

The ratio of the contributions and activation energies to phosphorus diffusion from doubly negatively charged and triply negatively charged vacancies in germanium

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Recently germanium has emerged as a promising candidate for the development of high performance devices (CMOS) and its optoelectronic applications. Knowing the parameters of the dopant diffusion in this material is essential to perform efficient Ge-Based devices. This study determine how the temperature dependence of the ratio of the contributions to phosphorus diffusion in germanium from doubly negatively charged (2-) and triply negatively charged (3-) vacancies with activation energies 3.09 eV and 2.4 eV, respectively. In this work we modulate phosphorus diffusion in Ge by the vacancy mechanism and numerical solution of Fick's second law, taking into account the dependence of the effective diffusion coefficient on the ratio of the contributions, and we simulate the experimental P diffusion profiles in Ge.

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1. Introduction

As dimensional scaling of CMOS devices reaches almost its fundamental limits, diverse research is being done to introduce novel structures and materials [1,2] in order to continue the historic progress in information processing and transmission. High intrinsic carrier mobility, small band gap for supply voltage scaling and possible monolithic integration with Si based devices have prompted renewed interest in germanium [3-8]. For optical applications, Ge has a smaller absorption coefficient, which makes it attractive for monolithic integration of optical components for the ultimate use in optical interconnects in the wavelength range of 1.3-1.55 μ m used in telecommunications [7]. This interest in Ge has stimulated studies on diffusion and activation of n- and p-type dopants in this semiconductor. The diffusion behavior of the n-type dopants in Ge is accurately described solely on the basis of the vacancy mechanism. In germanium the experimental observations indicated that the E center (a pair of a vacancy with a group V donor atom) has a double acceptor state [9,10] and supported the theoretical studies of Puska and Coutinho [11,12] about the existence of a V³⁻ (triply negatively charged vacancy) in germanium. This vacancy (V³⁻) contributes with V²⁻ (doubly negatively charged vacancy) on the intrinsic and extrinsic diffusion of phosphorus in germanium [13]. In this paper, we have simulated the phosphorus profiles, taken from ref. [14], measured by means of a spreading resistance profiler (SRP) and secondary ion mass spectrometry (SIMS) to determine the ratio of the contributions at different temperatures for the diffusion of phosphorus via doubly negatively charged and triply

negatively charged vacancies in germanium and then infer the activation energies for the diffusion of phosphorus via the two states of charge of the vacancies.

This work which explains how the phosphorus diffuses in Ge can be a contribution with other previous studies [13-15].

2. Model used

It is known in the literature that n-type dopants in germanium diffuse by a vacancy mechanism [13-18]. Taking into account that the diffusion of phosphorus occur via doubly and triply negatively charged vacancies[13] in the form of dopant-defect pairs or simple exchange, the effective diffusion coefficient takes the following form:

$$D^{\text{eff}} = h \cdot \left(D^{2-} \left(\frac{n}{n_i} \right)^2 + D^{3-} \left(\frac{n}{n_i} \right)^3 \right) \quad (1)$$

D^{2-} and D^{3-} successively presents the intrinsic diffusion coefficient via doubly negatively charged and triply negatively charged vacancies, where:

$$D^{2-} = \frac{\beta}{1 + \beta} \cdot D^i \quad (2)$$

$$D^{3-} = \frac{1}{1 + \beta} \cdot D^i \quad (3)$$

β is the ration of the contributions for the diffusion from V^{2-} and V^{3-} .

$$\beta = \beta_0 \exp\left[-\frac{\delta g}{KT}\right] \quad (4)$$

δg is the difference in the activation energies to P diffusion from Ge vacancies with the charge states 2- and 3-. T is the absolute temperature (in Kelvin), K is the Boltzmann constant and β_0 is an adjustment factor for the ratio of the contributions.

