

## The Temperature Dependence of the Quadratic Proportionality Factor of $P$ Diffusivity in Germanium with the Free Electron Density

A. Souigat<sup>1,2,\*</sup>, M.K. Bechki<sup>1</sup>, D. Slimani<sup>1</sup>

<sup>1</sup> *Ecole Normale Supérieure de Ouargla, Algeria*

<sup>2</sup> *Lab. Développement des Energies Nouvelles et Renouvelables en Zones Aride, Univ Ouargla, Fac. des Mathématiques et des Sciences de la Matière, 30000 Ouargla, Algeria*

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High intrinsic carrier mobility, small band gap for germanium and possible monolithic integration with Si based devices have prompted renewed interest in germanium to continue the historic progress of CMOS devices. To obtain efficient germanium-based electronic devices, it is necessary to understand the dopant diffusion in this semiconductor. Up to now,  $n$ -type dopant diffusion in germanium at most is modeled by diffusivity proportional to the square of the free electron density ( $n$ ). This study determines the temperature dependence of the quadratic proportionality factor of the  $P$  diffusivity with the free electron density, through simulations of experimental  $P$  diffusion profiles in the temperature range from 650 to 870 °C. Accurate simulation is achieved within that temperature range, taking into account the quadratic proportionality between the phosphorus diffusivity and the free electron density.

**Keywords:** Phosphorus, Diffusion, Proportionality factor, Germanium.

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### 1. INTRODUCTION

As dimensional scaling of traditional silicon CMOS devices approaches its fundamental limits, diverse research is being done to introduce novel structures and materials to accomplish this technological progress and to continue the historical progress in information processing and transmission [1-5]. In this context, recently germanium has emerged as a promising candidate in order to improve devices (CMOS), because of its distinctive physical characteristics such as high intrinsic carrier mobility, small band gap and possible monolithic integration with Si based devices [5-11]. For optical applications, germanium with smaller direct band gap (0.8 eV) offers a higher optical absorption, corresponding 1.3 to 1.55  $\mu\text{m}$  wavelength range. This makes germanium a good candidate for ultimate use in photodetector devices within that wavelength range, used in telecommunications [12, 13]. In addition, the smaller direct band gap, the lower melting point for germanium. This helps to fabricate electronic devices characterized by a scaled operating voltage and lowest thermal cost; this is consistent with the international technology roadmap for semiconductors [5, 12] and compatible with requirements of the thermal stability in integrating metal gate electrodes and novel high- $k$  dielectrics into developed transistors [14-16]. Knowing the parameters of  $n$ - and  $p$ -type dopants, diffusion in this semiconductor is necessary to obtain efficient germanium-based electronic devices.

The enhanced diffusion is directly associated with the characteristics of the point defects involved in the diffusion mechanisms. In the case of  $n$ -type dopant diffusion in Ge, the mass transport is mediated by vacancy mechanism [17-20]. Up to now,  $n$ -type dopant diffusion in germanium at most is modeled by diffusivity proportional to the square of the free electron density ( $n$ ) [19-23]. The quadratic proportionality is a result of

the difference charge between the substitutional dopant donor and the singly negatively charged mobile donor-vacancy pair [20, 22-24].

The aim of this work is devoted to the estimation of the quadratic proportionality factor of phosphorus diffusivity in germanium with the free electron density, through simulations of experimental  $P$  diffusion profiles in Ge, taken from reference [20], in the temperature range from 650 to 870 °C.

### 2. MODEL USED

In accordance with previous reports [19-24], we have taken into account the vacancy mechanism to model the diffusion of phosphorus in germanium. We considered that the diffusion occurs via doubly negatively charged vacancies in the form of dopant-defect pairs or simple exchange. This leads to quadratic proportionality between the phosphorus diffusivity and the free electron density, therefore the expression of the diffusivity of phosphorus ( $D$ ) in germanium takes the following form:

$$D = \alpha n^2, \quad (1)$$

where  $\alpha$  is the quadratic proportionality factor of  $P$  diffusivity in germanium with the free electron density.

The density of free electron carriers ( $n$ ) is calculated from the mass action law, assuming charge neutrality:

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

where  $C$  and  $n_i$  represent respectively the local phosphorus concentration and the intrinsic carrier density.

