Diffusion in Copper-rich Copper-Silicon Alloys

Yoshiaki Iijima*, Yoshihiro Wakabayashi**, Toshihiko Itoga*** and Ken-ichi Hirano*

The interdiffusion and intrinsic diffusion coefficients in Cu-rich Cu-Si alloys containing up to 8 at% Si have been determined in the temperature range between 900 and 1150 K by use of semi-infinite diffusion couples with the Kirkendall markers. Further, the tracer diffusion coefficient of $^{64}$Cu in pure Cu and the alloys containing up to 1.8 at% Si at 1130 K has been determined by the serial sectioning method. Non-linear enhancement of the Cu diffusivity in Cu-Si alloys by addition of Si has been observed, and the first and second order enhancement factors of the solvent diffusivity have been determined to be 19.4 and 188, respectively. The Gibbs free energy of binding between a vacancy and a silicon atom in Cu has been estimated to be $-11.8$ kJ mol$^{-1}$ at 1130 K. Using the values of the self-diffusion coefficient in pure Cu and the extrapolated values of interdiffusion coefficient and intrinsic diffusion coefficient of Cu to the infinite dilution of Si, the vacancy flow factor in the Cu-Si system at 1130 K has been estimated to be $-0.62$. From the first order enhancement factor and the vacancy flow factor, appropriate numerical values of the correlation factor and the three jump frequency ratios in the five-frequency model for the impurity diffusion of Si in Cu have been evaluated. By combining the above data, the five frequencies have been also estimated. These results suggest a weak interaction between a vacancy and a silicon atom in Cu.

(Received February 28, 1991)

Keywords: interdiffusion, intrinsic diffusion, tracer diffusion, enhancement factor, correlation factor, vacancy flow factor, Kirkendall effect, jump frequency, copper-silicon alloy

I. Introduction

It has been well known that a polyvalent solute atom such as indium, tin or antimony in a monovalent noble metal such as copper, silver or gold is characterized as the solute of high diffusivity which is ten or more times as large as the solvent diffusivity and that the diffusional jumps of the solute to a vacancy in the solvent are strongly correlated. Investigation of diffusion behavior of silicon in copper is of technological interest, because copper alloys containing silicon are used as a bonding wire in integrated circuit devices and failure in the bonding is a serious problem. However, detailed study on diffusion behavior of silicon in the noble metals has not been worked out, because suitable radioisotope of silicon for diffusion experiments is unavailable.

According to a recent experiment on interdiffusion in copper-rich Cu-Si alloys by Minamino et al. (19), the extrapolated value of interdiffusion coefficient to the infinite dilution of Si is about four times as large as the self-diffusion coefficient of Cu. This suggests that interaction between a vacancy and a silicon atom in copper is weaker than that between a vacancy and indium, tin or antimony in copper.

The correlation factor and the jump frequency ratios in the five-frequency model for the impurity diffusion can be determined by combining the following experimental data: the solvent and solute diffusivities in the pure solvent, the enhancement factor of the solvent diffusivity by a small addition of solute atom into the solvent metal, the isotope effect coefficient for the impurity diffusion, and the vacancy flow factor based on the Kirkendall effect in very dilute alloys. These data contribute complementarily to the evaluation of the correlation factor and the jump frequency ratios.

In the present work, three kinds of experiments, interdiffusion, intrinsic diffusion and solvent tracer diffusion, have been performed. The experiments of the solute diffusion of Si in Cu and the isotope effect in it are impossible because of lack of suitable radioactive isotopes of silicon. Concentration-penetration profiles and Kirkendall marker shifts in various semi-infinite interdiffusion couples consisting of pure Cu and copper-rich Cu-Si alloys have been examined, and the interdiffusion coefficients in the temperature range between 900 and 1150 K and the intrinsic diffusion coefficients at 1130 K have been determined. By the aid of the value of the intrinsic diffusion coefficient of Cu in Cu-Si alloys extrapolated to the infinite dilution of Si, the vacancy flow factor has been calculated. Further, the diffusion coefficient of $^{64}$Cu in copper-rich Cu-Si alloys at 1130 K has been measured to determine the solute enhancement factor for the solvent diffusion. From the values of the vacancy flow factor and the solute enhancement factor, appropriate numerical values of the correlation factor and the jump frequency ratios for impurity diffusion of Si in Cu have been calculated. By combining the above data, the five frequencies have been also evaluated. The Gibbs free energy of binding between a vacancy and a silicon atom in copper has been estimated from the first and second order enhancement factors for the solvent diffusion
and compared with those for various solutes in copper.

