STUDY OF SELF-DIFFUSION IN SEMICONDUCTORS BY STATISTICAL MOMENT METHOD

Vu Van Hung, Nguyen Quang Hoc and Phan Thi Thanh Hong

Hanoi University of Education

Abstracts. Using the statistical moment method, self-diffusion in semiconductors is studied including the anharmonic effects of lattice vibrations. The interaction energies between atoms in semiconductors are estimated by applying many-body potential. The activation energy Q and pre-exponential factor D_0 of the self-diffusion coefficient are given in closed forms. The values of Q and D_0 are calculated for Si and GaAs at high temperature region near the melting temperatures and they shown to be in good agreement with the experimental data

1. Introduction

The physical properties of crystalline solids, like electrical conductivity, atomic diffusivity and mechanical strength are generally influenced quite significantly by the presence of lattice defects [1]. The point defects like the vacancies and interstitials, play an important role in determining the atomic diffusions in crystals [2]. It is known that the self-diffusion in close-packed crystals is almost completely conducted by the thermal lattice vacancies. On the other hand, the mechanical properties of the materials, e.g., creep, aging, recrystallization, precipitation hardening and irradiation effects (void swelling), are also extensively controlled by atomic diffusions [1]. Therefore, it is of great significance to establish a theoretical scheme for treating atomic diffusion in crystalline solids.

The theory of atomic diffusion in solids has a long history. In 1905, Einstein used incidental chaotic model for investigating the diffusion [3]. Bardeen và Hering impoved this model so as to include the correlation effect [4]. Using the transition state theory [5], Glestom et al. have derived the diffusion coefficient and showed that the self-diffusion obeys the Arrhenius's law. Kikuchi discussed the atomic diffusion in metals and alloys by applying the path probability method [6]. In general, the atomic diffusion have been studied within the framework of the phenomenological theories and based on the simple theory of the thermal lattice vibrations. In the present study, we establish a theoretical scheme to treat the self-diffusion in semiconductors taking into account the anharmonicity of lattice vibrations. We use the moment method in statistical dynamics in order to calculate the pre-exponential factor D_0 and the activation energy Q for self-diffusion in semicoductor with diamond cubic and zincblende ZnS structures. We compare the calculated results of self-diffusion in semiconductors with the experimental data.

2. Theory of self-diffusion in semeconductors

In the case of the self-diffusion conducted by a vacancy mechanism. it has been generally assumed that the diffusion coefficient D is simply given as

$$D = a\nu \exp [- Q/ RT)], \; Q = g_v^f + g_v^m, \tag{1}$$

where a and ν are the jump distance and attempt frequency of the atom, respectively. The activation energy Q of the self-diffusion is the sum of the changes in the free energy for the formation g_v^f and migration g_v^m of the vacancy.

In this paper, we investigate the self-diffusion in semiconductors by using the moment method in statistical dynamics. We consider the self-diffusion via vacancy mechanism and do not take into account the contribution from di-vacancies and direct atomic exchange mechanisms. We take into account the global lattice expansion originated from the anharmonicity of thermal lasttice vibrations, but do not consider the detailed local lattice relaxation around the vacancies. In order to study the atomic diffusion in semiconductors, one must firstly determine the equilibrium lattice spacing and the free energy of the perfect crystal because the atomic diffusion occur at finite temperatures. The calculational procedure for obtaining thermodynamic quantities of the perfect crystals has been given in our previous studies [7,8]. We then derive the thermodynamic quantities of the crystal containing thermal lattice vacancies, which play a central role in the self-diffusion of semiconductors.

Let us consider a monoatomic crystal consisting of N atoms and n lattice vacancies. By assuming N >> n the Gibbs free energy of the crystal is given as

$$G(T, p) = G_0(T,p) + n\, g_v^f(T,p) - TS_C, \tag{2}$$

where T and p denote the absolute temperature and hydrostatic pressure, respectively. $G_0(T,p)$ is the Gibbs free energy of pefect crystal of N atoms, $g_v^f(T,p)$ is the change in the Gibbs free energy due to the formation of a single vacancy and S_C is the entropy of mixing

$$S_c = k_B \ln \frac{(N+n)!}{N!\,n!}$$

where k_B denotes the Boltzmann constant. It is noted here that $g_v^f(T,p)$ contains contribution from vibrational entropy of the system.

