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High concentration diffusion of P in Si : a percolation problem ?

D. Mathiot and J. C. Pfister

CNET-CNS, B.P. 42, Chemin du Vieux Chêne, 38240 Meylan, France

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Résumé. — Un nouveau modèle est développé pour la diffusion aux fortes concentrations du phosphore dans le silicium : nous montrons que la diffusion accélérée dans la région de surface est due à la percolation des lacunes entre les impuretés. La simulation numérique ainsi obtenue pour une diffusion à 1 000 °C montre un excellent accord avec le résultat expérimental.

Abstract. — A new model is developed for the high concentration diffusion of phosphorus in silicon : it is shown that the accelerated diffusion in the surface region is due to vacancy percolation between the impurities. The corresponding numerical simulation for a 1 000 °C diffusion is in excellent agreement with the experimental result.

1. Introduction. — High concentration phosphorus diffusion in silicon is of long-standing interest, both for technology and basic understanding. Very large nonlinear effects are observed when the diffusion is performed with surface concentrations higher than 10^{20} at. cm^{-3} , and various partial explanations have been proposed in the literature. Among the various proposed models, the most detailed and complete is the pair diffusion model, or diffusion *via* E centres, which was first proposed by Yoshida [1, 2]. In this model it is assumed that phosphorus can diffuse only *via* the diffusion of E centres (phosphorus-vacancy pairs). Fair and Tsai [3] have postulated that, at high phosphorus concentration, the diffusion is dominated by the $\text{P}^+ \text{V}^-$ pairs, the dissociation of which at a well-defined Fermi level position creates excess V^- vacancies which enhance the tail region diffusivity.

Recently we have shown [4] that a numerical solution incorporating the proposed effects within a consistent thermodynamic frame is possible and leads to satisfactory profile simulations for concentrations below $2.5 \times 10^{20} \text{ cm}^{-3}$. Unfortunately, it is impossible to obtain with this model the plateau which is observed in the surface region for diffusions at higher concentrations in the case of highly soluble impurities P and As, because the high supersaturation of vacancies enhancing the tail diffusivity also causes an important backwards contribution to the phosphorus flux in the surface region. Yoshida [2] has also found that this simple model is not suitable to describe the experimental shape of phosphorus profiles at very high concentration and he developed a model in which the vacancy formation energy is a quadratic function of impurity concentration [5]. This model leads to satisfactory fits to experimental diffusion profiles, but the physical basis for the decrease in vacancy formation energy is not clear and no satisfactory fit to isoconcentration results is obtained with parameters suitable for chemical diffusion.

In this letter we develop a new concept to explain the plateau region. We show that the very fast diffusion at high concentration is due to vacancy percolation between the impurities. The corresponding equations are solved numerically, and the theoretical result is compared with experimental data for phosphorus diffusion at 1 000 °C.

2. Theoretical analysis. — **2.1 LOW CONCENTRATIONS.** — In the low concentration region — the limit of which is defined later — we consider that the pair diffusion model applies, and we use the set of equations described in reference [4].

The relative concentrations of the charged vacancies are given by (in n-type silicon the concentration of positively charged vacancies is negligible) :

$$C_{V^-} = \left(\frac{n}{n_i}\right)^2 \exp\left(\frac{2e_i - e^- - e^+}{kT}\right) \cdot C_{V^0} = \delta^- \left(\frac{n}{n_i}\right)^2 C_{V^0} \quad (1a)$$

$$C_{V^+} = \frac{n}{n_i} \exp\left(\frac{e_i - e^-}{kT}\right) \cdot C_{V^0} = \delta^- \frac{n}{n_i} \cdot C_{V^0} \quad (1b)$$

where e_i is the intrinsic Fermi level, e^- and e^+ are the two acceptor levels of the vacancy and n , n_i , k , T have the usual meanings. The flux of free vacancies is :

$$J_V^{\text{Low}} = -D_V \left[1 + \delta^- \frac{n}{n_i} + \delta^+ \left(\frac{n}{n_i}\right)^2 \right] \frac{\partial C_{V^0}}{\partial x} \quad (2)$$

if the vacancy diffusivity D_V is assumed independent of the charge state of the vacancy.