II. Experimental Procedure

1. Interdiffusion in Cu-rich Cu–Si alloys

Rods of pure Cu and Cu–Si alloys containing 1.0, 2.0, 4.0, 6.0 and 8.0 at% Si were made by vacuum-melting oxygen-free copper chips of 99.99% purity together with silicon flakes of 99.99% purity in an alumina crucible and casting into a steel mold 15 mm in diameter and machined to 12 mm in diameter. To cause grain growth, the rods of pure Cu and the alloys were annealed in high purity argon gas at temperatures 50 K below their solidus temperatures for 7 days. The resultant grain size, 2 to 4 mm in the pure Cu and 1 to 2 mm in the alloys, was large enough to avoid the influence of grain boundary diffusion on the concentration-penetration profile by volume diffusion. The rods were cut to make the disc specimens 7 mm in thickness. The cut surfaces were ground on abrasive papers and polished on a buff with fine alumina paste. As the Kirkendall marker, a tungsten wire of 2.4 μm in diameter was put between two discs. Semi-infinite couple consisted of the two discs was put in a stainless steel holder with two screws, pressed by the screws and diffused-welded by heating in a stream of argon gas at 1073 K for 4.5 ks. The couple was removed from the holder and sealed in a quartz tube with argon gas. Diffusion anneals were carried out at temperatures in the range from 900 to 1150 K for 0.43 to 2.59 Ms in a furnace controlled within ±1 K.

After the diffusion, the couple was cut parallel to the diffusion direction, and the cut surfaces were polished on a buff with fine alumina paste to examine the concentration-penetration profile by an electron probe microanalyzer (Shimadzu ARL-II), operated under the following conditions: accelerating voltage, 20 kV; take-off angle of Si–Kα X-ray, 0.916 rad; specimen current, 30 to 200 nA; line scanning speed, 1.66 or 2.33 μm s⁻¹. By the aid of the standard alloy specimens the calibration curve was obtained. It was shown that the relative intensity of the Si–Kα X-ray emitted from the specimen was proportional to the mole fraction of Si. The interdiffusion coefficient was determined as a function of solute concentration by Matano’s method. In the Cu–Si alloys containing less than 8 at% of Si, the molar volume is proportional to the mole fraction of Si, indicating that the partial molar volume of each component is independent of concentration of Si, therefore, the mole of Si per cubic meter can be used as the unit of concentration in the analysis for the determination of diffusion coefficient. The Kirkendall marker shift was determined by measuring the distance between the marker and the position of the Matano interface determined by analyzing the concentration-penetration profile.

2. Diffusion of 64Cu in Cu-rich Cu–Si alloys

For the tracer diffusion experiment the pure Cu and six Cu–Si alloys containing 0.3, 0.6, 0.9, 1.2, 1.5 and 1.8 at% Si prepared in the same way as described above were used. The rods of pure Cu and the alloys were cut to make disc specimens 12 mm in thickness. The cut surfaces were ground on abrasive papers and polished on a buff with fine alumina paste. To obtain strain-free surface, the specimens were annealed at 1173 K for 16 h in high purity hydrogen gas. The radioisotope 64Cu (γ-rays, 0.092 and 0.184 MeV; half-life, 61.9 h) was produced by the 300 MeV linear accelerator of Tohoku University by using the 64Zn(γ, p)65Cu reaction. The γ-ray generated by the bremsstrahlung of 60 MeV electron beam with a platinum converter was applied to a bulk target of 99.99% purity Zn. The radioisotope 64Cu was separated chemically from the Zn target into HCl solution and electroplated on the surface of the specimen. The intensity of the γ-rays from the specimen just after the electroplating was about 3 × 10⁶ Bq. The specimens were then sealed in quartz tubes with high purity argon gas and diffused at 1130 K for 6.0 × 10⁴ s in a furnace controlled within ±1 K.