The total flux  $J$  of phosphorus in germanium, by inserting the arising term due to an internal electric field, can be described as follows:

\* [souigataek@gmail.com](mailto:souigataek@gmail.com)

$$J = -D \frac{\partial C}{\partial x} - D \frac{C}{n} \frac{\partial n}{\partial x}. \quad (3)$$

The conservation of the diffused mass quantity is expressed by the continuity equation:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}. \quad (4)$$

From the equations (1)-(4), diffusion of phosphorus in Ge can be described by the following diffusion equation:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D^{eff} \frac{\partial C}{\partial x} \right), \quad (5)$$

where  $x$  and  $t$  represent respectively the spatial coordinate and the time,  $D^{eff}$  is the effective diffusion coefficient. It is expressed as follows:

$$D^{eff} = h \alpha n^2, \quad (6)$$

where  $h$  is an enhancement factor arising due to an internal electric field:

$$h = 1 + \frac{C}{2n_i} \left( \left( \frac{C}{2n_i} \right)^2 + 1 \right)^{-1/2}. \quad (7)$$

### 3. NUMERICAL SIMULATION

#### 3.1 Numerical Treatment of Diffusion Equation

Because  $D^{eff}$  depends on the dopant concentration, the equation (5) can be written as:

$$\frac{\partial C}{\partial t} = \frac{\partial D^{eff}}{\partial x} \frac{\partial C}{\partial x} + D^{eff} \frac{\partial^2 C}{\partial x^2}. \quad (8)$$

We use finite difference method to solve equation (8), exactly, the implicit finite difference scheme. This scheme is characterized by an accuracy of order  $O(\Delta t, \Delta x^2)$  and unconditionally stable. We divide the space into  $k$  slices and we replace the partial derivatives in the equation (8) by the following finite difference approximations:

$$\mathbf{B} = \begin{pmatrix} 1 + \delta_2^j & -\delta_2^j & 0 & \dots & \dots & \dots & \dots & \dots & \dots \\ -\delta_2^j & 1 + \delta_2^j + \delta_3^j & -\delta_3^j & 0 & \dots & \dots & \dots & \dots & \dots \\ 0 & -\delta_3^j & 1 + \delta_3^j + \delta_4^j & -\delta_4^j & 0 & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & 0 & -\delta_i^j & 1 + \delta_i^j + \delta_{i+1}^j & -\delta_{i+1}^j & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & 0 & -\delta_k^j & 1 + \delta_k^j \end{pmatrix}.$$

#### 3.2 Features of Our Program for Simulating the Diffusion

To simulate the experimental profiles of the phosphorus diffusion in germanium at the indicated temperatures and times in Table 1, we accomplished a program by FORTRAN language where we relied on to solve the

$$\frac{\partial C}{\partial x} = \frac{1}{\Delta x} (C_{i+1}^j - C_i^j), \quad (9)$$

$$\frac{\partial C}{\partial t} = \frac{1}{\Delta t} (C_i^j - C_i^{j-1}), \quad (10)$$

$$\frac{\partial D^{eff}}{\partial x} = \frac{1}{\Delta x} \left( (D^{eff})_{i+1}^j - (D^{eff})_i^j \right), \quad (11)$$

and

$$D^{eff} \frac{\partial^2 C}{\partial x^2} = (D^{eff})_i^j \frac{C_{i-1}^j - 2C_i^j + C_{i+1}^j}{\Delta x^2}. \quad (12)$$

Here,  $\Delta x$ ,  $\Delta t$ ,  $i$ ,  $j$  represent respectively the space step, the time step, the space index and the time index.

From the equations (8)-(12), we get the relationship expressing the concentration at time  $j\Delta t$  and the concentration at time  $(j-1)\Delta t$ :

$$C_i^{j-1} = -\delta_i^j C_{i-1}^j + (1 + \delta_i^j + \delta_{i+1}^j) C_i^j - \delta_{i+1}^j C_{i+1}^j, \quad (13)$$

where  $\delta_i^j = \delta_0 (D^{eff})_i^j$  and  $\delta_0 = \frac{\Delta t}{\Delta x^2}$ .