We have also derived the total phosphorus and E^i centres concentrations as functions of n and C_{V^0} (see Ref. [4] for more details) :

$$C_P^i = \frac{n^2 - n_i^2}{n} \cdot \frac{1 + K_{E^-} \cdot C_{V^0} n^2}{1 - K_{E^-} \cdot C_{V^0} n^2} \quad (3a)$$

$$C_{E^0} = K_{E^0} \cdot \frac{n^2 - n_i^2}{1 - K_{E^-} \cdot C_{V^0} n^2} \cdot C_{V^0} \quad (3b)$$

$$C_{E^-} = \frac{n}{n^-} C_{E^0} \quad (3c)$$

$$C_{E^+} = \frac{n^+}{n} C_{E^0} \quad (3d)$$

with :

$$n^- = \frac{K_{E^0}}{K_{E^-}} \quad \text{and} \quad n^+ = \frac{K_{E^+}}{K_{E^0}}.$$

The K_{E^i} are the mass action law constants for the reactions of formation of the E centres in the various charge states, corresponding to the association of P^+ with $V^=$, V^- and V^0 respectively :

$$C_{E^-} = K_{E^-} \cdot n^2 \cdot C_{P^+} \cdot C_{V^0} \quad (4a)$$

$$C_{E^0} = K_{E^0} \cdot n \cdot C_{P^+} \cdot C_{V^0} \quad (4b)$$

$$C_{E^+} = K_{E^+} \cdot C_{P^+} \cdot C_{V^0}. \quad (4c)$$

The existence of E^+ is not experimentally established, but for generality and following Fair and Tsai [3] we do not neglect its possible contribution to the diffusion.

In the pair diffusion model the total flux of P is the flux of E centres, thus :

$$J_P^{\text{Low}} = J_E = -D_{E^0} \left(1 + \rho^- \frac{n}{n^-} + \rho^+ \frac{n^+}{n} \right) \cdot \frac{\partial C_{E^0}}{\partial x} \quad (5)$$

with $\rho^- = D_{E^-}/D_{E^0}$ and $\rho^+ = D_{E^+}/D_{E^0}$. The D_{E^i} are the diffusivities of the E^i centres.

2.2 HIGH CONCENTRATIONS. — It is obvious that the pair diffusion model holds only if the E centres can be considered as isolated entities during their whole diffusion process. It is known that, in order to diffuse, the E centre has to partially dissociate : the saddle point for the diffusion corresponds to the vacancy on the third neighbour position from the phosphorus atom, and the remaining binding energy between the vacancy and the phosphorus atom ensures the cohesion of the E centre. If we now consider that the phosphorus concentration is high enough to have the situation depicted in figure 1a (for simplicity this figure shows a two dimensional hexagonal lattice, but the same is true with the actual silicon structure) where an E centre is formed by the

Fig. 1. — a) Configuration of P atoms at high concentration. b) Corresponding energy of the vacancy.

binding of a vacancy to a phosphorus atom P_1 , and a second phosphorus atom P_2 or P'_2 is on a fifth neighbour position from P_1 . In this case the third neighbour site (3) from P_1 is also a second neighbour site (2') from P_2 or P'_2 , thus the vacancy has the same energy in this site as in site (2) (see Fig. 1b), and it can diffuse directly from P_1 to P_2 or P'_2 with a potential barrier height smaller than that existing for the diffusion of an isolated E centre. If a sufficient number of P atoms are connected in such a way, the vacancy can freely diffuse through the corresponding cluster, and this accelerated diffusion of the vacancies also causes an accelerated diffusion of the impurity atoms *via* a substitutional mechanism. In these clusters the effective energy of formation of the vacancy is decreased by E'_B , the binding energy between phosphorus and the vacancy on a second neighbour site (see Fig. 1b). The effective concentration of vacancies is thus increased by a factor $F = \exp(E'_B/kT)$, and the corresponding fluxes are given by :

