Near Equilibrium in Dissociative Diffusion of Nickel in Silicon

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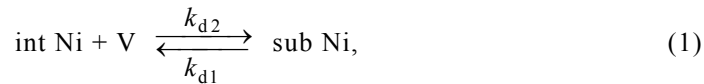E-mail: myoshida@ws.ipc.fit.ac.jp

1. Introduction

In 1964, Yoshida and Furusho [1] studied the diffusion of Ni in Si at 750~1200K and concluded that most of the Ni atoms are located at the interstitial sites. In 1967, Yoshida and Saito [2] further studied the Ni diffusion and concluded that about one thousandth of the total number of Ni atoms are electrically active and are located at the substitutional sites, and that Ni diffuses dissociatively. In ref. 2, the near equilibrium represented by $C_i C_V / C_s = C_i^{eq} C_V^{eq} / C_s^{eq}$ was assumed, where subscripts i, V, and s represent interstitial Ni atoms, vacancies, and substitutional Ni atoms, respectively, superscript eq represents the thermal equilibrium, and C_A is the concentration of component A. However, the assumption of the near equilibrium was not verified experimentally, because it is difficult to measure the concentration of vacancies in Si.

In the present work, the simultaneous diffusion equations of the dissociative mechanism are solved numerically by double-precision FORTRAN without assuming the near equilibrium, under the condition of in-diffusion of Ni into a Si specimen of thickness $L = 0.15$ cm. The solutions of C_s, C_i, and C_V thus obtained are termed the general solutions. On the basis of the general solutions, the near equilibrium is studied.

2. Mathematical Treatment of Near Equilibrium

The dissociative mechanism of Ni in Si is expressed by the chemical reaction,

$$\text{int Ni} + \text{V} \xrightleftharpoons[k_{d1}]{k_{d2}} \text{sub Ni,} \tag{1}$$

where k_{d1} and k_{d2} are the rate constants. We have [3]

$$k_{d2} = 4\pi \alpha_d r_{iV} (D_i + D_V), \tag{2}$$

where $\alpha_d = 10^n$ is a factor for the dissociative mechanism, r_{iV} is the shortest distance for the recombination of interstitial Ni atom and vacancy, and D_A is the diffusion coefficient of component A. The overall reaction rate of reaction (1), R_{dis}, is given by

$$R_{dis} = k_{d1} C_s - k_{d2} C_i C_V. \tag{3}$$

At the thermal equilibrium, we have

$$R_{dis} = k_{d1} C_s^{eq} - k_{d2} C_i^{eq} C_V^{eq} = 0, \tag{4}$$

resulting in
$$k_{d1} = k_{d2} C_i^{eq} C_V^{eq} / C_s^{eq}. \tag{5}$$

At the near equilibrium, we have $R_{dis} \approx 0$ of eq. (3). Because $R_{dis} \approx 0$ is not suitable

for mathematical treatment, R_{dis} of eq. (3) is assumed to be $R_{dis} = 0$, and we have

from eqs. (3) and (5) $C_i C_V / C_s = C_i^{eq} C_V^{eq} / C_s^{eq}$.   (6)

On the basis of eq. (6), Normalized $C_i C_V / C_s$ is defined as

$$\text{Normalized } C_i C_V / C_s = \frac{C_i C_V / C_s}{C_i^{eq} C_V^{eq} / C_s^{eq}} .$$ (7)

Effect of dislocations as sinks and sources of vacancies is also taken into account.

3. Results and Conclusions

Using $C_s^{eq} = 3.40 \times 10^{13}$, $C_i^{eq} = 1.44 \times 10^{17}$, $C_V^{eq} = 7.00 \times 10^{10}$ cm^{-3}, $D_i = 1.00 \times 10^{-4}$, $D_V = 1.70 \times 10^{-5}$ cm^{2}s^{-1}, $n_d = 3.00 \times 10^3$ cm^{-2} and $r_{iV} = r_0 = 2.35 \times 10^{-8}$ cm, where n_d is the dislocation density and r_0 is the shortest distance from a dislocation for the capture of a vacancy by a dislocation, the time dependence of Normalized $C_i C_V / C_s$ obtained from the general solutions at $x = L/2$ with a parameter n of $\alpha_d = 10^n$ is shown in Fig. 1. When Normalized $C_i C_V / C_s$ changes from 1.01 to 1.00 at $t = t^{ne}$ with increasing t, t^{ne} is defined as the time at which the near equilibrium is reached. t^{ne} is shown by circles in Fig. 1. Figure 1 shows the establishment of the near equilibrium. At $n = 0$, the near equilibrium is reached at $t^{ne} = 5.5 \times 10^{-1}$ s. Then the general solutions of C_i, $C_s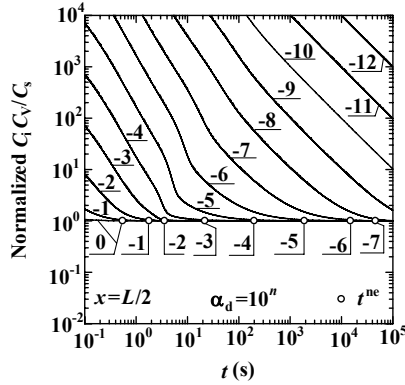$, and C_V reach C_i^{eq}, C_s^{eq}, and C_V^{eq} at $t = 1.4 \times 10^2$, 1.1×10^5, and 1.2×10^5 s, respectively.

On the basis of these results, it is concluded that the near equilibrium is a transitional process which continues until the thermal equilibrium is reached. After the near equilibrium is reached, the very small difference of two nearly equal terms, $k_{d1} C_s$ and $k_{d2} C_i C_V$ of eq. (3), is an important factor in solving the diffusion equations, or high accuracy is necessary to solve the diffusion equations. It is concluded that the accuracy of double-precision FORTRAN is sufficiently high in the case of the numerical values described above.

Fig. 1: Time dependence of Normalized $C_i C_V / C_s$ at $x = L/2$.

References

[1]   M. Yoshida, K. Furusho, Jpn. J. Appl. Phys. 3 (1964) 521-529.
[2]   M. Yoshida, K. Saito, Jpn. J. Appl. Phys. 6 (1967) 573-581-.
[3]   A. C. Damask and G. J. Dienes: *Point Defects in Metals* (Gordon and Breach, New York, 1963) p. 81.