For treatment of boundary conditions, we use no-flux boundary conditions, and then we find:

$$C_0^j = C_1^j, \quad (14)$$

$$C_k^j = C_{k+1}^j. \quad (15)$$

From (13)-(15), we get the tridiagonal matrix systems that bind the concentration at time  $j\Delta t$  and the concentration at time  $(j-1)\Delta t$  in the form  $Bc = a$ , where

$$\mathbf{a} = \begin{pmatrix} C_1^{j-1} \\ C_2^{j-1} \\ C_3^{j-1} \\ \dots \\ C_i^{j-1} \\ \dots \\ C_k^{j-1} \end{pmatrix}, \quad \mathbf{c} = \begin{pmatrix} C_1^j \\ C_2^j \\ C_3^j \\ \dots \\ C_i^j \\ \dots \\ C_k^j \end{pmatrix}$$

and

tridiagonal matrix systems that have been reached, using the Thomas algorithm, which is based on LU decomposition method.

Because the effective diffusion coefficient depends on the dopant concentration, which is varied during the diffusion, it has to be recalculated for every time step.

We chose the values of  $a$  at diffusion temperature  $T$ , which bring the coincidence of simulated profiles and experimental profiles. We have chosen the values of intrinsic carrier density according to the reference [20].

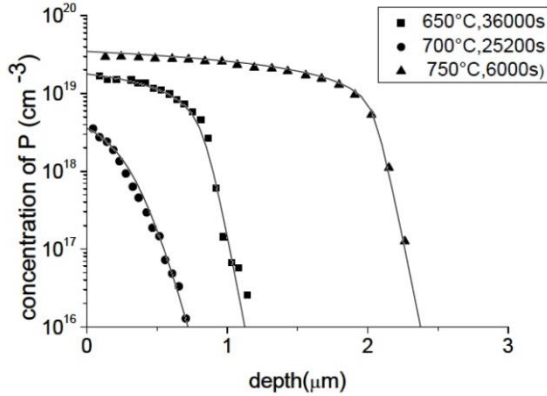
The phosphorus concentration  $C_0$  at surface of the germanium sample is considered constant during the diffusion  $C_j^{-1} = C_0$  ( $j = 1, 2, \dots, n$ ), where the initial conditions are  $C_i^0 = 0$  ( $i = 2, 3, \dots, k$ ),  $k$  and  $n$  represent respectively the total number of space steps and total number of time steps.

**Table 1**–  $C_0$  at surface, time and  $a$  corresponding to diffusion temperature  $T$  used for these simulations

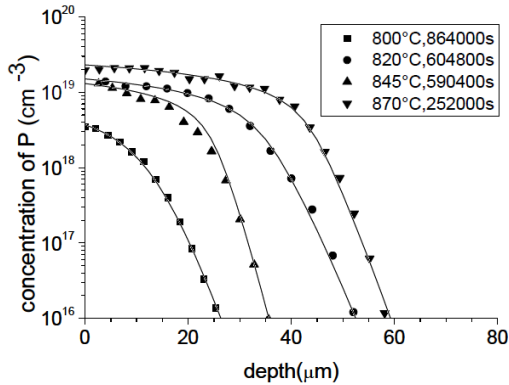
$C_0$ ( $\text{cm}^{-3}$ )	$t$ (s)	$T$ ( $^{\circ}\text{C}$ )	$\alpha$ ( $\text{cm}^8\text{s}^{-1}$ )
$1.8 \times 10^{19}$	36000	650	$2.31 \times 10^{-52}$
$3.6 \times 10^{18}$	25200	700	$6.00 \times 10^{-52}$
$3.5 \times 10^{19}$	6000	750	$2.68 \times 10^{-51}$
$3.7 \times 10^{18}$	864000	800	$1.35 \times 10^{-50}$
$1.3 \times 10^{19}$	604800	820	$2.17 \times 10^{-50}$
$1.5 \times 10^{19}$	590400	845	$3.02 \times 10^{-50}$
$2.3 \times 10^{19}$	252000	870	$5.51 \times 10^{-50}$

#### 4. RESULTS AND DISCUSSION

Fig. 1 and Fig. 2 show the simulated profiles (solid lines). We have obtained and compared them with the experimental profiles of phosphorus diffusion in Ge at the indicated temperatures and times.



