Uphill diffusion of Si-interstitial during boron diffusion in silicon

Vu Ba Dung

Indian Journal of Physics

ISSN 0973-1458
Volume 91
Number 10

Indian J Phys (2017) 91:1233-1236
DOI 10.1007/s12648-017-1024-0

Springer

Indian J Phys (October 2017) 91(10):1233–1236
DOI 10.1007/s12648-017-1024-0

ORIGINAL PAPER

Uphill diffusion of Si-interstitial during boron diffusion in silicon

V B Dung*

Department of Physics, Hanoi University of Mining and Geology, Hanoi, Vietnam

Received: 11 August 2016 / Accepted: 9 March 2017 / Published online: 24 May 2017

Abstract: The phenomenon of uphill diffusion has been considered because of its frequent appearance in multicomponent systems. Several studies have been carried out to recommend the treatment for uphill diffusion and it is found that the diffusion flux of any component coupled with its partner species is the cause of uphill diffusion. In this paper, a new diffusion equation system based on irreversible thermodynamics theory is presented. With the system, uphill diffusion in ternary systems in silicon (simultaneous diffusion of boron, Si-interstitial and vacancy in silicon) can be treated.

Keywords: Diffusion of ternary system in silicon; Simultaneous diffusion equation; Uphill diffusion of Si-interstitial

PACS Nos: 66.30.-h; 66.30.Lw

1. Introduction

Uphill diffusion, the diffusion of a component up its own concentration gradient, which can take place in single component systems [1, 2]. However, Uphill diffusion often occurs in multicomponent systems [3–18]. A number of different approaches have been proposed for the treatment of uphill diffusion in ternary systemshfrt such as Darken [3], Oishi [4], Gupta and Cooper [5], Dayananda and Kim [6], Zhang [8], Trial and Spera [10], Krishna and Wesselingh [11], Nishiyama [12], Bozek and Danielewski [17]. In 1948, the first time, uphill diffusion was discussed and described by Darken's phenomenological equations. Darken [3] presented his phenomenological analysis of diffusion on binary systems. He developed equations that describes a dynamic phenomenon in terms of a thermodynamic state function and describes the interactions between the elements influences diffusion, and how it could lead to uphill diffusion. Recently, in 2015, Bożek et al. [17] showed that Darken method is consistent with Onsager phenomenology for the treatment of uphill diffusion. In the following, the author presented an equation system that can describe the simultaneous diffusion for ternary systems, which is determined by Onsager's equations. This equation system can be developed to treat uphill diffusion of Si-interstitial in simultaneous diffusion of boron, Si-interstitial and vacancy in silicon.

2. Simultaneous diffusion equation of ternary component systems

Many diffusion processes are simultaneous diffusions of multi-component. Based on irreversible thermodynamics, simultaneous diffusion of ternary components can be described by Onsager's equation system [17, 19, 20].

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3 \tag{1}$$

$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \tag{2}$$

$$J_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3 \tag{3}$$

where J_1, J_2, J_3 are diffusion fluxes of component 1, 2, 3; L_{11}, L_{22}, L_{33} parameters are related to diffusivities. The coefficients L_{12}, L_{21}, L_{13}, L_{31}, L_{23}, L_{32} measure the extent of the coupling between J_1, J_2, J_3; X_1, X_2, X_3 are driving forces on component 1, 2, 3. The fluxes J_1, J_2, J_3 are relative to each other by formula [19–21]

$$J_1 + J_2 + J_3 = 0 \tag{4}$$

As the temperature is uniform, the driving forces are related via the Gibbs–Duhem equation [20]

$$C_1X_1 + C_2X_2 + C_3X_3 = 0 \tag{5}$$

C_1, C_2 and C_3 are the concentration of component 1, 2, 3. Based on Eqs. (1, 2, 3), (4) and (5) J_1, J_2 and J_3 are determined

