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SIMULATION OF SEMICONDUCTOR DEVICES AND PROCESSES Vol. 4
Edited by W. Fichtner, D. Aemmer - Zurich (Switzerland) September 12-14, 1991 - Hartung-Gorre

On Limitations of Pair-Diffusion Models for Phosphorus Diffusion

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Abstract

In recent time there have been several attempts to develop unified diffusion models for application in process simulation programs. Accurate prediction of phosphorus diffusion is one of the important aims of these efforts. Comparisons between experimental results and simulations presented here, however, indicate that pair-diffusion models proposed so far are incomplete. A pragmatic extension of a standard pair-diffusion model allows the simulation of phosphorus diffusion with a fixed set of parameters.

1   Introduction

New approaches to impurity diffusion in silicon suggested by various authors are based on point defect-impurity pair mechanisms [1,2,3]. Anomalous diffusion phenomena like kink and tail which can be observed especially in case of high concentration phosphorus diffusion are qualitatively reproduced by numerical solutions of the resulting model equations. As has been shown by several authors, it is possible to approach individual experimental profiles by adapting model parameters accordingly [1,2]. The general validity of pair-diffusion models, however, has not yet been ascertained. It will be shown that using a standard model which has been derived on the basis of generally accepted assumptions, it is not possible to simulate a series of experimental profiles with a fixed set of parameters. A consistent model extension has been developed which includes cluster effects in a pragmatic way. This model ex-

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tension allows simulations of a series of experimental profiles with a fixed set of parameters although deviations between simulations and measurements for profiles implanted with medium doses still occur. It is therefore concluded that commonly used pair-diffusion models are incomplete. In general, modifications of these models are necessary. The extension suggested here, however, has to be considered as one of several possible ways to improve the describtion of diffusion phenomena.

2 Theory

2.1 Standard pair-diffusion model

Numerical simulations of phosphorus diffusion have been performed using a simplified standard pair-diffusion model [4] which includes all important features of pair-diffusion. In this model, the behavior of defects is described by a time-independent equation:

$$\left(D_{AI}\left(C_{A^+}\frac{\partial}{\partial x}\frac{C_{I^0}}{C_I^{eq}} + \frac{C_{I^0}}{C_I^{eq}}\frac{\partial C_{A^+}}{\partial x} + C_{A^+}\frac{C_{I^0}}{C_I^{eq}}\frac{\partial}{\partial x}\ln\frac{n}{n_i}\right)\right) +$$

$$\left(D_I C_I^{eq}\right)\frac{\partial}{\partial x}\frac{C_{I^0}}{C_I^{eq}} -$$

$$\left(D_{AV}\left(-C_{A^+}\left(\frac{C_I^{eq}}{C_{I^0}}\right)^2\frac{\partial}{\partial x}\frac{C_{I^0}}{C_I^{eq}} + \frac{C_I^{eq}}{C_{I^0}}\frac{\partial C_{A^+}}{\partial x} + C_{A^+}\frac{C_I^{eq}}{C_{I^0}}\frac{\partial}{\partial x}\ln\frac{n}{n_i}\right)\right) +$$

$$\left(D_V C_V^{eq}\right)\left(\frac{C_I^{eq}}{C_{I^0}}\right)^2\frac{\partial}{\partial x}\frac{C_{I^0}}{C_I^{eq}} = 0 \tag{1}$$

where C_A+ is the concentration of phosphorus ions, C_{I^0} is the concentration of neutral self interstitials and C_I^{eq} is the concentration of interstitials in thermal equilibrium. The concentration of electrons is given by n, and n_i is the intrinsic carrier concentration.

D_{AI} and D_{AV} are the Fermi-level dependent phosphorus diffusion coefficients according to interstitial-mechanism and to vacancy-mechanism. The products $D_I C_I^{eq}$ and $D_V C_V^{eq}$ depend on the Fermi-level, too:

$$D_I C_I^{eq} = D_{I^0} C_I^{eq} + D_{I^-} C_{I^-,i}^{eq}\left(\frac{n}{n_i}\right) + D_{I^=} C_{I^=,i}^{eq}\left(\frac{n}{n_i}\right)^2$$

$$D_V C_V^{eq} = D_{V^0} C_V^{eq} + D_{V^-} C_{V^-,i}^{eq}\left(\frac{n}{n_i}\right) + D_{V^=} C_{V^=,i}^{eq}\left(\frac{n}{n_i}\right)^2$$

where, e.g. $D_{V^-} C_{V^-,i}^{eq}$ is the contribution of vacancies in single negative charge state for intrinsic conditions $(n = n_i)$. A continuity equation describes the diffusion of phosphorus:

$$\frac{\partial C_{A^+}}{\partial x} = \frac{\partial}{\partial x}\left(\left(D_{AI}\frac{C_{I^0}}{C_I^{eq}} + D_{AV}\frac{C_I^{eq}}{C_{I^0}}\right)\left(\frac{\partial C_{A^+}}{\partial x} + C_{A^+}\frac{\partial}{\partial x}\ln\frac{n}{n_i}\right)\right) +$$

$$\frac{\partial}{\partial x}\left(C_{A^+}\left(D_{AI} - D_{AV}\left(\frac{C_I^{eq}}{C_{I^0}}\right)^2\right)\frac{\partial}{\partial x}\frac{C_{I^0}}{C_I^{eq}}\right) \tag{2}$$

Within the pure formalism of pair-diffusion, no effects from clustering and precipitation are taken into account.