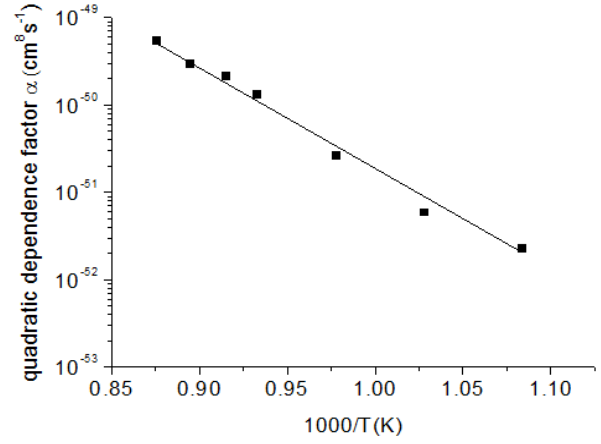
**Fig. 1** – Simulated profiles (solid lines) and experimental profiles (Ref. [20]) of phosphorus diffusion in Ge measured with SIMS



**Fig. 2** – Simulated profiles (solid lines) and experimental profiles (Ref. [20]) of phosphorus diffusion in Ge measured with SRP

The simulated profiles and the experimental profiles concordance in Fig. 1 and Fig. 2 confirm that the phosphorus diffusivity is proportional to the square of the free electron density.

Fig. 3 shows the change of the quadratic proportionality factor  $a$  depending on the inverse of the temperature, given by our simulation data.



**Fig. 3** –  $a$  variation with the inverse of the temperature

The temperature dependence of the quadratic proportionality factor is best reproduced by the following expressions:

$$\alpha = 572.3 \times 10^{-42} \exp\left(-\frac{2.28(\text{eV})}{k_B T}\right) \text{cm}^8\text{s}^{-1}, \quad (16)$$

where  $T$  is the temperature in kelvins,  $k_B$  is the Boltzmann constant.

#### 5. CONCLUSIONS

In this work, an accurate simulation of experimental P diffusion profiles in germanium is achieved based on the modeling of phosphorus diffusion by the vacancy mechanism, taking into account the quadratic proportionality between the phosphorus diffusivity and the free electron density. This simulation allowed us to determine the relationship between the quadratic proportionality factor and the temperature. The quadratic proportionality factor of phosphorus diffusivity in germanium with the electron density determined from our simulations data in the temperature range from 650 to 870  $^{\circ}\text{C}$  is best reproduced by Eq. (16).

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## Температурна залежність квадратичного коефіцієнта пропорційності дифузії фосфору в германій із вільними електронами

A. Souigat<sup>1,2</sup>, M.K. Bechki<sup>1</sup>, D. Slimani<sup>1</sup>

<sup>1</sup> *Ecole Normale Supérieure de Ouargla, Algeria*

<sup>2</sup> *Lab. Développement des Energies Nouvelles et Renouvelables en Zones Aride, Univ Ouargla, Fac. des Mathématiques et des Sciences de la Matière, 30000 Ouargla, Algeria*

Висока внутрішня мобільність носіїв, невелика заборонена зона для германію та можлива монолітна інтеграція з пристроями на основі Si спонукали відновити інтерес до германію у продовженні історичного прогресу пристроїв CMOS. Для отримання ефективних електронних пристроїв на основі германію необхідно зрозуміти дифузію домішки у цьому напівпровіднику. До цього часу, дифузія домішок *n*-типу в германії моделювалася, головним чином, дифузією, пропорційною квадрату концентрації вільних електронів (*n*). У дослідженні вивчається температурна залежність квадратичного коефіцієнта пропорційності дифузії *P* від концентрації вільних електронів шляхом моделювання експериментальних профілів дифузії *P* у діапазоні температур від 650 до 870 °C. Точне моделювання досягається у цьому температурному діапазоні з урахуванням квадратичної пропорційності між дифузійною рухливістю атомів фосфору та концентрацією вільних електронів.

**Ключові слова:** Фосфор, Дифузія, Коефіцієнт пропорційності, Германій.