

BORON AND PHOSPHORUS DIFFUSION IN SILICON: INTERSTITIAL, VACANCY AND COMBINATION MECHANISMS

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Abstract. *The diffusion of boron B and phosphorus P in silicon has been investigated by using the statistical moment method (SMM). Temperature dependence of activation energy, Q , and diffusion coefficient, D , of B and P in silicon obey interstitial, vacancy and combination mechanisms has been studied. The effects of anharmonicity and the different mechanisms on diffusion of B and P in silicon are calculated. Experimental results for B and P diffusion in silicon and SMM calculations of the activation energy for B and P diffusion by interstitial mechanism are in quantitative agreement.*

I. INTRODUCTION

IC (Integrated Circuit) fabrication is accomplished by selectively changing the electrical properties of silicon through the introduction of impurities commonly referred to as dopants. In recent years, integrated circuit fabrication, deep semiconductor junctions required doping processes followed by a drive-in step to diffuse the dopants to the desired depth, i.e. diffusion was required to successfully fabricated devices. In modern state-of-the-art IC fabrication the required junction depths have become so shallow that dopants are introduced into the silicon at the desired depth by ion implantation and any diffusion of the dopants is unwanted. Therefore, atomic processes of impurity diffusion in Si are of great scientific and technological interest. In particular, the problem of identifying the dominant diffusion mechanism has attracted considerable attention [1]. Both experimental observations and theoretical calculations indicate that diffusion of common dopants in Si mediated by interstitials (I), vacancies (V) or a concerted exchange (CE) mechanism [2, 3, 4, 5, 6, 7].

The development of theoretical calculations of atomic diffusion in silicon is of great interest. Namely, The First-principles total-energy calculations [2, 3], the Ab initio calculations [4, 8], the Tight-binding molecular dynamics (TBMD) [9], the Density functional theory (DFT) [10], the Local density approximation (LDA) [11],...In these papers, authors has been studied diffusion of impurities: B, P, As, Sb,... in silicon, calculated activation energy for an atom diffusion. They find that B, P, and As diffusion have substantial interstitial components, while Sb diffusion is vacancy dominated. Parallel with theoretical

methods, the diffusivity of dopant impurities in silicon have been measured. Instance for, the Secondary ion mass spectrometry (SIMS) [6, 7], the Radioisotope [12],...

In order to understand the diffusion of impurities in silicon, one should be careful to study the local behavior of impurities close to the vacancy and the interstitial. In the present study we used the moment method in statistical dynamics within the fourth order moment approximation, to calculate the activation energy, Q , pre-exponential, D_0 , and diffusion coefficient, D , of B and P in silicon at zero pressure. We also compare the calculated results for diffusion of B and P in silicon with the experimental data and the different theoretical calculations.

II. THEORY

Impurity atoms may occupy either substitutional or interstitial positions in the Si lattice. Vacancy diffusion occurs when a substitutional atom exchanges lattice positions with a vacancy- requires the presence of a vacancy. Interstitial diffusion occurs when an interstitial atom jumps to another interstitial position. Combination diffusion results from silicon self-interstitials displacing substitutional impurities to an interstitial position- requires the presence of silicon self-interstitials, the impurity interstitial may knock a silicon lattice atom into a self-interstitial position (Fig.1).

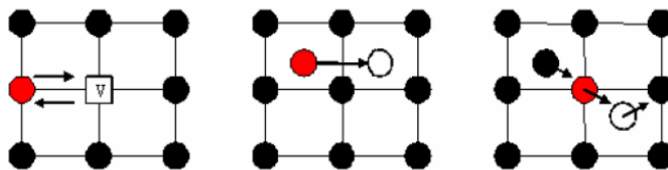


Fig. 1. Vacancy, interstitial and combination mechanisms

For all diffusion mechanisms, under equilibrium conditions, the diffusion coefficient, D , exhibits Arrhenius behavior over a wide range of temperatures [2]:

$$D = D_0 \exp\left\{-\frac{Q}{k_B T}\right\}, \quad (1)$$

where the pre-exponential factor, D_0 , and the activation energy, Q , can be temperature dependent, k_B is Boltzmanns constant, and T is the absolute temperature.