*Corresponding author, E-mail: zung305@gmail.com

$$J_1 = \left(L_{11} - L_{13}\frac{C_1}{C_3}\right)X_1 + \left(L_{12} - L_{13}\frac{C_2}{C_3}\right)X_2 \quad (6)$$

$$J_2 = \left(L_{21} - L_{23}\frac{C_1}{C_3}\right)X_1 + \left(L_{22} - L_{23}\frac{C_2}{C_3}\right)X_2 \quad (7)$$

$$J_1 = -(J_2 + J_3) \quad (8)$$

in which X_1, X_2 and X_3 are determined [21]

$$X_1 = -\frac{\partial \mu_1}{\partial x} = -\frac{kT}{C_1}\frac{\partial C_1}{\partial x} \quad (9)$$

$$X_2 = -\frac{\partial \mu_2}{\partial x} = -\frac{kT}{C_2}\frac{\partial C_2}{\partial x} \quad (10)$$

k is Boltzmann constant, T is temperature. Combining Eq. (4) with Eqs. (1, 2, 3), we have

$$L_{11} + L_{12} + L_{13} = 0;\ L_{21} + L_{22} + L_{23} = 0;\ L_{31} + L_{32} + L_{33} = 0 \quad (11)$$

According to Ongager's theory, we have [19–21]

$$L_{12} = L_{21};\ L_{13} = L_{31};\ L_{32} = L_{23} \quad (12)$$

based on Eqs. (11) and (12), we have

$$L_{12} = \frac{L_{33} - L_{11} - L_{22}}{2};\ L_{13} = \frac{L_{22} - L_{33} - L_{11}}{2};\ L_{23} = \frac{L_{11} - L_{22} - L_{33}}{2};\ L_{23} = \frac{L_{11} + L_{33} - L_{22}}{2} \quad (13)$$

where

$$L_{11} = \frac{C_1 D_1}{kT};\ L_{22} = \frac{C_2 D_2}{kT};\ L_{33} = \frac{C_3 D_3}{kT} \quad (14)$$

in which D_1, D_2, D_3 are diffusivities of component 1, 2, 3. Substituting Eqs. (14) into (13), L_{12}, L_{13}, L_{23} become

$$L_{12} = \frac{1}{2kT}(C_3D_3 - C_1D_1 - C_2D_2) \quad (15)$$

$$L_{13} = \frac{1}{2kT}(C_2D_2 - C_1D_1 - C_3D_3) \quad (16)$$

$$L_{23} = \frac{1}{2kT}(C_1D_1 - C_2D_2 - C_3D_3) \quad (17)$$

substituting Eqs. (9, 10), (13), (14) and (15, 16, 17) into (6), (7), (8) we have

$$J_1 = -D_{11}\frac{\partial C_1}{\partial x} - D_{12}\frac{\partial C_2}{\partial x} \quad (18)$$

$$J_2 = -D_{21}\frac{\partial C_1}{\partial x} - D_{22}\frac{\partial C_2}{\partial x} \quad (19)$$

$$J_3 = -(J_1 + J_2) \quad (20)$$

in which

$$D_{11} = \frac{1}{2}\left(2D_1 + D_3 + \frac{D_1C_1 - D_2C_2}{C_3}\right) \quad (21)$$

$$D_{12} = \frac{1}{2}\left(D_3 - D_2 + \frac{D_3C_3 - D_1C_1}{C_2} + \frac{D_1C_1 - D_2C_2}{C_3}\right) \quad (22)$$

and

$$D_{21} = \frac{1}{2}\left(D_3 - D_1 + \frac{D_3C_3 - D_2C_2}{C_1} + \frac{D_2C_2 - D_1C_1}{C_3}\right) \quad (23)$$

$$D_{22} = \frac{1}{2}\left(2D_2 + D_3 + \frac{D_2C_2 - D_1C_1}{C_3}\right) \quad (24)$$

D_{11}, D_{22} are called intrinsic diffusivities, and D_{12}, D_{21} are called mutual diffusivities. Equations (18, 19, 20) describe the diffusion of ternary systems.