From the previous equations the effective diffusion coefficient is described by the following expression:

$$D^{\text{eff}} = \frac{h}{1+\beta} \left[\beta \left(\frac{n}{n_i}\right)^2 + \left(\frac{n}{n_i}\right)^3 \right] D^i \quad (5)$$

D^i and n_i represent successively the intrinsic diffusion coefficient and the intrinsic carrier density. h is an enhancement factor arising due to an internal electric field:

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

and n is the concentration of free electron carriers which is calculated from the mass action law, assuming charge neutrality:

$$n = \frac{1}{2} \left(c + \sqrt{c^2 + 4n_i^2} \right) \quad (7)$$

where c is the dopant concentration.

3. Numerical simulation

3.1. Numerical solution method of Fick's second law

In macroscopic one-dimensional, scale, diffusion of phosphorus in Ge can under equilibrium conditions be described by Fick's second law:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D^{\text{eff}} \frac{\partial C}{\partial x} \right] \quad (8)$$

$$\frac{\partial C}{\partial t} = D^{\text{eff}} \frac{\partial^2 C}{\partial x^2} + \frac{\partial C}{\partial x} \cdot \frac{\partial D^{\text{eff}}}{\partial x} \quad (9)$$

Where x is the spatial coordinate and t is the time.

We solve equation (9) numerically, using finite difference approximations, specifically, the Backward Euler method. This method is an implicit finite difference method, which is unconditionally stable and has an accuracy of order $O(\Delta t, \Delta x^2)$. We discrete the space into N slices and we replace the partial derivatives in the equation (9) by the following finite difference approximations:

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

$$\frac{\partial C}{\partial x} = \frac{c_{i+1}^j - c_i^j}{\Delta x} \quad (11)$$

$$\frac{\partial D^{\text{eff}}}{\partial x} = \frac{\left(D^{\text{eff}}\right)_{i+1}^j - \left(D^{\text{eff}}\right)_i^j}{\Delta x} \quad (12)$$

and:

$$D^{\text{eff}} \frac{\partial^2 C}{\partial x^2} = \left(D^{\text{eff}}\right)_i^j \frac{c_{i-1}^j - 2c_i^j + c_{i+1}^j}{\Delta x^2} \quad (13)$$

Where i is the space index, j is the time index, Δx is the space increment and Δt is the time increment.

From the equations (9) - (13) we get the relationship expressing the concentration at time $j\Delta t$ and the concentration at time $(j-1)\Delta t$:

$$c_i^{j-1} = -\delta_i^j c_{i-1}^j + \left[1 + \delta_i^j + \delta_{i+1}^j\right] c_i^j - \delta_{i+1}^j c_{i+1}^j \quad (14)$$

Where: $\delta_i^j = \delta_0 \cdot \left(D^{\text{eff}}\right)_i^j$ and $\delta_0 = \frac{\Delta t}{\Delta x^2}$

The boundary conditions are:

$$c_0^j = c_1^j \quad (15)$$

$$c_N^j = c_{N+1}^j \quad (16)$$

From (14), (15), (16) we get the matrix that bind the concentration at time $j\Delta t$ and the concentration at time $(j-1)\Delta t$:

$$\begin{bmatrix} c_1^{j-1} \\ c_2^{j-1} \\ \text{M} \\ c_i^{j-1} \\ \text{M} \\ c_N^{j-1} \end{bmatrix} = \begin{bmatrix} 1+\delta_2^j & -\delta_2^j & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\delta_2^j & 1+\delta_2^j+\delta_3^j & -\delta_3^j & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \text{O} & & & & & & & & & & \\ 0 & 0 & 0 & 0 & -\delta_i^j & 1+\delta_i^j+\delta_{i+1}^j & -\delta_{i+1}^j & 0 & 0 & 0 & 0 \\ \text{O} & & & & & & & & & & \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\delta_N^j & 1+\delta_N^j & \end{bmatrix} \begin{bmatrix} c_1^j \\ c_2^j \\ \text{M} \\ c_i^j \\ \text{M} \\ c_N^j \end{bmatrix}$$

3.2. Features of our program for simulating the diffusion

To simulate the experimental profiles of the phosphorus we accomplished a program by FORTRAN language where we relied on to solve the matrix equations that have been reached. The phosphorus concentration (c_0) at surface of the sample is considered

constant during the diffusion, and the phosphorus diffused in germanium according to the equation (14). D^{eff} has to be recalculated for every time step. We chose the values of the ratio of contributions which bring the coincidence of simulated profiles and experimental profiles. We have chosen the values of intrinsic carrier density and intrinsic diffusion coefficient according to the reference. [14].