After the diffusion, the cylindrical surface of the specimen was removed to a depth of about 0.5 mm by a precision lathe to eliminate the anxious effect of the surface diffusion along the cylindrical surface. To determine the volume diffusion coefficient of 64Cu, the serial sectioning method was employed. The flat surface layer of the specimen was removed successively by grinding on abrasive papers 6 cm wide and 12 cm long. After each grinding, the abrasive paper was collected together with the powder of the removed section of the specimen. The loss in the collection of each ground section was less than about 3%. The intensity of γ-ray emitted by 64Cu in each section was measured by a well-type Ti-activated NaI scintillation detector in conjunction with a 1024 channels pulse height analyzer.

III. Results

1. Concentration and temperature dependence of interdiffusion coefficient

Figure 1 shows the concentration dependence of the inter-diffusion coefficient, \( D \), in Cu–Si alloys determined with semi-infinite couples consisting of pure Cu and Cu–8 at%Si alloy in the temperature range between 900 and 1300 K and with a semi-infinite couple consisting of pure Cu and Cu–6 at%Si alloy at 1150 K. The logarithm of \( D \) increases with increase of Si content at all the temperatures, in agreement with the generally recognized trend that the self-diffusion coefficient in alloys increases with decrease of the melting temperature. The temperature dependence of the interdiffusion coefficient is shown in Fig. 2 in comparison with that of the self-diffusion in Cu. The frequency factor, \( D_0 \), and the activation energy, \( Q \), for the interdiffusion are determined by the least square fits of the plots of \( D \) in Fig. 2 to the Arrhenius equation and listed in Table 1 together with the probable error. The values of \( D_0 \) and \( Q \) determined by the present work are in fair agreement with those by
Minamino et al.\(^{(10)}\) for each concentration of Si. With increase of Si content, \(\dot{Q}\) decreases linearly, but logarithm of \(\dot{D}_0\) increases almost linearly. This is contrary to the general decreasing tendency of \(\dot{D}_0\) corresponding to decrease of \(\dot{Q}\) with increase of solute.

According to Darken’s relation\(^{[12]}\), the extrapolated value of interdiffusion coefficient to the infinite dilution of Si can be regarded as the impurity diffusion coefficient of Si in Cu, the value of which at 1047 K determined in such a way by the present work is \(7.0 \times 10^{-15}\) m\(^2\) s\(^{-1}\) and about three times as large as the self-diffusion coefficient in Cu\(^{[19]}\), but smaller than \(1.0 \times 10^{-14}\) m\(^2\) s\(^{-1}\) by Minamino et al.\(^{(10)}\).

### 2. Kirkendall effect and intrinsic diffusion coefficients

In all the interdiffusion couples, movement of the Kirkendall marker toward the Cu-rich side has been observed. This indicates faster diffusion of Cu atom than Si atom in Cu–Si alloys. The Kirkendall voids with diameter less than 10 \(\mu\)m have been observed only in (pure Cu)–(Cu-6 at%Si alloy) and (pure Cu)–(Cu-8 at%Si alloy) couples diffused at 1130 K for 2.56 Ms which is the longest time in the present experiments. In other couples the Kirkendall void has not been observed as far as an optical microscope is used. It has been confirmed that the concentration of Si at the marker position is independent of diffusion time, and the marker shift is proportional to the square root of diffusion time, as shown in Fig. 3. The intrinsic diffusion coefficients, \(D_{Si}\) and \(D_{Cu}\), at the concentration of the marker position have been calculated, based on the experimental data on the interdiffusion coefficient, the marker shift, the partial molar volumes of both components\(^{(7)}\) (\(V_Cu = 7.11 \times 10^{-6}\) m\(^3\) mol\(^{-1}\) and \(V_Si = 7.51 \times 10^{-6}\) m\(^3\) mol\(^{-1}\)) and Darken’s relations\(^{[12]}\).