The equilibrium cocentration of a vacancy n_v in semiconductors can be calculate from the Gibbs free energy of the system. To obtain the equilibrium concentration n_v, we use the minimization condition of the free energy with respect to n_v under the condition of constant p, T and N as

$$(\partial G/ \partial n_v)_{p,T,N} = 0. \tag{4}$$

This minimization condition leads to the concentration of the vacancy as

$$n_v = \exp\left[\frac{g_v^f(T,p)!}{\theta}\right] \tag{5}$$

with $\theta = k_B T$. Then, the Gibbs free energy of the crystal containing equilibrium thermal vacancies can be given by

$$g_v^f \cong -(n_1 + n_2)\psi_0^* + n_1\psi_1^* + n_2\psi_2^* + \Delta\psi_0^*, \tag{6}$$

where

$$\psi_0^* = 3\{U_0/6 + \theta[x + \ln(1 - e^{-2x})]\}, \tag{7a}$$

$$U_0 = \Sigma\, \varphi_{0i}(|\mathbf{r}_i|), \tag{7b}$$

$$\mathbf{r}_i = \mathbf{r}_0 + \Delta\mathbf{r}_i. \tag{7c}$$

Here, $x = \hbar\omega/2\theta$, ω denotes the atomic vibrational frequency, n_1 and n_2 denote numbers of the first and second nearest-neighbours, respectively. $\psi_0^* = \psi_0/N$ denotes the Helmholtz free energy per single atom in the perfect crystal[6],ψ_1^* and ψ_2^* represent the free energy of the atoms located at the nearest-neighbour and next nearest-neighbour sites of the vacancy, respectively, φ_{0i} is the interaction energy between zeroth and i-th atoms, $\mathbf{r}_i$ indicates the position of the i-th atom located at the neighbouring sites of the central 0-th atom or the nearest distance of the i-th atom at temperature T, $\mathbf{r}_0$ determines the nearest distance of the i-th atom at temperature 0K, $\Delta\mathbf{r}_i$ indicates the displacement of the i-th atom from the equilibrium position at temperature T or the thermal expansion depending on temperature of lattice and it is determined as in [9]. It must be noted that we take into account the anharmonicity of the thermal lattice vibration and therefore the temperature dependent thermal lattice expansion and vibrational force constants are considered.

To calculate the interaction energy U_0 of the perfect crystal, we use the empirical pair potentials and take into account the contributions up to the second nearest-neighbours. $\Delta\psi_0^*$ denotes the change in the Helmholtz free energy of the central atom which creates a vacancy by moving itself to the certain sinks (e.g., crystal surface, or to the core region of the dislocation and grain boundary) in the crystal

$$\Delta\psi_0^* = \psi_0^{*\prime} - \psi_0^* \equiv (B - 1)\,\psi_0^*, \tag{8}$$

where $\psi_0^{*\prime}$ denotes the free energy of the central atom after moving to a certain sink sites in the crystal. In this respect, it is noted that the vacancy formation energies

of the real crystals are measured experimentally as an average value over all those values corresponding to the possible sink sites.

In the theoretical analysis, it has been often assumed that the central atom originally located at the "vacancy site" moves to the special atomic sites, i.e., kink sites on the surface or in the core region of the edge dislocation in the bulk crystal which are thermodynamically eqivalent to bulk atoms [10]. This assumption simply leads to $B = 1$ in the above eq. (8). In the present study, we take the average value for B as

$$B \approx \frac{1}{2} + \frac{-(1+n_1+n_2)\psi_0^* + n_1\psi_1^* + n_2\psi_2^*}{-2\psi_0^*} \tag{9}$$

This is equivalent to the condition that the half of the broken bonds are recovered at the sink sites. We do not take into account the lattice relaxation around a vacancy, because the change in the free energy due to the lattice relaxation is a minor contribution compared to the formation energy of a vacancy, especially for high temperature region near the melting temperature.

We now derive the thermodynamic quantities of the semiconductor lattice containing thermal vacancies and discuss the self-diffusion via vacancy mechanism. From (2), the Gibbs free energy of the semiconductor lattice containing thermal vacancies can be written in the form

$$G = H - TS, \tag{10}$$

where $S = -(\partial G/\partial T)_p$ is the entropy and H represents the enthalpy of the system. Thus, the change in the Gibbs free energy g_v^f due to the creation of a vacancy can be written as

$$g_v^f(T,p) = G(T,p) - G_0(T,p) = h_v^f(T,p) - TS_v^f(T,p), \tag{11}$$

where h_v^f and S_v^f are the enthalpy and entropy of formation of a vacancy.