In summary: Based on irreversible thermodynamics, the simultaneous diffusion of ternary components could be found out, which can be applied to the simultaneous diffusion of boron and point defect in silicon.

3. Uphill diffusion of Si-interstitial during boron diffusion in silicon

Boron impurity diffusion in silicon from a high surface concentration is accompanied by generation of point defects [22] that diffuse simultaneously with boron. So boron diffusion in silicon is simultaneous diffusion of boron (B), Si-interstitial (I) and vacancy (V).

Based on Eqs. (18, 19, 20), current fluxes of boron (J_B), Si-interstitial (J_I) and vacancy (J_V) can be written as

$$J_B = J_{BB} + J_{BI} \quad (25)$$

$$J_I = J_{IB} + J_{II} \quad (26)$$

$$J_V = -(J_B + J_I) \quad (27)$$

in which

$$J_{BB} = -D_{BB}\frac{\partial C_B}{\partial x} \quad (28)$$

$$J_{BI} = -D_{BI}\frac{\partial C_I}{\partial x} \quad (29)$$

$$J_{II} = -D_{II}\frac{\partial C_I}{\partial x} \quad (30)$$

$$J_{IB} = -D_{IB}\frac{\partial C_B}{\partial x} \quad (31)$$

where

$$D_{BB} = \frac{1}{2}\left(2D_B + D_V + \frac{D_BC_B - D_IC_I}{C_V}\right) \quad (32)$$

$$D_{BI} = \frac{1}{2}\left(D_V - D_I + \frac{D_VC_V - D_BC_B}{C_I} + \frac{D_BC_B - D_IC_I}{C_V}\right) \quad (33)$$

$$D_{II} = \frac{1}{2}\left(2D_I + D_V + \frac{D_I C_I - D_B C_B}{C_V}\right) \quad (34)$$

$$D_{IB} = \frac{1}{2}\left(D_V - D_B + \frac{D_V C_V - D_I C_I}{C_B} + \frac{D_I C_I - D_B C_B}{C_V}\right) \quad (35)$$

Equations (25), (26) show that: the diffusion flux of any component (B or I) depends on concentration gradient of its partner (I or B), which is called coupled effect. Diffusivities D_{BB}, D_{BI} of boron depend on B_I, D_V, C_I, C_V and D_{II}, D_{IB} of Si-interstitial depend on B_B, D_V, C_B, C_V. This shows that there is interaction between B, I and V.

Diffusion flux Eqs. (25, 26, 27) give the following nonlinear diffusion equations:

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left(D_{BB}\frac{\partial C_B}{\partial x}\right) + \frac{\partial}{\partial x}\left(D_{BI}\frac{\partial C_I}{\partial x}\right) \quad (36)$$

$$\frac{\partial C_I}{\partial t} = \frac{\partial}{\partial x}\left(D_{IB}\frac{\partial C_B}{\partial x}\right) + \frac{\partial}{\partial x}\left(D_{II}\frac{\partial C_I}{\partial x}\right) \quad (37)$$

$$\frac{\partial C_V}{\partial t} = -\left(\frac{\partial C_B}{\partial t} + \frac{\partial C_I}{\partial t}\right) \quad (38)$$

The numerical solution of equation system (36, 37, 38) can be solved in one direction ($0 \le x \le L$) with boundary and initial conditions

$$C_B(0,t) = C_{B0}; C_B(x,0) = 0; C_B(L,t) = 0 \quad (39)$$

$$C_I(0,t) = C_I(L,t) = C_I(x,0) = C_{I0} \quad (40)$$

$$C_V(0,t) = C_V(L,t) = C_V(x,0) = C_{V0} \quad (41)$$

When boundary, initial conditions are chosen [23–25]: $C_{B0} = 10^{19}$ cm^{-3}; $D_B = 1.28 \times 10^{-14}$ cm^2 s^{-1}; $C_{I0} = 1.1 \times 10^{12}$ cm^{-3}; $D_I = 2.57 \times 10^{-11}$ cm^2 s^{-1}; $C_{V0} = 1.0 \times 10^{15}$ cm^{-3}; $D_V = 3.21 \times 10^{-10}$ cm^2 s^{-1}; T = 1273 K; L = 1 μm, we have the result of numerical solution of equation system (36, 37, 38) with boundary and initial conditions (39, 40, 41) as presented in Table 1.