Figure 4 shows that the logarithm of \(D_{Si}\) and \(D_{Cu}\) at 1130 K increases linearly with the Si content. As shown in Figs. 1 and 4, also the logarithm of \(\dot{D}\) at 1130 K increases linearly with the Si content. Thus by the least square fits, the following relationships have been obtained for \(\dot{D}, D_{Si}\) and \(D_{Cu}\) in the range of mole fraction of Si, \(N_{Si}\), from 0 to 0.05:

\[
\dot{D}(N_{Si}) = 3.9 \times 10^{-14} \text{ exp}(29.2N_{Si}) \text{ m}^2\text{s}^{-1},
\]

and

\[
D_{Si}(N_{Si}) = 3.9 \times 10^{-14} \text{ exp}(29.1N_{Si}) \text{ m}^2\text{s}^{-1},
\]
where $f_0 (=0.781)$ is the correlation factor for self-diffusion in pure f.c.c. metals. According to Darken’s relation$^{(12)}$, $D_{0}^{*}(0)$ is equivalent to $\tilde{D}(0)$. Putting the values of $\tilde{D}(0) = D_{Si}^{*}(0)$, $D_{Cu}^{*}(0)$ and $D_{Cu}(0)$ and the value of $\tilde{V}_{Si}/\tilde{V}_{Cu}$ into eq. (4), the vacancy flow factor, $G$, is determined to be $-0.62$ at 1130 K. This value is larger than those obtained in other copper-base alloys such as Cu-Sn$^{(13)}$ ($G = -0.84$ at 1089 K), Cu-In$^{(14)}$ ($G = -0.71$ at 1005 K) and Cu-Sb$^{(15)}$ ($G = -1.20$ at 1005 K).

3. Concentration dependence of tracer diffusion coefficient of copper in Cu-Si alloys

For one-dimensional volume diffusion of a tracer from an infinitesimally thin surface layer into a sufficiently long rod analyzed by the serial sectioning method, the solution of Fick’s second law is given by

$$C(X, t) = \frac{M}{\sqrt{\pi D^* t}} \exp \left( -\frac{X^2}{4D^* t} \right), \quad (5)$$

where $C(X, t)$ is the concentration of the radioactive tracer at a distance $X$ from the original surface, $D^*$ the volume diffusion coefficient of the tracer, and $t$ the time of diffusion. $M$ is the total amount of tracer deposited on the surface before the diffusion.

Figure 5 shows the plots of $ln C(X, t)$ vs $X^2$ for the diffusion of $^{65}Cu$ in Cu-Si alloys at 1130 K. The linearity observed in Fig. 5 proves that eq. (5) holds, thus the

$$D_{Cu}^*(N_{Si}) = 4.1 \times 10^{-14} \exp (29.7N_{Si}) \text{ m}^2 \text{ s}^{-1}. \quad (3)$$

According to Heumann$^{(5)}$, the vacancy flow factor, $G$, defined by the ratio of the phenomenological coefficients of the flux equations for $N_{Si}=0$ can be evaluated in terms of the self- and impurity diffusion coefficients in pure solvent Cu, $D_{Cu}^*(0)$ and $D_{Si}^*(0)$, and the intrinsic diffusion coefficient of the solvent in pure solvent, $D_{Cu}(0)$, by the following equation:

$$G = \frac{\left( \tilde{V}_{Cu}/\tilde{V}_{Si} \right)}{\left( \frac{D_{Cu}(0)}{D_{Si}^*(0)} \right) \left( \frac{1}{f_0} \frac{D_{Cu}(0)}{D_{Cu}^*(0)} \right)}.$$

Fig. 4 Concentration dependence of interdiffusion coefficient ($\tilde{D}$), intrinsic diffusion coefficients ($D_{Cu}$ and $D_{Si}$) and tracer diffusion coefficient of copper ($D_{Cu}^*$) in Cu-Si alloys at 1130 K.