Table 1: Parameters used for these simulations.

C_0 (cm ⁻³)	t(s)	T (°C)	β	n_i (cm ⁻³)	D^i (cm ² s ⁻¹)
1.8×10^{19}	36000	650	1.43	3.68×10^{18}	2.52×10^{-15}
3.5×10^{18}	25200	700	2	4.89×10^{18}	0.85×10^{-14}
3.5×10^{19}	6000	750	3.57	6.67×10^{18}	8.37×10^{-14}
2.7×10^{19}	1200	910	10	1.47×10^{19}	6.56×10^{-12}
3.7×10^{18}	864000	800	4	5.50×10^{18}	3.78×10^{-13}
1.3×10^{19}	604800	820	5	6.37×10^{18}	5.8×10^{-13}
1.5×10^{19}	590400	845	5.26	6.45×10^{18}	1.14×10^{-12}
2.3×10^{19}	252000	870	6.78	6.67×10^{18}	2.29×10^{-12}
1.1×10^{19}	72000	920	11.11	8.87×10^{18}	7.8×10^{-12}

4. Results and discussion

The simulated profiles and the experimental profiles concordance, in Fig. 1 and Fig. 2, confirm the contribution with V^{2-} and V^{3-} on the diffusion of phosphorus in germanium.

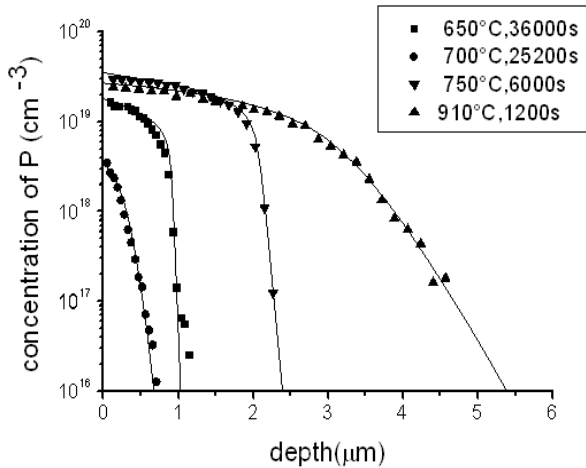


Fig. 1. Simulated profiles (solid lines) and experimental profiles (Ref. [14]) of phosphorus diffusion in Ge measured with SIMS.

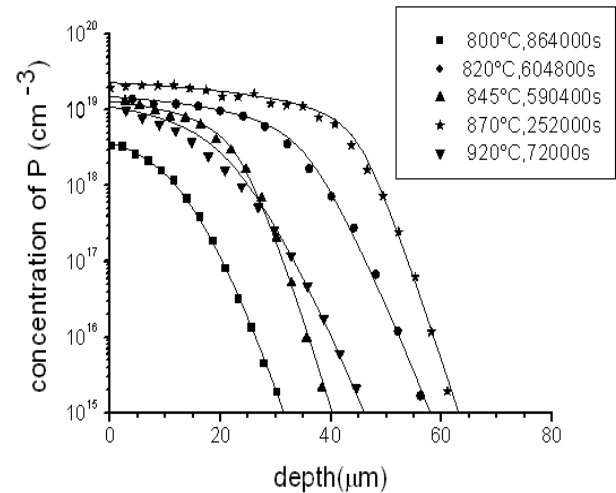


Fig. 2. Simulated profiles (solid lines) and experimental profiles (Ref. [14]) of phosphorus diffusion in Ge measured with SRP.

Fig. 3 shows that the ratio of the contributions to phosphorus diffusion via doubly negatively charged and triple negatively charged vacancies in germanium depends on the temperature from 650°C to 920 °C. According to Eq.

4, β is then given, in this temperature range, by the expression:

$$\beta = 79.32 \times 10^2 \exp \left[-\frac{(0.69) \text{ eV}}{KT} \right] \quad (17)$$

Where 0.69eV is the value of δg .

