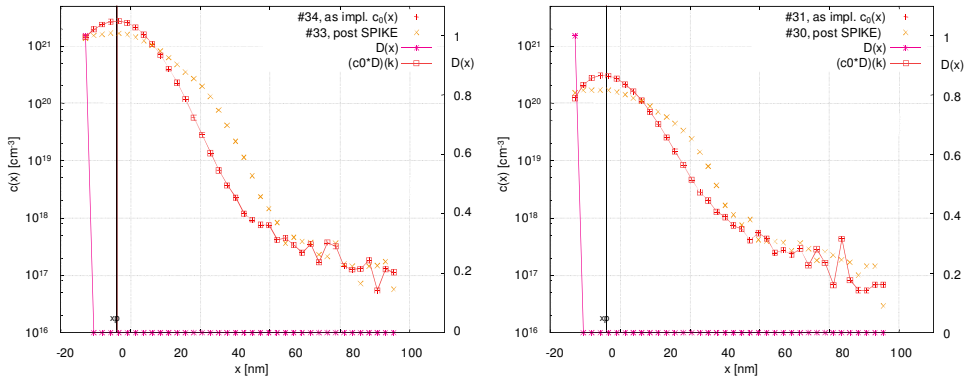


Figure 4: Arsenic SIMS spectra post implant and diffusion $c(x)$ of samples #29-#34 (simulation parameters are given in Tab. 3), shown together with LDD model approximations by the convolution approach "$(c_0*D)(k)$" as given in Equ. 1 (initial implant profile $c_0(x)$, $D(x)$ is LDD model's diffusivity function).

Table 3: LDD model approximation parameters x_i for diffusion profiles shown in Fig. 4. Sample preparation conditions are listed in Tab. 1. For all approximations a global LDD model parameter of x=0.33 is used.

(1)	(2)	(3)
Sample	Projected Implant Penetration x_p [nm]	LDD Model Parameter x_i [nm]
#As34	Reference	
#As33	16	21
#As32	16	36
#As31	Reference	
#As30	16	21
#As29	16	25

To illustrate the LDD model parameter x_i impact on the approximated diffusion length, the simulation in Fig. 5 for samples #33 and #30 (compare Fig. 4a and 4c) is shown. Under applied simulation condition x_i<=4nm in Fig. 5, the LDD model approximates the initial Arsenic concentration slope $c_0(x)$ perfectly. Diffusion length is represented by model parameter x_i therefore and is given in Tab. 3 for the analyzed samples. An error of approximately 4 nm is estimated because of the measurement resolution.



a) b)

Figure 5: LDD model simulation test with parameter condition x_p=16nm and x_i minimal (<=4 nm, depending on measured profile resolution) and the convolution approach in Equ. 1 for a) high dose (5×10^{15}cm^{-2}) and b) low dose (5×10^{14}cm^{-2}) Arsenic implant profiles $c_0(x)$ (pls. compare Fig. 4a,c). Under this condition the initial Arsenic profile $c_0(x)$ is approximated by the LDD model perfectly

By comparing the Arsenic concentration slopes $c(x)$ in Fig. 4b (low dose) with 4d (high dose), the SIMS profiles clearly show different diffusion lengths. This is also approximated by the model based diffusion lengths x_i of 36 nm versus 25 nm in column 3 of Table 3 (samples #32 vs. #29). The same Soak anneal was applied to both samples. Because of the equivalent conditions while processing the samples, this shift in parameter x_i is assumed to be Arsenic concentration related. This observation has to be justified by a more detailed investigation before conclusions can be drawn. There are however arguments for and against this effect:

Arguments for this effect : This observation points to a known, so called anomalous diffusion behavior: “Anomalous diffusion is the rule in concentration-dependent diffusion processes” [7]. Anomalous diffusion was discussed for Boron in Silicon widely, but resolved by interstitial diffusion and high concentration agglomeration as the major effect [8]. Furthermore, a non linear “local density

diffusivity coefficient *d*(LDD)" was already proposed for Phosphorus and Arsenic diffusion in [4] (see Fig.4 in Ref. [4]), related to concentration-dependent diffusion.

Arguments against: In general, if the observed effect indicates an increased Arsenic diffusivity at high concentration, this will contradict Arsenic clustering effects, predicted by *ab inito* calculations [9].

By comparison of the fit and residuals of the LDD approximation "$(c_0*D)(k)$" to the $c(x)$ slope in Fig. 4b, a raise in residuals magnitude at large diffusion lengths can be seen. This indicates, that the LDD approximation and convolution with the initial concentration profile slope $c_0(x)$ does not always predict the future concentration slope $c(x)$ precisely. Caused may be by the limited resolution of the initial concentration slope measurement or by measurement errors or secondary effects in the host lattice implant damage. The host lattice disorder along the diffusion path post-implant seems to be of relevant impact for LDD approximation, because the post-surface diffusion experiments in Fig. 3 are fitted precisely at every diffusion length. This is even true for the largest diffusion lengths.

Summary

The LDD approximation approach as given in Equ. 1 is used first time for post-surface diffusion and post-implant diffusion experimental results at the same time. It is shown, that the surface concentration level c_0 of a delta function profile reflects the total impurity amount measured post-diffusion, instead of the commonly applied surface concentration level itself. The LDD model is found to be applicable for Arsenic diffusion in Silicon under both surface and implant experimental conditions by using the same empiric model parameter r=0.33. It should be noted that the LDD model parameter x_i reflects the diffusion distance. This parameter is now called the LDD model based diffusion length, and is naturally specified within an experimental error given by measurement resolution.

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