In addition to these coupled differential equations, a third equation providing charge neutrality has to be considered:

$$p + C_{A^+} = n \tag{3}$$

where p denotes the concentration of holes. The above system of equations has been implemented in PROMIS [5] to provide numerical solutions. As has been shown in [4], calculated profiles agree well with experimental phosphorus profiles at least in some cases especially when maximum concentrations are not to high. It is, however, not possible to achieve good agreement between simulations and experimental profiles in general.

2.2 Extended model

In the model described above, high concentration effects like clustering or precipitation are not included. Experimetal results, however, indicate that in the regime of high phosphorus concentration precipitation occurs and that the total atomic phosphorus concentration differs from the electrical active concentration [6]. Since anomalous phosphorus diffusion phenomena are observed especially in cases of high concentrations, these effects are expected to play an important role. To describe such phenomena, an extension of the model described above based on a simple cluster model [7] has been developed. The total concentration of phosphorus C_{total} is then given by:

$$C_{total} = C_{A^+} + C_{sol} m \left(\frac{C_{A^+} n}{C_{sol}^2} \right)^m \tag{4}$$

where C_{sol} is a measure for the solubility limit and m denotes the number of atoms which are combined in an electrical inactive cluster. If redistribution of clusters or clustered atoms during high temperature processes is taken into account, equation (2) has to be written in a modified form:

$$\frac{\partial C_{total}}{\partial t} = \frac{\partial}{\partial x} \left(\left(D_{AI} \frac{C_{I^0}}{C_I^{eq}} + D_{AV} \frac{C_I^{eq}}{C_{I^0}} \right) \left(\frac{\partial C_{A^+}}{\partial x} + C_{A^+} \frac{\partial}{\partial x} \ln \frac{n}{n_i} \right) \right) +$$

$$\frac{\partial}{\partial x} \left(C_{A^+} \left(D_{AI} - D_{AV} \left(\frac{C_I^{eq}}{C_{I^0}} \right)^2 \right) \frac{\partial}{\partial x} \frac{C_{I^0}}{C_I^{eq}} \right) +$$

$$\frac{\partial}{\partial x} \left(D_{eff} m^2 n_i^m C_{sol}^{1-2m} \left(C_{A^+} \frac{n}{n_i} \right)^{m-1} \left(\frac{n}{n_i} \frac{\partial C_{A^+}}{\partial x} + C_{A^+} \frac{\partial}{\partial x} \frac{n}{n_i} \right) \right) \tag{5}$$

where D_{eff} is the effective diffusion coefficient of clusters or clustered atoms. Equations (1) and (3) remain valid in the form given in section 1.1.

It is important to note that the treatment of the high concentration effects as described here has to be considered as a pragmatic model modification because it is not based on a physical interpretation of the behavior of clusters or precipitates. Since physical

understanding of these effects is still poor, the treatment presented here should be considered as a first approximation. The system of equations described in this section has been implemented in PROMIS, too.

In order to simplify the fit procedure a different formulation of the diffusion coefficient is convenient:

$$D = D_{AI}\frac{C_{P^0}}{C_I^{eq}} + D_{AV}\frac{C_I^{eq}}{C_{P^0}} =$$

$$D_{int}\frac{f_I^0 + f_I^1\beta\frac{n}{n_i} + f_I^2\gamma\left(\frac{n}{n_i}\right)^2}{1 + \beta + \gamma}\frac{C_{P^0}}{C_I^{eq}} +$$

$$D_{int}\frac{\left(1 - f_I^0\right) + \left(1 - f_I^1\right)\beta\frac{n}{n_i} + \left(1 - f_I^2\right)\gamma\left(\frac{n}{n_i}\right)^2}{1 + \beta + \gamma}\frac{C_I^{eq}}{C_{P^0}}$$

Here D_{int} is the intrinsic diffusion coefficient, the coefficients f_I^r ($r = 0,1,2$) describe the fractional diffusion via interstitials in different charge states, and β and γ are factors to account for Fermi-level dependend diffusion.

It has to be pointed out that the concept of pair-diffusion can account for the electrically inactive part of the phosphorus concentration without modifications when a high concentration of neutral pairs is assumed. Since this assumption is not supported by experimental evidence no improved simulation results can be expected.