The diffusion of impurities (Ga, As, Al, Au) in Si for vacancy mechanism has been investigated in our paper [13]. Therefor, the activation energy Q , and the pre-exponential D_0 is given by

$$Q = -u_0 + \Delta\psi_0 - \Delta\psi_1 + TS_V^f, \quad (2)$$

$$D_0 = n_1 f \frac{\omega}{2\pi} r_1^2 \exp\left\{\frac{S_V^f}{k_B}\right\}, \quad (3)$$

with u_0 represent the sum of effective pair interaction energies between the zero-th atom (the central atom) and i -th atoms in crystal, $\Delta\psi_0$ denotes the change in the Helmholtz free energy of the central impurity atom upon moving itself to the certain sinks by creating a vacancy in the crystal, $\Delta\psi_1$ is change in the Gibbs free energy associated with the exchange of the vacancy with the neighboring impurity atoms, S_V^f is entropy of the formation a vacancy, f is the correlation factor and r_1 is the jump distance at temperature T , and n_1 denotes the number of the first nearest neighbor.

In this context, we present the diffusion of impurities in Si by interstitial mechanism. The silicon atoms symbol for A, the interstitial atoms is B. When an interstitial atom B jumps from one interstitial position (position 1) to another interstitial position (position 3) must go past intermediate position (position 2) - Fig. 2.

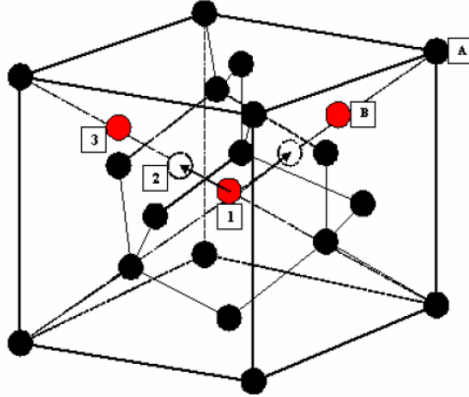


Fig. 2. The interstitial diffusion mechanism in Silicon.

The diffusion coefficient, D , will rate with the frequency of fluctuation and the transition probability of an interstitial atom (given by the Boltzman factor $\exp\{-\frac{E_a}{k_B T}\}$) [14].

$$D = g \frac{\omega}{2\pi} r_1^2 \exp\left\{-\frac{E_a}{k_B T}\right\}, \quad (4)$$

where g is a coefficient which depends on the crystalline structure and the mechanism of diffusion

$$g = n_1 f, \quad (5)$$

where f is the correlation factor, and n_1 denotes the number of adjacent sites in order to atom B can move to there, E_a is the activation energy ($E_a = Q$) is given by [7]

$$Q = h_I^f + h_I^m, \quad (6)$$

with h_I^f is the formation enthalpy of an interstitial, and h_I^m is the migration enthalpy of an interstitial atom as

$$h_I^f = -u_0^B + \Delta\psi_2^A, \quad (7)$$

$$h_I^m = \Delta\psi^B = \psi_2^B - \psi_1^B, \quad (8)$$

where u_0^B is the sum of the effective pair interaction energies between the interstitial atom, B, at position 2 and the surrounding silicon atoms, A; $\Delta\psi_2^A$ denotes the change in the Helmholtz free energy of the atoms, A, when atom B occupies position 2 in order to jumps to position 3, and as

$$\Delta\psi_2^A = \psi_2'^A - \psi_2^A = \frac{u_0^B}{2}, \quad (9)$$

ψ_1^B, ψ_2^B are the Helmholtz free energies of atom B at position 1 and position 2, respectively.

Substituting equations (7) and (8) into equation (6), we can be rewritten as

$$Q = -\frac{u_0^B}{2} + \psi_2^B - \psi_1^B, \quad (10)$$

Equation (4) can be rewritten as

$$D = D_0 \exp\left\{-\frac{Q}{k_B T}\right\}, \quad (11)$$

with

$$D_0 = n_1 f \frac{\omega}{2\pi} r_1^2 \quad (12)$$

For the combination mechanism, the total diffusion coefficient is of the form [2]

$$D = D_I + D_V \quad (13)$$

III. NUMERICAL RESULTS AND DISCUSSIONS

We now perform the statistical moment method (SMM) calculate the activation energy, Q , pre-exponential, D_0 , and diffusion coefficient, D , of B and P diffusion in silicon at zero pressure. Using the empirical many-body potential was developed for silicon [15]

$$\varphi = \sum_{i<j} U_{ij} + \sum_{i<j<k} W_{ijk}, \quad (14)$$

$$U_{ij} = \varepsilon \left[\left(\frac{r_0}{r_{ij}} \right)^{12} - 2 \left(\frac{r_0}{r_{ij}} \right)^6 \right], \quad (15)$$

$$W_{ijk} = Z \frac{(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(r_{ij} r_{jk} r_{ki})^3}, \quad (16)$$

where r_{ij} is the distance between the i -th atom and j -th atom in crystal; ε , r_0 , Z is the potential parameters are taken from [15]. These parameters are determined so as to fit the experimental lattice constants and cohesive properties.

