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ACTIVATION VOLUME FOR DIFFUSION IN SILICON

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Abstract. *The activation volume is the difference between the volume of system in two states: one has atom diffuse and another has not. In this study, we used the statistical moment method (SMM) with the four order expansion of interaction potential energy, i.e, we have taken into account the effects of anharmonic lattice vibration, to calculate activation volumes for self-diffusion and impurity-diffusion in silicon crystal. Numerical results for Si, B, P, and As diffusion in silicon are performed and compared to experimental data showing a good agreement with the experimental data and other theories.*

I. INTRODUCTION

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]. A study of the dependence of the atomic diffusivity on pressure, p, can provide valuable direct information to elucidate atomistic diffusion mechanisms [2, 3]. It can permit conclusions to be drawn about the predominant point defect mechanism independent of the assumptions inherent in the currently used kinetic models. The hydrostatic pressure dependence of the diffusivity, which is commonly characterized by the activation volume V^* is the difference between the volume of system in two states: one has atom diffuse and another has not. Measurements of the activation volume V^* , for B, P, As, Sb,... diffusion in silicon under hydrostatic pressure are executed by Zhao, Aziz and coworkers [4, 5, 6, 7, 8]. Atomistic calculations using molecular statics or dynamics have provided activation volumes under hydrostatic conditions for self-diffusion and impurity-diffusion in silicon crystal [9, 10].

In this paper, we us the moment method in statistical dynamics with the four order expansion of interaction potential energy, to calculate the lattice constants a of the silicon crystal at temperature T. Then, we us results of the theory presented in section II to determine activation volume V^* for self-diffusion and impurity-diffusion in silicon crystal at temperature T. The numerical results obtained by this method will be compared with the experimental data and previous theoretical calculations.

II. THEORY

According to the previous studies [3, 4, 5, 6, 7, 8, 11], the effect of pressure, p on the diffusion coefficient D is characterized by the activation volume V^*

$$V^* = -k_B T \frac{\partial lnD(p,T)}{\partial p}, \tag{1}$$

where k_B is the Boltzmann constant and T is the absolute temperature.

When negligible correction terms are omitted, the activation volume V^* is the sum of the formation volume V^f and the migration volume V^m [3, 7, 8, 11]:

$$V^* = V^f + V^m, \tag{2}$$

The formation volume V^f is the volume change in the system upon the formation of a defect in its standard state. The migration volume V^m is the additional volume change when the defect reaches the saddle point in its migration path. V^f and V^m for a simple vacancy and interstitialcy mechanism are shown schematically in Figure 1.

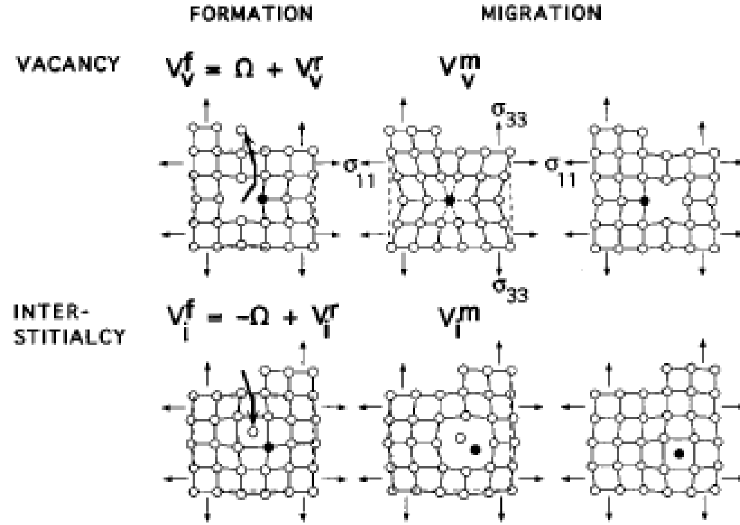

Figure.1. *Schematic volume changes (see dashed lines) upon point defect formation and migration for simple vacancy and interstitialcy mechanisms.*

The volumes V^f and V^m are given by Aziz [3, 11]:

$$V^f = (\frac{\partial G^f}{\partial p})_T = \pm\Omega + V^r, \tag{3}$$

$$V^m = (\frac{\partial G^m}{\partial p})_T, \tag{4}$$

where G^f is the standard free energy of formation of the mobile species, G^m is the additional change in free energy when the species move to the saddle point of its migration path, Ω is the atomic volume at temperature T, and the plus sign is for vacancy formation, and the minus sign is for interstitial formation. The relaxation volume V^r is the amount of outward relaxation of the sample surfaces (if the relaxation is inward, V^r is negative) due to the newly-created point defect.