3   Experimental Procedure

FZ-grown <100> Silicon wafers were thermally oxidized in dry oxygen to grow an SiO_2 layer of about 50nm thickness. Subsequently, phosphorus was implanted at an energy of 150keV, the implantation dose was varied between $1 \cdot 10^{14}cm^{-2}$ and $3 \cdot 10^{16}cm^{-2}$ to produce a wide range of different surface concentrations. Residual damage was removed during annealing at 1000°C for 20s by rapid thermal annealing

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to produce the initial profiles for the diffusion experiments which were performed at 1000°C for 60min in inert atmosphere. Phosphorus profiles were determined by secondary ion mass spectroscopy (SIMS).

4 Results

Figure 1 shows the experimental profiles after diffusion together with simulations using the standard pair-diffusion model as described in section 1.1. All simulations presented in this paper have been obtained by including temperature ramping steps which have been performed during sample processing. For clarity, initial profiles determined by SIMS are not included in Figure 1. Good agreement is achieved by adjusting model parameters for each profile separately. It is not possible, however, to simulate all profiles with a consistent set of parameters. As an example,
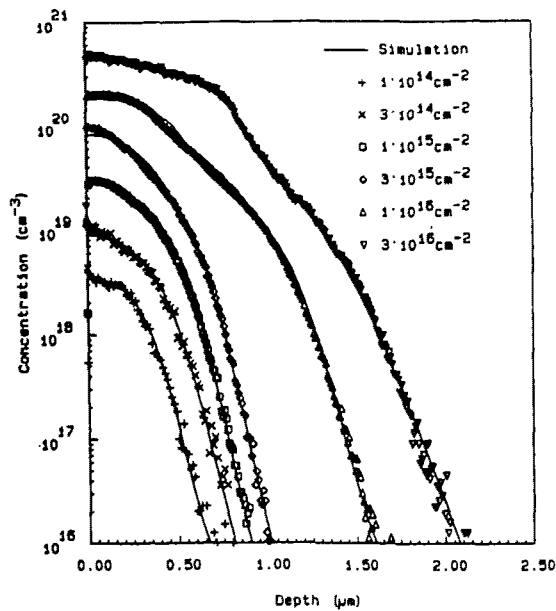

Figure 1: Experimental profiles and simulations after diffusion at 1000°C for 60min. Simulations have been performed using the standard model with parameters adjusted for each curve.
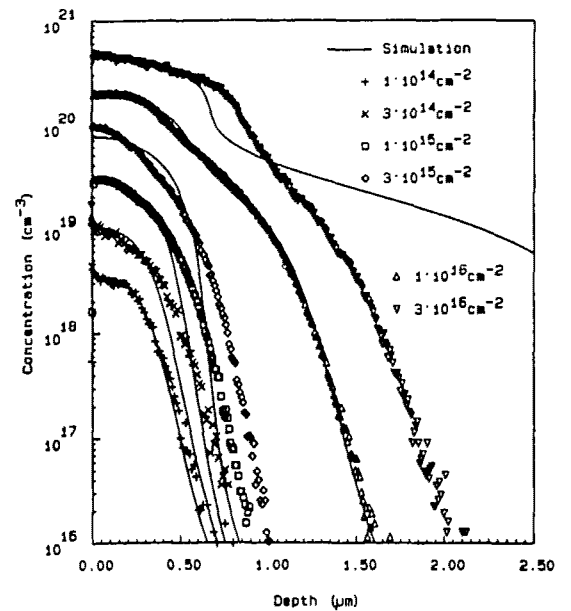
Figure 2: Experimental profiles and simulations after diffusion at 1000°C for 60min. Simulations have been performed using the standard model with a single set of parameters.