Fig. 5 Penetration profiles for diffusion of $^{65}Cu$ in Cu-Si alloys at 1130 K for $6.0 \times 10^5$ s.
volume diffusion has been concerned. The tracer diffusion coefficients of Cu in Cu-Si alloys at 1130 K, \( D^*_A \), determined from the slope of \( \ln C(X, t) / X^2 \) plots by use of eq. (5), are plotted in Fig. 4 as a function of the Si concentration. The value of the self-diffusion coefficient in Cu at 1130 K determined by the present experiments, \( 1.50 \times 10^{-14} \text{ m}^2 \text{ s}^{-1} \), is in good agreement with those obtained by Fujikawa and Hirano\(^{11}\) and Rothman and Peterson\(^{16}\).

### IV. Discussion

According to LeClaire\(^{16}\), the enhancement effect of the solvent diffusivity by a small addition of solute atom is generally expressed by the following polynomial equation:

\[
D^*_A(N_b) = D^*_A(0)[1 + b_1 N_b + b_2 N_b^2 + b_3 N_b^3 + \cdots], \tag{6}
\]

where \( D^*_A(N_b) \) is the diffusion coefficient of solvent A at the mole fraction of solute B, \( N_b, b_1, b_2 \) and \( b_3 \) are the first, second and the third order enhancement factor, respectively. Equation (6) has been used to determine the enhancement factors by many authors, so far. Recently, Hagschulte and Heumann\(^{17}\) have shown that eq. (6) is insufficient for determination of the veritable enhancement factors. Taking into account theoretical considerations of the enhancement factors\(^{18}\) and the general equations of the equilibrium vacancy concentration in alloys\(^{19}\), Hagschulte and Heumann\(^{17}\) have approximated the enhancement effect by

\[
D^*_A(N_b) = D^*_A(0) \exp (b_1 N_b) \tag{7}
\]

\[
= D^*_A(0) \left[ 1 + b_1 N_b + \frac{1}{2} b_2 N_b^2 + \frac{1}{6} b_3 N_b^3 + \cdots \right]. \tag{8}
\]

Therefore, the enhancement factor \( b_1 \) can be obtained from a linear fit to the logarithm of the solvent diffusion coefficients plotted versus concentration. According to eq. (8), the higher order enhancement factors \( b_2 \) and \( b_3 \) are given by \( b_2 = (1/2) b_1^2 \) and \( b_3 = (1/6) b_1^3 \). Hagschulte and Heumann\(^{17}\) have recommended this way to determine the enhancement factors.

As shown in Fig. 4, the logarithm of \( D^*_A \) increases linearly with increase of the Si content in agreement with eq. (8), and by the least square fits to eq. (8) we have

\[
D^*_A(N_b) = 1.49 \times 10^{-14} \exp [(19.4 \pm 0.5) N_b] \text{ m}^2 \text{ s}^{-1}. \tag{9}
\]

Thus, the enhancement factors \( b_1 \) and \( b_2 \) have been determined to be 19.4 and 188, respectively.

Theoretically, the first order enhancement factor for the solvent diffusivity, \( b_1 \), can be related to the jump frequencies, \( \omega_i \), of a vacancy neighboring a solute atom as follows\(^{20}\):

\[
b_1 = -18 + \frac{4 \omega_i}{f_i} \left( \frac{\omega_1}{\lambda_3} \frac{7}{2} \right). \tag{10}
\]

where \( \omega_i \) represents the jump frequency in the five-frequency model for impurity diffusion, defined as follows:

- \( \omega_1 \) the jump frequency of a vacancy from a nearest neighbor site of an impurity to another nearest neighbor site;
- \( \omega_2 \) the jump frequency for an impurity-vacancy exchange;
- \( \omega_3 \) the jump frequency of a vacancy from a nearest neighbor site of an impurity to non-nearest neighbor positions;
- \( \omega_4 \) the frequency of the reverse jump to the jump \( \omega_2 \); and
- \( \omega_0 \) the jump frequency of a vacancy unaffected by an impurity.

