Negative diffusivity and uphill diffusion of vacancy during boron diffusion in silicon

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***Abstract* - In this paper, the author presents study results about the diffusivity and the diffusion of vacancy during B diffusion in silicon. Results showed that: i) During boron diffusion in silicon, which makes vacancy is generated and interacts with vacancy; ii). The interaction between boron impurity and vacancy is cause of the dependence of the vacancy diffusion flux on the concentration gradient of boron; iii) The interaction makes the coupled diffusion effect occurs in silicon; iv) Interaction between boron impurity and vacancy is the cause of negative mutual diffusivity and uphill diffusion of vacancy in silicon.**

Keywords: Negative mutual diffusivity, Uphill diffusion of vacancy.

I. INTRODUCTION

Diffusion of dopants such as boron (B), arsenic (As), phosphorus (P) in silicon is generally controlled by intrinsic point defects [1-6], these can generate Si-interstitials and vacancies [1]. Point defects diffuse simultaneously and interact with dopants. The interaction between impurity and point defects makes diffusion process and diffusivities become more complex and this can be caused of the anomalous diffusion (Emitter-push, Buried marker layer, Base retardation) [7-9] and uphill diffusion. Several approaches are proposed for treatment of multicomponent diffusion [10-12], one of them is the base on Onsager's equation system, the simultaneous diffusion equations of B, I and V (a ternary system) has been found out [13]:

$$J_B = -D_{BB}\frac{\partial C_B}{\partial x} - D_{BI}\frac{\partial C_I}{\partial x} \qquad (1)$$

$$J_I = -D_{IB}\frac{\partial C_B}{\partial x} - D_{II}\frac{\partial C_I}{\partial x} \qquad (2)$$

$$J_V = -(J_B + J_I) \qquad (3)$$

in which:

$$D_{BB} = \frac{1}{2}\left(2D_B + D_V + \frac{D_B C_B - D_I C_I}{C_V}\right) \qquad (4)$$

$$D_{BI} = \frac{1}{2}\left(D_V - D_I + \frac{D_V C_V - D_B C_B}{C_I} + \frac{D_B C_B - D_I C_I}{C_V}\right) \qquad (5)$$

$$D_{II} = \frac{1}{2}\left(2D_I + D_V + \frac{D_I C_I - D_B C_B}{C_V}\right) \qquad (6)$$

$$D_{IB} = \frac{1}{2}\left(D_V - D_B + \frac{D_V C_V - D_I C_I}{C_B} + \frac{D_I C_I - D_B C_B}{C_V}\right) \qquad (7)$$

where C_B, C_I, C_V are concentrations and D_B, D_I, D_V are diffusivities of boron, interstitial and vacancy; D_{BB}, D_{II} and D_{BI}, D_{IB} are intrinsic diffusivity ad mutual diffusivity of boron and interstitial.

Uphill diffusion is diffusion process, in which the diffusion flux goes up to a higher concentration area. Uphill diffusion often occurs in multicomponent systems [14-19]. A number of different approaches have been proposed for the treatment of uphill diffusion in binary and ternary systems, such as Y. Oishi (1965) [14], M. Dayananda, C. Kim (1979) [15], Y. Zhang (1993) [16], R. Krishna, J. Wesselingh (1997) [17], T. Nishiyama (1998) [18], R. Krishna (2019) [19]. They have shown that: i) the coupled diffusion effect (diffusion flux of any component depends on the concentration gradient of its partner component) is the cause of uphill diffusion in the multicomponent diffusion systems for gas, liquid and metal. However, the uphill diffusion can occur in semiconductor material [20, 21].

In the following, the coupled diffusion effect, negative diffusivity and uphill diffusion of vacancy, during boron diffusion in silicon material are presented and discussed.

Table 1. Distribution of concentration of B, I and V in Si for 10 diffusion minutes at 1000 °C.

X (cm)	C_B (cm^{-3})	C_I (cm^{-3})	C_V (cm^{-3})
0.00	1.0×10^{19}	1.1×10^{12}	1.0×10^{15}
5.3×10^{-6}	6.5×10^{18}	2.0×10^{13}	5.8×10^{13}
1.1×10^{-5}	4.4×10^{18}	2.6×10^{13}	4.5×10^{13}
2.1×10^{-5}	1.6×10^{18}	2.4×10^{13}	4.8×10^{13}
3.2×10^{-5}	4.0×10^{17}	1.7×10^{13}	6.9×10^{13}
4.2×10^{-5}	7.2×10^{16}	1.0×10^{13}	1.1×10^{14}
5.3×10^{-5}	9.6×10^{15}	5.6×10^{12}	2.0×10^{14}
6.4×10^{-5}	9.8×10^{14}	2.9×10^{12}	4.0×10^{14}
7.4×10^{-5}	7.8×10^{13}	1.4×10^{12}	8.2×10^{14}
1.0×10^{-4}	5.5×10^{10}	4.5×10^{11}	2.5×10^{15}