simulations of all profiles have been performed using the same set of parameters which has been extracted from the simulation of the profile with an implantation dose of $1 \cdot 10^{16} cm^{-2}$. The results of these simulations are shown in Figure 2. Remarkable deviations between measurements and simulations can be observed especially in case of an implantation dose of $3 \cdot 10^{16} cm^{-2}$. Here, precipitation effects are expected to become important. Moreover, the parameter set contains values for self-diffusion coefficients which are not in agreement with literature values. It can be concluded that the standard model described in section 1.1 is incomplete and does not account for all diffusion phenomena. Furthermore it has to be pointed out that the validity of pair-diffusion models can not be confirmed by comparing a single experimental profile to a calculated profile. For the simulations in Figure 3, the extended model which has been described in section 1.2 and a single set of parameters have been used. The intrinsic diffusion coefficient of phosphorus D_{int} has been determined independently and the self-diffusion coefficients in silicon are taken from the literature [8] as well as the value for C_{sol} [9]. In agreement with experimental evidence, phosphorus is assumed to diffuse entirely via interstitials. Values for the prefactor and the activation energy of the effective diffusion coefficient D_{eff} and for m have been obtained by fitting. The complete set of parameters is listed in Table 1. The profiles in the different concentration regimes are described well by the simulations. However, deviations are observed especially for implantation doses of $3 \cdot 10^{14} cm^{-2}$ and $1 \cdot 10^{15} cm^{-2}$. Additional simulations show that these profiles can be fitted well only by adjusting the intrinsic diffusion coefficient whereas the influence of all other parameters is small. It is therefore neither possible to account for these deviations by changing parameters of the pair-diffusion model nor by changing the Fermi-level dependence of diffusion. Further investigations are necessary to examine these effects.
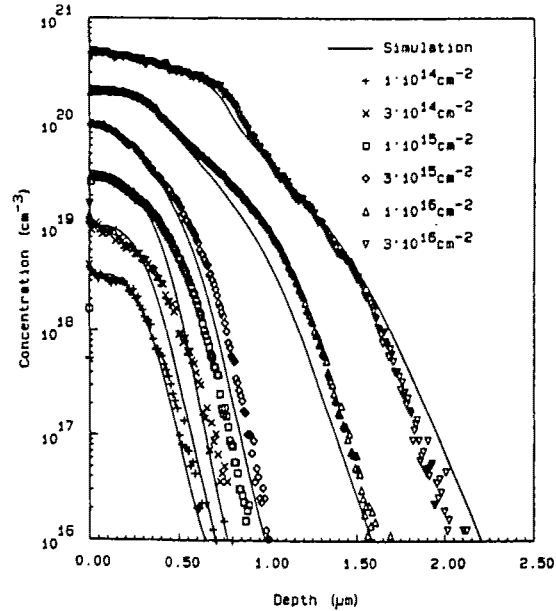

Figure 3: Experimental profiles and simulations after diffusion at 1000°C for 60min. Simulations have been performed using an extended model with a single set of parameters (see Table 1).

Table 1   Parameters used for the simualtions with the extended model

	prefactor	activation energy (eV)		prefactor	activation energy (eV)
D_{int}	8.51 cm^2/s	3.75	$D_{I0}C_I^{eq}$	$2\cdot10^{26}$ $cm^{-1}s^{-1}$	5.0
β	0.085	-	$D_{V0}C_V^{eq}$	$2\cdot10^{24}$ $cm^{-1}s^{-1}$	4.6
γ	0	-	$D_\Gamma, D_I =$	0	-
f_I^0	1	-	$D_{V'}, D_V =$	0	-
f_I^1	1	-	C_{sol}	$1.8\cdot10^{22}$ cm^{-3}	0.4
f_I^2	1	-	m	3	-
			D_{eff}	$3.5\cdot10^3$ cm^2/s	4

5   Conclusion

As has been shown by various authors, it is possible to describe single profiles well by using standard pair-diffusion models. Comparing simulations to a series of profiles covering a wide range of implantation doses, it is concluded that the capability of the pure pair-diffusion formalism to fit a single profile is mainly caused by the great number of parameters which can be varied. In general, model modifications and extensions are necessary for improved description of diffusion profiles in all concentration regimes.

A pragmatical model extension concerning situations where solid solubility is exceeded is suggested. Although this extension is not based on a physically motivated description of phenomena like clustering or precipitation, it has the advandage that simulations can be performed by using indepently determined parameters.

Besides the problems arising in situations where solid solubility is exceeded it has been

shown that simulation results for phosphorus profiles implanted with medium doses are not satisfying. Further investigations will be neccessary to clarify these effects.

References

[1]   B.J.Mulvaney, W.B.Richardson, Appl. Phys. Lett. **51**, 1439 (1987)

[2]   M.Orlowski, Appl. Phys. Lett. **53**, 1323 (1988)

[3]   W.B.Richardson, B.J.Mulvaney, J. Appl. Phys. **65**, 2243, (1989)

[4]   R.Dürr, P.Pichler in Proc. ESSDERC 1989 Conf., Berlin, 1989, 297

[5]   P.Pichler, W.Jüngling, S.Selberherr, E. Guerrero, H.W. Pötzl, IEEE Trans. Electron Devices **ED-32**, 1940 (1985)

[6]   D.Nobili, A.Armigliato, M.Finetti, S.Solmi, J. Appl. Phys. **53**, 1484 (1982)

[7]   H.Ryssel, K.Haberger, K.Hoffmann, G.Prinke, R.Dümcke, A.Sachs, IEEE Trans. Electron Devices **ED-27**, 1484 (1980)

[8]   F.F.Morehead, R.F.Lever, Mat. Res. Soc. Symp. Proc. **104**, 99 (1987)

[9]   D.Nobili in: Properties of Silicon, EMIS Data Reviews No.4, INSPEC, p.394, (1988)

Acknowledgement