$$J_V^{\text{Perc}} = F \cdot J_V^{\text{Low}} \quad (6a)$$

$$J_P^{\text{Perc}} = -F \cdot D_V \frac{C_V^t}{N_s} \left(\frac{\partial C_P^t}{\partial x} + C_P^t \frac{1}{n} \cdot \frac{\partial n}{\partial x} \right) \quad (6b)$$

where $C_V^i = \left[1 + \delta^- \frac{n}{n_i} + \delta^+ \left(\frac{n}{n_i} \right)^2 \right] C_{V0}$ is the total concentration of vacancies,

$$N_s = 5 \times 10^{22} \text{ cm}^{-3}$$

is the number of silicon sites, and in (6b) the effect of the built-in electric field on the ionized P atoms is taken into account. In the high concentration region the total fluxes of vacancies and phosphorus are a combination of the fluxes caused by each mechanism.

If p is the probability that a given P atom belongs to a cluster large enough to have the accelerated diffusion, the total fluxes are given by :

$$J_V = (1 - p) J_V^{\text{Low}} + p J_V^{\text{Perc}} \quad (7a)$$

$$J_P = (1 - p) J_E + p J_P^{\text{Perc}}. \quad (7b)$$

2.3 ESTIMATION OF THE PROBABILITY p . — Let us consider the network of phosphorus atoms in the sample. Two atoms will be considered connected by an easy vacancy diffusion path if they are in fifth neighbour positions or closer in the Si lattice (positions P_2 or P'_2 of figure 1a, or closer). Connecting neighbouring atoms with this rule will generate clusters within which the lattice vacancies can move with high mobility. Although the phosphorus network is not a regular lattice, it is clear that for high enough concentrations C_P^i very large clusters can be formed and percolation phenomena are expected : for C_P^i above a threshold value C_P^* an infinite phosphorus cluster exists through the silicon lattice [6].

We have used a value of the probability p corresponding to the probability (P_∞ in percolation theory) that a phosphorus atom belongs to the infinite cluster [6] :

$$p = 0 \quad \text{for} \quad C_P^i \leq C_P^* \quad (8a)$$

$$p = K \left(\frac{C_P^i}{C_P^*} - 1 \right)^{0.4} \quad \text{for} \quad C_P^i > C_P^*. \quad (8b)$$

C_P^* is estimated from the percolation threshold value for FCC lattices ($p_c \cong 0.2$ [6]) since the number of equivalent fifth neighbour positions is 12. Simple geometrical considerations lead then to the critical phosphorus concentration :

$$C_P^* \cong 3 \times 10^{20} \text{ cm}^{-3}. \quad (9)$$

In fact this parameter appears to be very sensitive in the numerical simulations and good fits with experimental data are obtained only if C_P^* lies between 2.5 and $3 \times 10^{20} \text{ cm}^{-3}$.

On the other hand it is found that the value of K in (8b) is not critical, and the presented result is obtained with $K = 0.85$, so that $p = 1$ for $C_P^i \geq 2.5 C_P^*$.

3. Results and discussion. — The distributions $C_P^i(x, t)$ and $C_{V0}(x, t)$ can be calculated using the expressions derived above and the continuity equations [4] :

$$\frac{\partial C_P^i}{\partial t} = - \frac{\partial J_P}{\partial x} \quad (10a)$$

$$\frac{\partial C_V^i}{\partial t} = - \frac{\partial J_V}{\partial x} - \frac{\partial J_E}{\partial x} - \frac{\partial C_E^i}{\partial t} + \left[1 + \delta^- \frac{n}{n_i} + \delta^+ \left(\frac{n}{n_i} \right)^2 \right] D_V \frac{C_V^{\text{eq}} - C_{V0}}{L_V^2} \quad (10b)$$

with $C_E^i = C_{E-} + C_{E0} + C_{E+}$, C_V^{eq} is the equilibrium value of C_{V0} and L_V is the vacancy diffusion length ($L_V \cong 30 \mu\text{m}$ at $T \cong 1\,000^\circ\text{C}$ [7]).