Table 1 Numerical result of the simultaneous diffusion equation of B, I and V in Si for 10 diffusion minutes at 1000 °C

x (cm)	C_B	C_I	C_V
$x_0 = 0.00$	1.0×10^{19}	1.1×10^{12}	1.0×10^{15}
$x_1 = 5.3 \times 10^{-6}$	6.5×10^{18}	2.0×10^{13}	5.8×10^{13}
$x_2 = 1.1 \times 10^{-5}$	4.4×10^{18}	2.6×10^{13}	4.5×10^{13}
$x_3 = 2.1 \times 10^{-5}$	1.6×10^{18}	2.4×10^{13}	4.8×10^{13}
$x_4 = 3.2 \times 10^{-5}$	4.0×10^{17}	1.7×10^{13}	6.9×10^{13}
$x_5 = 4.2 \times 10^{-5}$	7.2×10^{16}	1.0×10^{13}	1.1×10^{14}
$x_6 = 5.3 \times 10^{-5}$	9.6×10^{15}	5.6×10^{12}	2.0×10^{14}
$x_7 = 6.4 \times 10^{-5}$	9.8×10^{14}	2.9×10^{12}	4.0×10^{14}
$x_8 = 7.4 \times 10^{-5}$	7.8×10^{13}	1.4×10^{12}	8.2×10^{14}
$x_9 = 1.0 \times 10^{-4}$	5.5×10^{10}	4.5×10^{11}	2.5×10^{15}

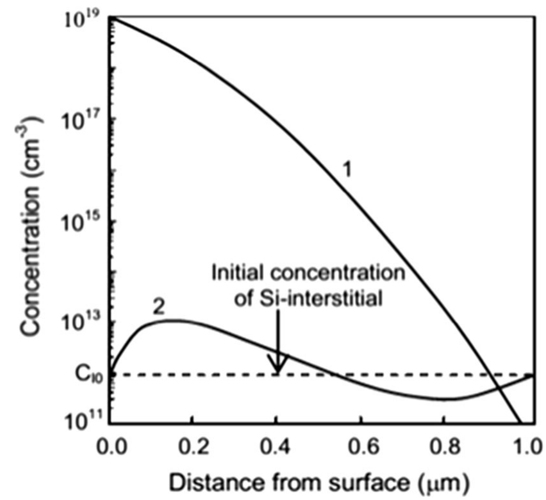

Fig. 1 Concentration profiles of boron (curve 1) and Si-interstitial (curve 2) in Si for 10 diffusion minutes at 1000 °C

Table 2 Dependent of D_{II} and D_{IB} on diffusion depth

x (cm)	D_{IB} (cm^{2}s^{-1})	D_{II} (cm^{2}s^{-1})
$x_1 = 5.3 \times 10^{-6}$	-6.5×10^{-10}	-3.3×10^{-10}
$x_2 = 1.1 \times 10^{-5}$	-5.2×10^{-10}	-2.0×10^{-10}
$x_3 = 2.1 \times 10^{-5}$	-1.2×10^{-10}	2.0×10^{-10}
$x_4 = 3.2 \times 10^{-5}$	1.5×10^{-11}	3.4×10^{-10}
$x_5 = 4.2 \times 10^{-5}$	2.3×10^{-11}	3.4×10^{-10}
$x_6 = 5.3 \times 10^{-5}$	1.7×10^{-11}	3.4×10^{-10}
$x_7 = 6.4 \times 10^{-5}$	1.9×10^{-11}	3.4×10^{-10}
$x_8 = 7.4 \times 10^{-5}$	1.5×10^{-10}	3.4×10^{-10}
$x_9 = 1.0 \times 10^{-4}$	5.8×10^{-10}	3.4×10^{-10}

Figure 1 shows concentration profiles of boron (curve 1) and Si-interstitial (curve 2). Values and signs of D_{II} and D_{IB}- at the distances from surface about (0 ÷ 1 μm) are calculated and presented in Table 2 and Fig. 2.