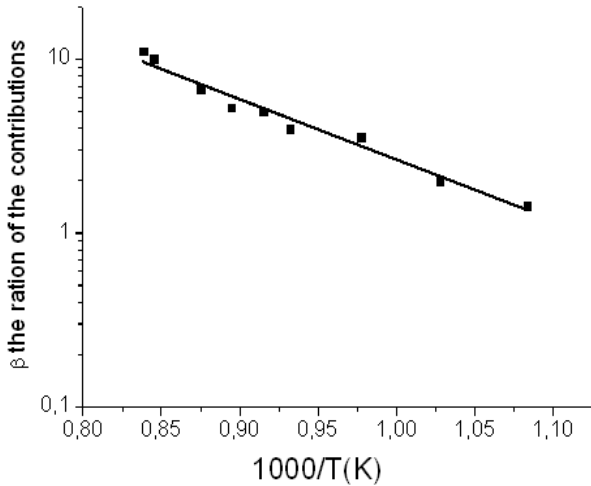


Fig. 3. β variation with the inverse of the temperature.

Fig. 4 shows the change of the diffusion coefficients via doubly and triply negatively charged vacancies depending on the inverse of the temperature, given by our simulation data.

The temperature dependence of the intrinsic diffusion coefficients of P via Ge vacancies with the charge states 2- and 3- are best reproduced by the following Arrhenius expressions:

$$D^{2-} = 83.29 \exp \left[-\frac{3.09 \text{ eV}}{KT} \right] (\text{cm}^2 \text{ s}^{-1}) \quad (18)$$

$$D^{3-} = 1.05 \times 10^{-2} \exp \left[-\frac{2.4 \text{ eV}}{KT} \right] (\text{cm}^2 \text{ s}^{-1}) \quad (19)$$

Where 3.09 eV and 2.4 eV respectively are the values of activation energies for phosphorus diffusion through doubly negatively charged and triply negatively charged vacancies.

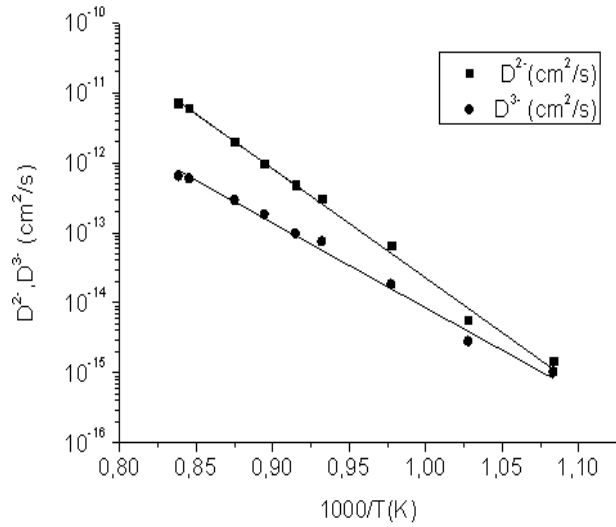


Fig. 4. Variation of D^{2-} and D^{3-} with the inverse of the temperature.

5. Conclusions

The phosphorus diffusion in germanium is performed by the vacancy mechanism via doubly negatively charged and triply negatively charged vacancies, where the ratio of the contributions is associated with temperature. This association is a result of the difference in the activation energies for phosphorus diffusion via the two states of charge of the vacancies which is estimated 0.69(eV). The ratio of the contributions to phosphorus diffusion via doubly negatively charged and triple negatively charged vacancies in germanium determined from the analysis of phosphorus diffusion in Ge is best reproduced by Eq. (17). The values of activation energies are 3.09 eV and 2.4 eV respectively, for phosphorus diffusion through doubly negatively charged and triply negatively charged vacancies. The intrinsic diffusion coefficients of P via Ge vacancies with the charge states 2- and 3-, are given by Eq. (18) and Eq.(19), respectively. The understanding of phosphorus diffusion in Ge will contribute to meet the requirements for the fabrication of modern electronic nanodevices.

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