\( \chi_1 \) and \( \chi_2 \) are the mean partial correlation factors defined by Howard and Manning\(^{20}\) and given as functions of three jump frequency ratios, \( \omega_2 / \omega_1, \omega_3 / \omega_1 \) and \( \omega_4 / \omega_0 \), respectively. The correlation factor \( f_i \) for the impurity diffusion is related to the three jump frequency ratios by the following equation\(^{21}\):

\[
f_i = \frac{1 + (7F/2)(\omega_3 / \omega_1)}{1 + (\omega_2 / \omega_1) + (7F/2)(\omega_3 / \omega_1)}, \tag{11}
\]

where \( F \) is expressed by the jump frequency ratio \( \omega_4 / \omega_0 \) as follows\(^{22}\):

\[
F = 1 - \frac{10(\omega_2 / \omega_0)^4 + 180.5(\omega_2 / \omega_0)^3 + 927(\omega_2 / \omega_0)^2 + 1341(\omega_2 / \omega_0)}{72(\omega_4 / \omega_0)^4 + 40.2(\omega_4 / \omega_0)^3 + 254(\omega_4 / \omega_0)^2 + 597(\omega_4 / \omega_0) + 436}. \tag{12}
\]

and

\[
D^*_A(0)/D^*_A(0) = (f_i/f_0)(\omega_2 / \omega_1)(\omega_3 / \omega_3)(\omega_4 / \omega_0). \tag{13}
\]

Furthermore, the vacancy flow factor \( G \) can be related to the jump frequency ratios as follows\(^{23}\):

\[
G = -2 + 3(\omega_2 / \omega_1) + (\omega_3 / \omega_1)(\omega_0 / \omega_0 - 1)(7 - 7F) \tag{14}
\]

\[
1 + (7F/2)(\omega_3 / \omega_1)
\]

Thus, a numerical set of \( f_i, \omega_2 / \omega_1, \omega_3 / \omega_1 \) and \( \omega_4 / \omega_0 \) can be determined by putting the empirical values of \( b_1, D^*_A(0)/D^*_A(0) \) and \( G \) into eqs. (10) ~ (14).

In the present work, at first \( b_1 \) is calculated as a function of \( \omega_4 / \omega_0 \) with the aid of eqs. (10) ~ (13) and the values of \( \chi_1 \) and \( \chi_2 \) computed by Howard and Manning\(^{20}\),
the corresponding line of \( f_i \) across the point of intersection, we can determine graphically the value of \( \omega_4 / \omega_0 \) and \( f_i \) to be 1.7 and 0.74, respectively. Then, putting these values into eqs. (11), (12) and (13), the values of \( \omega_5 / \omega_1 \) and \( \omega_6 / \omega_1 \) are calculated to be 0.42 and 0.69, respectively, as listed in Table 2. The error in this calculation is estimated to be less than 20%. It is noted that \( f_i < f_0 (= 0.7811) \), \( \omega_0 < \omega_1 \) and \( \omega_0 < \omega_0 \), thus the interaction between a silicon atom and a vacancy in the Cu matrix lattice is weak and that a vacancy makes more exchanges with neighboring Cu atoms rather than the Si atom. This characteristic of Si atom in Cu is in contrast with the behavior of In, Sn or Sb in Cu\(^{20} \), for which \( f_i < f_0, \omega_5 > \omega_1, \omega_6 > \omega_1 \) and \( \omega_5 > \omega_0 \), and the intense attraction between a solute atom and a vacancy makes them very much consecutive exchanges between them, and less exchanges between a vacancy and the atom neighboring it.

Another important jump frequency ratio is \( \omega_4 / \omega_3 \), which is connected with the Gibbs free energy of binding, \( \delta g \), between a vacancy and a solute atom by

\[
\frac{\omega_4}{\omega_3} = \exp \left( - \frac{\delta g}{RT} \right).
\]  

According to Faupel and Hehenkamp\(^{18} \), \( \delta g \) is related with the first and the second enhancement factors for solvent diffusivity, \( b_1 \) and \( b_2 \), defined by eq. (6), respectively, as follows:

\[
\delta g = -RT \ln \left[ \frac{(b_1/55 + b_2/5.5 + 1)/(b_1/11 + 1)}{0.818} \right].
\]  

Putting the present experimental values, \( b_1 = 19.4 \) and \( b_2 = 188 \) into eq. (16), \( \delta g \) is calculated to be \(-11.8 \) kJ mol\(^{-1}\) for the solute silicon atom in Cu at 1130 K. Then putting this value of \( \delta g \) into eq. (15), \( \omega_4 / \omega_3 \) is calculated to be 3.5. Thus, all the four jump frequency ratios have been calculated, as shown in Table 2.