Results show that:

1. Initially, although concentration is uniform ($C_I = C_{I0}$), the diffusion process of Si-interstitial still takes place. This is an osmotic diffusion. In this case, the diffusion equation of Si-interstitial (26) becomes

$$J_I = J_{IB} = -D_{IB}\frac{\partial C_B}{\partial x} \quad (42)$$

2. After the initial period, concentration gradient of Si-interstitial does not vanish, but concentration gradient values of Si-interstitial are very small and almost negligible. Thus, diffusion of Si-interstitial is also described by Eq. (19). This shows that diffusion flux of Si-interstitial depends on concentration gradient of

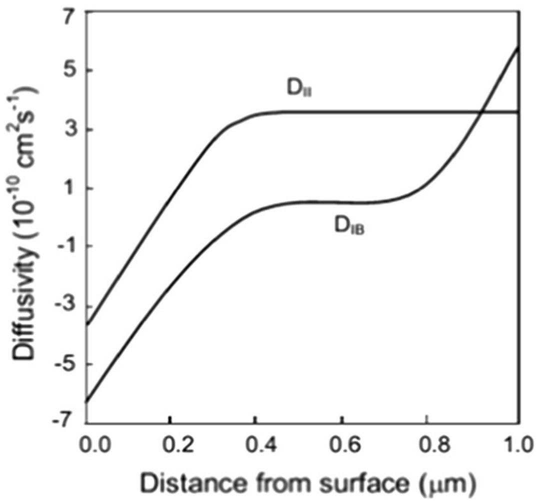

Fig. 2 Graph of depending of D_{II} and D_{IB} on diffusion depth during diffusion of boron in Si

Table 3 Value and sign of Si-interstitial flux in silicon at the time after 10 min of diffusion

Δx	$\Delta C_B/\Delta x$ (cm^{-4})	D_{IB} ($cm^2\ s^{-1}$)	$J_I \approx J_{IB}$ ($cm^{-2}\ s^{-1}$)	Type of diffusion
x_1–0	-6.6×10^{23}	-6.5×10^{-10}	-4.3×10^{14}	Uphill
x_2–x_1	-3.7×10^{23}	-5.2×10^{-10}	-1.9×10^{14}	Uphill
x_3–x_2	-2.8×10^{23}	-3.0×10^{-10}	-8.4×10^{13}	Uphill
x_4–x_3	-1.1×10^{23}	-1.2×10^{-10}	-1.3×10^{13}	Uphill
x_5–x_4	-3.3×10^{22}	1.5×10^{-11}	5.0×10^{11}	Downhill
x_6–x_5	-5.6×10^{21}	2.3×10^{-11}	1.3×10^{11}	Downhill
x_7–x_6	-7.8×10^{20}	1.7×10^{-11}	1.3×10^{10}	Downhill
x_8–x_7	-9.0×10^{19}	1.9×10^{-11}	1.7×10^{9}	Downhill
x_9–x_8	-3.0×10^{18}	1.5×10^{-10}	4.5×10^{8}	Downhill

boron impurity. It means the cause of Si-interstitial diffusion is coupled effect.

Values and signs of diffusion flux of Si-interstitial calculated and presented in Table 3 shows that:

1. In the near surface area (x = 0.0 ÷ 0.5 μm), D_{IB} is negative and diffusion flux J_I goes to the area of higher boron concentration. It means Si-interstitial diffuses uphill;
2. In the far surface area (x = 0.5 ÷ 1.0 μm), D_{IB} is positive and diffusion flux J_I goes to the area of lower boron concentration. It means Si-interstitial diffuses downhill (normal diffusion). According to A. Willoughby and S. Hu, in simultaneous diffusion of multi-components in silicon, any component can interact (electric interaction [22, 26]) with its partners. In the near surface area, boron concentration is very high, so the interaction is very strong. Strong interaction makes D_{IB} become negative and Si-interstitial diffuses uphill.