II. DIFFUSION EQUATION OF VACANCY IN SILICON

Equation system (1, 2, 3) describe the diffusion process of boron, interstitial and vacancy in silicon. However, the concentration gradient value of interstitial is very small and almost negligible [22], so equation (1, 2, 3) become:

$$J_B = -D_{BB}\frac{\partial C_B}{\partial x} \tag{8}$$

$$J_I = -D_{IB}\frac{\partial C_B}{\partial x} \tag{9}$$

$$J_V = -(J_B + J_I) \tag{10}$$

Diffusion equation of boron, interstitial and vacancy in silicon can be written by the Fick's 2nd equation [13] as follow:

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left(D_{BB}\frac{\partial C_B}{\partial x}\right) \tag{11}$$

$$\frac{\partial C_I}{\partial t} = \frac{\partial}{\partial x}\left(D_{IB}\frac{\partial C_B}{\partial x}\right) \tag{12}$$

$$\frac{\partial C_V}{\partial t} = -\left(\frac{\partial C_B}{\partial t} + \frac{\partial C_I}{\partial t}\right) \tag{13}$$

The numerical solutions of equation system (11, 12, 13) have been solved on distance from silicon surface x = 0 ÷ 1.2 μm and boundary, initial conditions are chosen [13]: $C_B(t=0) = 10^{19}$ cm^{-3}; $D_B = 1.28\text{x}10^{-14}$ cm^{2}s^{-1}; $C_I(t=0) = C_{I0} = 1.1\text{x}10^{12}$ cm^{-3}; $D_I = 2.57\text{x}10^{-11}$ cm^{2}s^{-1}; $C_V(t=0) = C_{V0} = 1.0\text{x}10^{15}$ cm^{-3}; $D_V = 3.21\text{x}10^{-10}$ cm^{2}s^{-1}; T = 1273K. The numerical solution of equation system (11, 12, 13) is presented in table 1.

Figure 1 is the graphs of diffusion profile of boron and vacancy, which are plotted by the data in table 1. These graphs show that the diffusion of boron is normal diffusion process (boron diffusion goes down to a lower concentration area), but based on the concentration profile of vacancy, we can predict the uphill diffusion can occur for vacancy.

For survey the diffusivity and diffusion process of vacancy, the equation diffusion and diffusivity express of vacancy must be found out. Based on equations (8), (9) and (10), diffusion flux of vacancy can be written by:

$$J_V = (D_{BB} + D_{IB})\frac{\partial C_B}{\partial x} = D_{VB}\frac{\partial C_B}{\partial x} \tag{14}$$

in which, mutual diffusivity of vacancy D_{VB} is determined by:

$$D_{VB} = -\frac{1}{2}\left(2D_V + D_B + \frac{D_V C_V - D_I C_I}{C_B}\right) \tag{15}$$

Equation (14) is equation diffusion vacancy and express (15) is mutual diffusivity, which shows that the diffusion flux of vacancy is determined by concentration gradient of boron and mutual diffusivity D_{VB}. It means diffusion of vacancy in silicon depends on coupled diffusion effect. Properties of the diffusion and diffusivity of vacancy can be studied by the diffusion flux (Eq. 14) and the mutual diffusivity D_{IB} (Eq. 15). Equation 14 shows that the diffusion of vacancy in silicon does not depend on concentration gradient of vacancy, but it depends on concentration gradient of boron and mutual diffusivity D_{VB} depends on boron concentration (this dependence can be the interaction of boron with vacancy [1]). It means the cause of diffusion of vacancy in silicon is the coupled diffusion effect [17, 18]. Thus, the equation (14) can describe the coupled diffusion effect and the mutual diffusivity D_{VB} can describe the interaction of vacancy with boron.

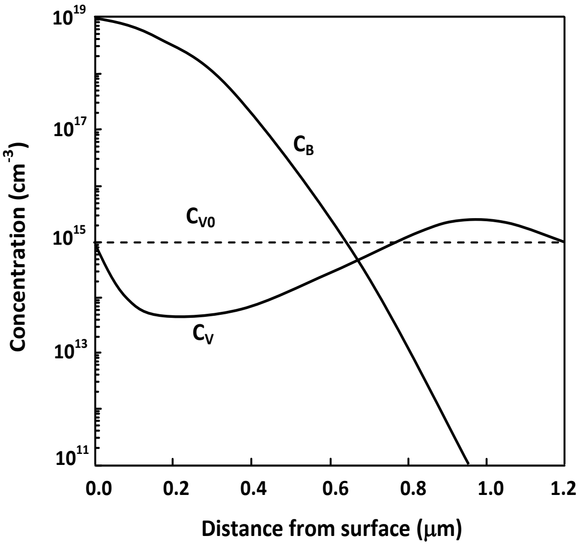

Figure 1. Concentration profiles of boron (curve C_B) and Si-interstitial (curve C_V) in Si for 10 diffusion minutes at 1000°C (line C_{V0} is initial vacancy concentration).