Fig. 2. — a) Diffusion profile of P in Si at 1 000 °C. The values used for the simulation are :

$$\begin{aligned}
 n_i &= 9.38 \times 10^{18} \text{ cm}^{-3}; \quad \delta^- = 9.55 \times 10^{-1}; \quad \delta^+ = 9.61 \times 10^{-3}. \\
 C_{V^0}^{\text{eq}} &= 4 \times 10^{12} \text{ cm}^{-3}; \quad D_V = 2 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}; \quad L_V = 30 \text{ } \mu\text{m}. \\
 K_{E^-} \cdot C_{V^0}^{\text{eq}} &= 5.5 \times 10^{-42} \text{ cm}^6; \quad n^- = 1.5 \times 10^{19} \text{ cm}^{-3}. \\
 D_{E^0} &= 1.25 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}; \quad \rho^- = 5.40 \times 10^{-2}; \quad n^+ \rho^+ = 2.92 \times 10^{18} \text{ cm}^{-3}. \\
 C_P^* &= 3 \times 10^{20} \text{ cm}^{-3}; \quad F = 1 \text{ } 100.
 \end{aligned}$$

b) Corresponding neutral vacancy distribution.

Figure 2a shows the result of the numerical simulation for a 60 min. phosphorus diffusion from an infinite source at 1 000 °C; the calculated curve is compared with SIMS data published by Fair and Tsai [3], and it can be seen that the agreement is very good. The corresponding vacancy distribution is given in figure 2b. The numerical values of the constants used for the calculation are given in the figure caption.

Among these constants there are only four independent fitting parameters. Indeed δ^- and δ^+ are given by the relation (1) using $e_c - e^- = 0.1 \text{ eV}$ and $e_c - e^+ = 0.6 \text{ eV}$ [8], the position of e_i is calculated from Morin and Maita's values of n_i and e_g [9] and $e_c - e_i = \frac{1}{2}(e_g - kT \cdot \ln N_V/N_c)$ with $N_V/N_c = 0.57$ [10].

The value $K_{E^-} \cdot C_{V^0}^{\text{eq}} \cong 5 \times 10^{-42} \text{ cm}^6$ is obtained by fitting the equation (3a) on Fair and Tsai's experimental results (Fig. 5 of Ref. [3]).

Otherwise $C_{V^0}^{\text{eq}}$ and D_V have to satisfy the relation :

$$D_{SD} = \frac{1}{2}(1 + \delta^- + \delta^+) \frac{C_{V^0}^{\text{eq}}}{N_s} \cdot D_V \quad (11)$$

where D_{SD} is the self-diffusion coefficient of Si. The chosen values lead to

$$D_{SD} \cong 1.6 \times 10^{-17} \text{ cm}^2 \cdot \text{s}^{-1}$$

which is in agreement with the published experimental values [11, 12], and $C_{V^0}^{\text{eq}} = 4 \times 10^{12} \text{ cm}^{-3}$ is very close to the value estimated in [8].

Furthermore n^- , ρ^- , n^+ , ρ^+ and D_{E^0} are bound by two other relations :

i) From the relation (22) in [4] we have (with $K_E - C_{V^0}^{\text{eq}} n_i^2 \ll 1$) :

$$D_i = D_{E^0} \cdot K_E - C_{V^0}^{\text{eq}} \cdot (\rho^- n_i^2 + n^- n_i + \rho^+ n^- n^+) \quad (12)$$

where $D_i = 1.3 \times 10^{-14} \text{ cm}^2 \cdot \text{s}^{-1}$ [13] is the intrinsic diffusivity of P.

ii) It has been found [14] that the difference in the migration energies of E^- and E^0 is due to the difference between their binding energies. If the same assumption is made for E^0 and E^+ , the ratios D_{E^-}/D_{E^0} and D_{E^+}/D_{E^0} are given by :

$$\rho^- = \exp \frac{E_{B^0} - E_{B^-}}{kT} \quad (13a)$$

$$\rho^+ = \exp \frac{E_{B^0} - E_{B^+}}{kT} \quad (13b)$$

and using the relations (9a)-(9b) in [4] we find the simple relationship :

$$\frac{\rho^-}{n^-} \cdot n^+ \rho^+ = \exp \frac{e^- - e^+}{kT} = \frac{\delta^-}{(\delta^-)^2} \quad (14)$$

It must be noted that the parameters mentioned above characterize the diffusivities and concentrations of vacancies and E centres, and that it is impossible to obtain the plateau in the profiles by any change in their values [4]. In fact, the new idea of percolation introduces only two new parameters C_p^* and F which are definitively determined by the position of the end of the plateau region and the concentration gradient in this area.