   In the far surface area, the concentration of boron is low, the interaction is weak and almost negligible. Thus, Si-interstitial diffuses normally.

4. Conclusions

Based on the Onsager's classic equations of thermodynamics, the equation system of simultaneous diffusion in the ternary system has been found out.

The diffusion of boron impurity in silicon is the diffusion in the ternary system (boron, Si-interstitial and vacancy), which can be described by simultaneous diffusion equation system.

During the diffusion of boron impurity in silicon, intrinsic and mutual diffusivities of Si-interstitial can be negative and Si-interstitial can diffuse uphill.

The coupled effect and the interaction between boron and vacancy with Si-interstitial are the causes of the uphill diffusion of Si-interstitial in silicon.

References

[1] V B Dung *Far East J. Dyn. Syst.* **27** 79 (2015)
[2] V B Dung and B H Nguyen *J. Phys. Conf. Ser.* **726** 012021 (2016)
[3] L S Darken *Trans. AIME* **174** 184 (1948)
[4] Y Oishi *J. Chem. Phys.* **43** 1611 (1965)
[5] P Gupta and A Cooper *Physica* **54** 39 (1972)
[6] M Dayananda and C Kim *Metall. Trans.* A **10** 1333 (1979)
[7] J Anderson and J Agren *J. Appl. Phys.* **72** 1350 (1992)
[8] Y Zhang, *J. Geophys. Res.* **98** 11901 (1993)
[9] K Holly and M Danielewski *Phys. Rev. B* **50** 13336 (1994)
[10] A Trial and F Spera *Geochim. Cosmochim. Acta* **58** 3769 (1994)
[11] R Krishna and J Wesselingh *Chem. Eng. Sci.* **52** 861 (1997)
[12] T Nishiyama *Phys. Earth Planet. Inter.* **107** 33 (1998)
[13] R Duffy, V Venezia, A Heringa, T Husken, M Hustaken, M Cowern, P Griffin and C Wang *Appl. Phys. Lett.* **82** 3647 (2003)
[14] S Emmanuel, A Cortis and B Berkowitz *Chem. Phys.* **302** 21 (2004)
[15] E Watson and E Baxter *Earth Sci. Lett.* **353** 307 (2007)
[16] R Krishna *Chem. Soc. Rev.* **44** 2812 (2015)
[17] B Bożek, M Danielewski, K Tkacz-Śmiech and M Zajusz *Mater. Sci. Technol.* **31** 1633 (2015)
[18] M Danielewski, M Zajusz, B Bożek and K Tkacz-Śmiech *Defect Diffus. Forum* **369** 53 (2016)
[19] A C Lasaga *Kinetic Theory in the Earth Sciences*. (New Jersey: Princeton University Press) p 447 (1998)
[20] I Prigogine *Introduction to Thermodynamics of Irreversible Processes* (New York: Interscience) (1967)
[21] R E Howard and A B Lidiard *Rep. Prog. Phys.* **27** 161 (1964)
[22] A F W Willoughby *J. Phys. D: Appl. Phys.* **10** 476 (1977)
[23] H Bracht, N Stolwijk and H Mehrer *Phys. Rev.* **B52** 16542 (1995)
[24] H Gossman, C Rafferty, H Luftman, F Unterwald and T Boone Poate *Appl. Phys. Lett.* **63** 639 (1993)
[25] S W Jones *Diffusion in Silicon* (Copyright 2000 IC Knowledge LLC—All rights reserved) (2008)
[26] S M Hu and S Schmidt *J. Appl. Phys.* **39** 4272 (1968)