The diffusion coefficient D of the semiconductor lattice can be obtained by assuming that it is proportional to the vacancy concentration n_v and the jump frequency Γ [2]. When the amplitude of the atomic vibration exceeds certain critical value in the nearest neighbour sites of the vacancy, one can expect that atomic exchange process with a vacancy occurs. The number of jumps Γ^* per unit time is proportional to the vibrational frequency of the atom ω and the square of the diffusion length a (or distance of jumping)

$$\Gamma^* \sim r_1^2\omega/(2\pi) = (r_0 + \Delta r_1)^2\omega/(2\pi). \tag{12}$$

The general expression of diffusion coefficient D can then be written in the form

$$D = g\Gamma n_v a^2, \tag{13}$$

where g is a coefficient which depends on the crystalline structure and the mechanism of self-diffusion. It is given with the correlation factor f as

$$g = n_1 f. \tag{14}$$

The attempt frequency Γ of the atomic jump is proportional to Γ^* and the transition probability of an atom

$$\Gamma = \frac{\varpi}{2\pi}\exp\left(\frac{\Delta\psi_1^*}{\theta}\right). \tag{15}$$

The change in the Gibbs free energy associated with the exchange of the vacancy with the neighbouring atoms is equal to the inverse sign of $\Delta\psi_1^*$ and

$$g_v^m = -\Delta\psi_1^* \equiv -(B'-1)\,\psi_1^*. \tag{16}$$

where B' is simply regarded as a numerical factor, which is analogous to the factor B defined for formation energy of the vacancy.

Summarizing eqs. (12)-(16), one can derive the diffusion constant D of semiconductors via the vacancy mechanism as

$$D = n_1 f\frac{\varpi}{2\pi}a^2\exp\left(-\frac{h_v^f - \Delta\psi_1^*}{\theta}\right)\exp\left(\frac{TS_v^f}{\theta}\right) \tag{17}$$

The above formula of the diffusion coefficient can be rewritten as

$$D = D_0\exp\left(-\frac{Q}{k_B T}\right),\ Q = h_v^f + h_v^m,\ D_Q = n_1 f\frac{\varpi}{2\pi}a^2\exp\left(\frac{S_v^f}{k_B}\right), \tag{18}$$

where the correlation factor of the self-diffusion f = 0,5 [14] for semiconductors with diamond cubic and zincblend structures.and the activation energy Q is given by

$$Q = -(n_1 + n_2)\,\psi_0^* + n_1\psi_1^* + n_2\psi_2^* + (B-1)\,\psi_0^* - (B'-1)\,\psi_1^* + p\Delta V. \tag{19}$$

It is noted here that the contribution from the entropy of migration S_v^m is included in the $-(B'-1)\psi_1^*$ term, and not seperated as S_v^f in eq.(18). On the other hand, the entropy S_v^f for the formation of a vacancy can be given in the next-nearest neighbour approximation as

$$S_v^f = \frac{1}{n_1 + n_2}k_B\ln\frac{(N+1)!}{N!} = \frac{k_B}{n_1 + n_2}\ln(N+1) \tag{20}$$

With the use of eqs.(18)-(20) one can determine the activation energy Q and the diffusion coefficients D_0 at temperature T and pressure p.

In the following section we shall use the above results for finding the diffusion coefficient D_0, the activation energy Q for Si and GaAs semiconductors and compare them with experimental data.

3. Results of numerical calculations and discussions

Recently the theorists developed extensively the interaction potentials between atoms in the form of simple model in order to calculate directly the structural and thermodynamic properties for complex systems, especially for semiconductors [11,12]. The pair potentials like the Lennard-Jones potential and và the Morse potential have been applied to study the inert gas, metal and ion crystal, but completely used to the strong valence systems like semiconductors. To study the valence systems it is necessary to use the many-body interaction potentials, e.g., the potentials were presented by Stillinger, Weber [11], Tersoff [12]. One of the emperical many-body potentials for Si has the following form [13]

$$\Phi = \sum_{i<j} U_{ij} + \sum_{i<j<k} W_{ijk}$$

$$U_{ij} = \varepsilon\left[\left(\frac{r_0}{r_{ij}}\right)^{12} - 2\left(\frac{r_0}{r_{ij}}\right)^{6}\right], \tag{21}$$

$$W_{ijk} = G\frac{1 + 3\cos\theta_i \cos\theta_j \cos\theta_k}{\left(r_{ij} r_{jk} r_{ki}\right)^3}$$

This potential firstly is parameterized for Si. The parameters are fitted in with the cohesive lenghth of dimer and trimer, the lattice parameter and the cohesive energy of the diamond structure. Same potentials are expanded for the systems of two components and three components like GaAs, SiAs, SiGa. SiGaAs,...

Applying the many-body potentials (21), we calculate the nearest-neighbour interaction and the next-nearest- neighbour interaction and take the interaction energy in semiconductors as

$$U_0 = \varepsilon\left[A_{12}\left(\frac{r_0}{r_1}\right)^{12} - 2A_6\left(\frac{r_0}{r_1}\right)^{6}\right] + \frac{0.078 n_1 G_1}{r_1^9} + \frac{1.375 n_2 G_2}{(v_2 r_1)^9}, \tag{22}$$

where A_6, A_{12} are the structural sums for semiconductor.