From the fitted value $\rho^- = 5.4 \times 10^{-2}$ the equation (13a) leads to $E_{B^-} - E_{B^0} \cong 0.32 \text{ eV}$ in remarkably good agreement with the value 0.35 eV found by DLTS measurements [14]. Moreover the position of the E centre level e_E can be calculated by the relation :

$$e_c - e_E = E_{B^-} - E_{B^0} + e_c - e^+ \quad (15)$$

This relation is obtained by comparison of the E^- centre formation either by interaction of P^+ with V^- and then ionization of the resulting E^0 , or by the ionization of V^- and then the interaction of P^+ with V^- . The relation (15) gives $e_c - e_E = 0.42 \text{ eV}$, which is also in excellent agreement with the 0.4 eV EPR value [15] and the 0.44 DLTS value [16].

Finally the fitted value $F = 1100$ leads to $E_B' = 0.77 \text{ eV}$ for the binding energy between a phosphorus atom and the vacancy on a second neighbour site. Since the doubly negatively charged vacancy is dominant in the concentration range of interest, this value is quite reasonable.

4. Conclusion. — We have shown that the plateau region observed in the phosphorus profiles for high concentration diffusions is caused by an acceleration of the diffusion due to the percolation of the vacancies between the impurities. This new model allows good numerical simulations of the diffusion profile at 1000 °C with physically reasonable values of the parameters. But finally it must be pointed out that the indicated values must be considered as first estimates. Indeed

more accurate values can be obtained only by fitting on a number of experimental profiles obtained with various diffusion conditions. This work is in progress in our laboratory and the results will be published later.

References

- [1] YOSHIDA, M., *Japan. J. Appl. Phys.* **10** (1971) 702.
 - [2] YOSHIDA, M., *J. Appl. Phys.* **48** (1977) 2169.
 - [3] FAIR, R. B., TSAI, J. C. C., *J. Electrochem. Soc.* **124** (1977) 1107.
 - [4] MATHIOT, D., PFISTER, J. C., to be published in *J. Appl. Phys.*
 - [5] YOSHIDA, M., *Japan. J. Appl. Phys.* **18** (1979) 479.
 - [6] STAUFFER, D., *Phys. Rep.* **54** (1979) 1.
 - [7] LECROSNIER, D., *et al.*, *Appl. Phys. Lett.* **34** (1979) 224.
 - [8] VAN VECHTEN, J. A., THURMOND, C. D., *Phys. Rev. B* **14** (1976) 3551.
 - [9] MORIN, F. J., MAITA, J. P., *Phys. Rev.* **96** (1954) 28.
 - [10] JAIN, R. K., VAN OVERSTRAETEN, R. J., *IEEE Trans.* **ED 21** (1974) 155.
 - [11] KALINOWSKI, L., SEGUIN, R., *Appl. Phys. Lett.* **35** (1979) 211.
 - [12] MAYER, H. J., *et al.*, Radiation Effects in Semiconductors. *Inst. Phys. Conf. Ser.* **31** (1977) 186.
 - [13] MAKIS, J., MASTERS, B. J., *J. Electrochem. Soc.* **120** (1973) 1252.
 - [14] KIMERLING, L. C., *et al.*, *Solid. State Commun.* **16** (1975) 171.
 - [15] WATKINS, G. D., CORBETT, J. W., *Phys. Rev.* **134** (1964) A 1359.
 - [16] KIMERLING, L. C., *Inst. Phys. Conf. Ser.* **31** (1977) 221.
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