However, the property of vacancy diffusion in silicon depends on sign of mutual diffusion D_{VB}.

Table 2. Values and signs of D_{VB} at the distances from surface (0 ÷ 0.64 μm) for 10 diffusion minutes.

x(cm)	$D_{VB}(cm^3s^{-1})$
$x_0 = 0.00$	-3.21×10^{-8}
$x_1 = 5.3 \times 10^{-6}$	-3.21×10^{-9}
$x_2 = 1.1 \times 10^{-5}$	-3.21×10^{-10}
$x_3 = 2.1 \times 10^{-5}$	-3.21×10^{-10}
$x_4 = 3.2 \times 10^{-5}$	-3.21×10^{-10}
$x_5 = 4.2 \times 10^{-5}$	-3.21×10^{-10}
$x_6 = 5.3 \times 10^{-5}$	-3.24×10^{-10}
$x_7 = 6.4 \times 10^{-5}$	-3.87×10^{-9}

III. NEGATIVE DIFFUSIVITY AND UPHILL DIFFUSION OF VACANCY IN SILICON

Equation (15) shows that mutual diffusivity of vacancy D_{VB} depended on boron concentration C_B, the cause of this dependence may be the interaction of vacancies with boron (according to A. Willoughby and S. Hu, this is the electric interaction [1, 7]. Based on equation (15) the value and sign mutual diffusivity of vacancy D_{VB} are calculated and presented in Table 2, Figure 2. The result shows that: during boron diffusion in silicon, mutual diffusivity of vacancy is negative.

Property of diffusion depends on diffusivity sign:

i) When diffusivity is positive, diffusion flux goes down to the lower concentration area, this is normal diffusion type (it is also called downhill diffusion;

ii) When diffusivity is negative, diffusion flux goes up to the higher concentration area, this is uphill diffusion type;

iii) When diffusivity equals to zero, but diffusion flux does not vanish, that is osmotic diffusion.

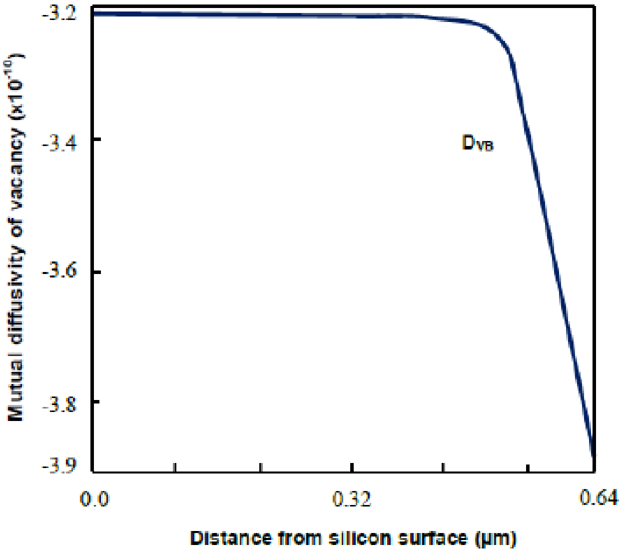

Figure 2. Graphs of Intrinsic and mutual diffusivities of vacancy in silicon are plotted by the data in table 2.

Uphill diffusion can occur in single component systems [23-25], but they often occur in multicomponent systems and their cause is coupled diffusion effect [12, 19, 26, 27]. During boron diffusion in silicon, vacancy is not only generated but also diffused simultaneously with boron. In silicon, the diffusivity of vacancy is negative, so vacancy diffuses uphill. It means diffusion flux of vacancy go up to the high concentration of vacancy in silicon.

Thus, during boron diffusion, vacancy is generated. Vacancy diffuses and interacts with boron impurity in silicon. This interaction is the cause of the coupled diffusion effect and the dependence of mutual diffusivity of vacancy on the concentration of boron impurity. This interaction makes diffusion flux of vacancy depend only on the concentration gradient of boron impurity. Interaction between boron impurity and vacancy is also the cause of negative mutual diffusivity and uphill diffusion of vacancy in silicon.

IV. CONCLUSION

During boron diffusion in silicon, which makes vacancy is generated and boron interacts with vacancy. This interaction is cause of the dependence of the vacancy diffusion flux on the concentration gradient of boron. It means the interaction makes the coupled diffusion effect occurs in silicon. Furthermore, interaction between boron impurity and vacancy is the cause of negative mutual diffusivity and uphill diffusion of vacancy in silicon.

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