Thus, in order to determined the activation volume V^* at temperature T we must determine the relaxation volume V^r and the migration volume V^m.

The relaxation volume V^r in units of Ω is given by [12]:

$$V^r_{I,V} = \frac{l^3_{I,V} - l^3_{eq}}{l^3_{eq}/N}, \tag{5}$$

here $l_{I,V}$ is the box length for interstitial (I) and vacancy (V) defects, respectively; l_{eq} is the original box length without defect; N is the number of atoms in the box. In the case of the box is a cubic lattice cell, the Eq. (5) can be rewritten as

$$V^r = \frac{a^3_d - a^3_p}{a^3_p/8}, \tag{6}$$

where, a_p or a_d denotes the lattice constants of the silicon crystal with perfect or defect, respectively.

From the schematic volume changes (see dashed lines) upon point defect formation and migration for simple vacancy and interstitialcy mechanisms (see Figure 1), we found that the migration volume V^m has the form analogous to Eq. (6)

$$V^m = \frac{a'^3_d - a^3_p}{a^3_p/8}, \tag{7}$$

here, a'_d is the lattice constant of the silicon crystal when defect moving.

The lattice constants a of the silicon crystal is determined according to formula

$$a = \frac{4}{\sqrt{3}} r_1, \tag{8}$$

where r_1 is the nearest neighbor distance between two atoms at temperature T, can be written as

$$r_1 = r_{10} + y_0, \tag{9}$$

with y_0 being the displacement of atom from equilibrium position at temperature T, which is determined by the SMM; r_{10} is the nearest neighbor distance between two atoms at absolute zero temperature ($T = 0K$) is determined from the equation of state [13]

$$pv = -r\left[\frac{1}{6}\frac{\partial u_0}{\partial r} + \frac{\hbar\omega}{4k}\frac{\partial k}{\partial r}\right], \tag{10}$$

where p denotes the hydrostatic pressure and v is the atomic volume; k denotes the vibrational constant and u_0 represents the sum of the effective pair interaction energies between the ith and 0th atoms:

$$u_0 = \sum_i \varphi_{i0}(|\vec{r_i}|), \tag{11}$$

$$k = \frac{1}{2}\sum_i \left(\frac{\partial^2 \varphi_{i0}}{\partial u_i^2}\right)_{eq} \equiv m\omega^2. \tag{12}$$

The vibrational constant k and sum of the effective pair interaction energies u_0 are calculated for the perfect, the self-interstitial defect and dopant-interstitial defect silicon crystal, then we solved Eq. (10) (In case pressure $p = 0$), and obtained the three following results:

i) The nearest neighbor distance r_{10p} for the perfect silicon crystal,

ii) The nearest neighbor distance r_{10d} for the self-interstitial defect silicon crystal,

iii) The nearest neighbor distance r'_{10d} for the dopant-interstitial defect silicon crystal.

Replace the values of r_{10p}; r_{10d}; r'_{10d} to Eq. (9), then using Eq. (8), we can find the lattice constants a_p; a_d; a'_d, respectively.

In previous interpreting atomistic calculations and experiments, the assumption has been made almost universally that V^m is negligible [3]. In the present study, we also assumed that the migration volume was negligible for self-diffusion and diffusion of impurities in silicon crystal via the vacancy mechanism.