The nearest neighbour distance $r_1(0)$ at temperature T = 0K is obtained by minimirizing the total energy of semiconductor or taking derivative

$$(\partial U_0/\partial r) = 0 \tag{23}$$

and is equal to

$$R_1(0) = \left[\frac{2\varepsilon A_{12} r_0^{12}}{\left(\Delta^2 + 4A_6 A_{12}\varepsilon^2 r_0^{18}\right)^{1/2} - \Delta} \right]^{1/3} \tag{24}$$

$$\Delta = 0.234G_1 + 0.0898G_2. \tag{25}$$

Using the experimental data for Si and GaAs (Table 1) and the formulae in the previous section, we obtain the values of the activation energy Q, the pre-exponential factor D_0 at various temoeratures for Si and GaAs. The numerical calculations are summirized in Tables 2 and 3. It is noted that the theoretical results can apply to GaAs though the analysis is more complex because of non-equal masses of atoms in the structure of ZnS type

Table 1: The parameters of the many-body potential for Si and GaAs [13]

Quantities	Si	GaAs
ε_A(eV)	2.817	
r_{0AA}(Å)	2.295	
G_{AAA}(eV.Å^9)	3484	
ε_{AB}(eV)		1.738
r_{0AB} (Å)		2.448
G_{AAB}(eV. Å ^{9})		1900
G_{ABB}(eV. Å ^{9})		4600

Table 2: The activation energy Q and the pre-exponential factor D_0 for Si

T(K)	200	400	600	800	1000	1200	1400
Q(kcal/mol)	85.95	87.56	89.21	90.88	92.565	94.25	95.96
D0(10^{-4}m^2/s)	6.18	6.55	6.95	7.24	7.44	7.58	7.72
a(Å)	5.1745	5.1840	5.1922	5.2001	5.2078	5.2162	5.2262

Table 3: The activation energy Q and the pre-exponential factor D_0 for GaAs

T(K)	200	400	600	800	1000	1200
Q(kcal/mol)	57.26	58.81	60.44	62.45	65.47	69.70
D_0(10^{-1}m^2/s)	3.83	4.09	4.64	-	-	-
a(Å)	5.5861	5.6002	5.6261	5.6767	5.7748	5.9389

For Si, from experimental data Q = 110 kcal/mol, D_0 = 1.8. 10^{-4}m^2/s [15], Q = 107.05 kcal/mol in the interval from 1128K to 1448K and Q = 109.82 kcal/mol in

the interval from 1473K to 1673K[16]. Therefore, the calculation results coincide relatively well with the experiment data.

For GaAs, from experimental data Q = 59.86 kcal/mol in the interval from 1298K to 1373K and Q = 128.92 kcal/mol in the interval from 1398K to 1503K[16]. The numerical results also agree relatively well with experiments. Both the activation energy and the diffusion coefficient for Si and GaAs increases when the temperature increases and this coincides with experiments.

This paper is finished by the financial sponsorship from the National Basic Research Programme in Natural Sciences..

References

1. R. W. Balluffi, A.V. Granato, *Dislocation in Solids* Vol.4, Dislocation in Metalurgy, ed. Nabarro F.R.N, North Holland,1998
2. N. I. Peterson, *Solid State Physics,* **22** (1968), 409
3. A.Einstein, *Ann. Physik,* **17**(105), 549
4. J. Bardeen, C. Herring, Atom Movement, *Ann. Soc. Metals,* Cleaveland, Ohio,1951, p.87
5. S. Gleston et al., *The Theory of Absolute Speed of Reaction*, Moskva,1948, p.543
6. R. Kikuchi , *J. Phys. Chem. Solids,* **20**(1961),17.
7. T. Nguyen, V. H. Vu, *Phys. Stat. Solidi,* **B149**(1988),511.
8. V. H. Vu et al., *J. Phys. Soc. Jpn,* **66**(1997), 3494.
9. V. H. Vu, T. M. H. Pham, *Hanoi University of Education J. of Science*, Natural Sciences Series N**1**(2002), 40.
10. K. Masuda-Jindo, *J. de Physique,* **47**(1986), 2087
11. F. Stillinger, T. Weber, *Phys. Rev.*, **B31**(1985), 5262.
12. J. Tersoff, *Phys. Rev.*, **B37**(1988),6991.
13. S. Erkoc, *Phys. Rep.,* **278**, **2**(1997), 81
14. V. H. Vu, V. T. Hoang, K. Masuda-Jindo , *J. Phys. Soc. Jpn* **69**(2000), 2691
15. N.A. Girifalco, *Statistical Physics of Material*, New York , 1973
16. R. L.. David, *Handbook of Chemistry and Physics*, 78th Edition, 1997-1998, p.104