Table 1: Potential parameters of the empirical many-body potential for Silicon [15]

ε (eV)	r_0 (Å)	Z (eV.Å ⁹)
2.817	2.295	3484

With the interstitial atoms, using the Pak-Doyam pair potential was developed for B and P [16]

$$\varphi_{ij} = \begin{cases} a(r_{ij} + b)^4 + c(r_{ij} + d)^2 + e, & r_{ij} < r_0 \\ 0, & r_{ij} \geq r_0 \end{cases} \quad (17)$$

The parameters for these potentials are presented in Table 2.

Table 2: Potential parameters of the Pak-Doyam pair potential for B and P [16]

	a	b	c	d	e	r_0 (Å)
φ_{BB} (eV)	-0.08772	-2.17709	0.79028	-2.85849	-0.09208	3.79
φ_{PP} (eV)	-0.07435	-2.60709	0.64791	-3.27885	-0.07531	4.21

Using the experiment data for Si and impurities B and P (Table 1 and Table2), and our theory in Section 2, we the obtain the values of activation energies Q , pre-exponential factor D_0 of B and P diffusion in Si with both interstitial and vacancy mechanisms. The SMM results are summarized in Table 3. The calculated results for the activation energies by the present theory are in good agreement with the experimental data, and the agreement is better with other theoretical methods.

Table 3: The SMM calculations with the experimental results and other calculations

	atoms	SMM	Expt	Other calculations	T(K)
Q(eV)	B_V	3.78	3.46 [14] 3.87 [17]	4.0 [2]	973- 1473 1113- 1523
	B_I	3.47	3.75 [6]	3.9 [2] 3.5 [4]	1123- 1273 -
	P_V	3.68	3.66 [14]	3.4 [2] 4.2 [3]	973- 1473
	P_I	3.02	2.81 [6]	3.8 [2] 4.0 [3]	- 1123- 1273
$D_0(cm^2/s)$	B_V	0.52	0.76 [14]	-	973- 1473
	B_I	$2, 73.10^{-2}$	7.78 [6]	-	1123- 1273
	P_V	0.32	3.85 [14]	-	973-
	P_I	$1, 60.10^{-3}$	$1, 71.10^{-3}$ [6]	-	1473 1123- 1273

For example, the activation energies, Q , calculated by the SMM for diffusion of P in Si with vacancy mechanism lie in the temperature range from 973K to 1473K is 3.68eV, while experimental result gives 3.66eV, but the Nicholss and Suginos calculations are 3.4eV and 4.2eV [2, 3]. Our calculation results show the activation energy for diffusion of B and P in Si by the interstitial mechanism is smaller than the vacancy mechanism, i.e., the dominant diffusion mechanism of B and P in Si is the interstitial mechanism, this result is agreement with conclusions by Nichols [2], Sugino [3], and Jones [14].

In Fig.3 and Fig.4 we show the temperature dependence of diffusion coefficient, D , of B and P in crystal Si obey combination mechanism. Our calculation results have been compared to available experimental data [6] showing a good agreement.

IV. CONCLUSIONS

In this paper we have performed the statistical moment method (SMM) to study temperature dependence of activation energy, Q , and diffusion coefficient, D , of B and P in silicon obey interstitial, vacancy and combination mechanisms. The calculated results for the activation energies by the present theory are in good agreement with the experimental data. We find that, B and P diffusion is mediated predominantly by interstitials, this conclusion confirm the conclusions of Nichols and Jones [3, 14].

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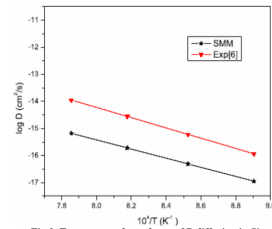


Fig.3. Temperature dependence of B diffusion in Si.

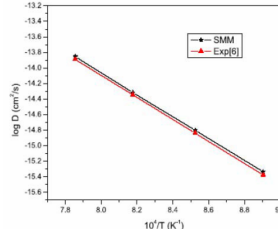


Fig.4. Temperature dependence of P diffusion in Si.

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