III. NUMERICAL RESULTS AND DISCUSSIONS

We now use the theory formulas presented in section II to calculate activation volume V^* for self-diffusion and diffusion of impurities: B, P, and As in silicon crystal. We used the empirical many-body potential developed for Si and As [14], as described by the following equations:

$$\varphi = \sum_{i<j} \Phi_{ij} + \sum_{i<j<k} W_{ijk}, \tag{13}$$

$$\Phi_{ij} = \varepsilon[(\frac{r_0}{r_{ij}})^{12} - 2(\frac{r_0}{r_{ij}})^6], \tag{14}$$

$$W_{ijk} = Z\frac{(1 + 3\cos\theta_i \cos\theta_j \cos\theta_k)}{(r_{ij}r_{jk}r_{ki})^3}, \tag{15}$$

here, r_{ij}, r_{jk}, and r_{ki} denote the distances between the i-th and j-th atoms, the j-th and k-th atoms, and the k-th and i-th atoms in crystal; θ_i, θ_j, θ_k are the inside angles of a triangle created from three atoms i, j and k; ε, r_0, Z are the potential parameters, which are taken from [14]. These parameters are determined so as to fit the experimental lattice constants and cohesive properties of crystal.

With the atoms B and P, we use the Pak-Doyam pair potential developed in work [15]:

$$\varphi_{ij} = \begin{cases} a(r_{ij} + b)^4 + c(r_{ij} + d)^2 + e\ , & r_{ij} < r_0 \\ 0, & r_{ij} \geq r_0 \end{cases} \tag{16}$$

where, a, b, c, d, e, r_0 are the potential parameters, taken from [15].

Using the interaction potentials of Eqs. (13) and (16) with formulas (11) and (12), it is straightforwatd to obtain expressions of the interaction energy, u_0 and the vibrational constant k. Using the potential parameters for Si and impurities (from refs.14 and 15) and the Maple program, Eq.(10) can be solved. Then we can find the values of the nearest neighbor distances, r_{10p}; r_{10d}; r'_{10d}, at absolute zero temperature and subsequently, the temperature dependence of the lattice constants a_p; a_d; a'_d, can be calculated. Using the calculated values of a_p; a_d; a'_d, and the Eqs. (6) - (7), the relaxation volume, V^r, and the migration volume, V^m, at temperature T are calculated. Therefore, with the aid of Eqs. (3) and (4), the activation volumes V^* of the diffusion of the atoms: Si, B, P, and As in silicon crystal at temperature T can be calculated. The calculated SMM values of V^* at temperature T are presented in Table 1.

Table 1: Comparison of the SMM calculated results of the activation volume V^* of Si, B, P and As in silicon with experiments and other calculations.

Diffusion Atoms	Expt. and calculations	V^*/Ω	T(K)	Diffusion mechanism
Si	SMM	0.82	0	Vacancy
	Ab-initio[9]	0.76	0	vacancy
	SMM	-0.30	0	Interstitial
	Ab-initio[9]	-0.28	0	Interstitial
B	SMM	-0.17	1083	Interstitialcy
	Expt.[8]	-0.16±0.05	1083	Interstitialcy
	Expt.[5]	-0.17±0.01	1083	Interstitialcy
	Ab-initio[8]	-0.26	0	Interstitialcy
	Ab-initio[8]	-0.15	0	Interstitialcy
	Ab-initio[8]	-0.11	0	Interstitialcy
P	SMM	0.04	1113	Interstitial
	Expt.[7]	0.09±0.11	1113	Interstitial
As	SMM	-0.42	1223	Interstitialcy
	Expt.[4]	-0.42±0.10	1223	Interstitialcy
	SMM	0.80	1273	Vacancy
	Ab-initio[16]	0.20	-	Vacancy

From Table 1, we can see that, with the self-diffusion in Si crystal, our numerical results for both vacancy and interstitial mechanisms are consistent with the calculations by the ab initio theory, the error of about 8% for the vacancy mechanism and about 7% for the interstitial mechanism. With the diffusion of B and As in silicon crystal via an interstitialcy mechanism, the calculated results for the activation volume by the present theory are in good agreement with the experimental data, the error with the experimental data approximate to zero. The activation volume, V^*, of P diffusion in silicon crystal calculated by the SMM is not really in good agreement with the experimental data. However, if we find the more suitable potential energy function, we may obtain the better result.

IV. CONCLUSIONS

In this paper, we have performed the statistical moment method to calculate the activation volume, V^*, of self-diffusion and impurity-diffusion in silicon crystal via both vacancy and interstitialcy mechanisms. The SMM calculated results for the the activation volume, V^*, are in good agreement with the experimental data and the other theory calculations.

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