The jump frequency \( \omega_0 \) in the solvent Cu is given by

\[
\omega_0 = \omega_0 \exp \left( \frac{S_m}{R} \right) \exp \left( - \frac{E_m}{RT} \right),
\]  

where \( \omega_0 \) is the attempt frequency which can be approximated by the Debye frequency of Cu\(^{22} \), \( 6.52 \times 10^2 \) s\(^{-1}\). \( S_m \) and \( H_m \) are the entropy and the enthalpy for migration of a vacancy in Cu, which have been estimated to be 1.72R and 81.0 kJ mol\(^{-1}\), respectively\(^{20} \). Putting these values into eq. (17), \( \omega_0 \) is calculated to be \( 6.5 \times 10^4 \) s\(^{-1}\) at 1130 K. Using the values of \( \omega_0 \) and the four jump frequency ratios, \( \omega_4 / \omega_0, \omega_5 / \omega_1, \omega_6 / \omega_1 \) and \( \omega_6 / \omega_3 \), the individual jump frequencies, \( \omega_1 \sim \omega_4 \) are calculated, as also shown in Table 2.

<table>
<thead>
<tr>
<th>Temperature /K</th>
<th>( f_i )</th>
<th>( \omega_4 / \omega_0 )</th>
<th>( \omega_5 / \omega_1 )</th>
<th>( \omega_6 / \omega_1 )</th>
<th>( \omega_6 / \omega_3 )</th>
<th>( \omega_1 )</th>
<th>( \omega_2 )</th>
<th>( \omega_3 )</th>
<th>( \omega_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1130</td>
<td>0.74</td>
<td>1.7</td>
<td>0.42</td>
<td>0.69</td>
<td>3.5</td>
<td>6.5</td>
<td>7.4</td>
<td>5.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 2 Correlation factor (\( f_i \)), jump frequency ratios (\( \omega_4 / \omega_0 \), \( \omega_5 / \omega_1 \), \( \omega_6 / \omega_1 \) and \( \omega_6 / \omega_3 \)) and jump frequencies (\( \omega_1 \sim \omega_4 \)) for impurity diffusion of Si in Cu at 1130 K.
Table 3  Gibbs free energy of binding ($\delta g$) between a vacancy and a solute atom in Cu and radius ($r$) of solute atom in Cu.
(radius of Cu atom, $r_{Cu}=1.278 \times 10^{-10}$ m)

<table>
<thead>
<tr>
<th>Group</th>
<th>Solute</th>
<th>Temperature T/K</th>
<th>$\delta g$ /kJ mol$^{-1}$</th>
<th>Reference for $\delta g$</th>
<th>Radius of solute atom, $r/10^{-10}$ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ib</td>
<td>Au</td>
<td>1133</td>
<td>-7.24</td>
<td>17</td>
<td>1.442</td>
</tr>
<tr>
<td>IIb</td>
<td>Zn</td>
<td>1168</td>
<td>-7.24</td>
<td>17</td>
<td>1.394</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>1076</td>
<td>-16.0</td>
<td>17</td>
<td>1.568</td>
</tr>
<tr>
<td>IIIb</td>
<td>In</td>
<td>1089</td>
<td>-17.9</td>
<td>17</td>
<td>1.663</td>
</tr>
<tr>
<td>IVb</td>
<td>Si</td>
<td>1130</td>
<td>-11.8</td>
<td>present work</td>
<td>1.319</td>
</tr>
<tr>
<td></td>
<td>Ge</td>
<td>1125</td>
<td>-13.5</td>
<td>27</td>
<td>1.369</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>1089</td>
<td>-19.5</td>
<td>17</td>
<td>1.545</td>
</tr>
<tr>
<td>Vb</td>
<td>Sb</td>
<td>1005</td>
<td>-24.2</td>
<td>17</td>
<td>1.59</td>
</tr>
</tbody>
</table>

The values of $\delta g$ for various solutes in the Cu matrix lattice are compiled in Table 3 with the values of the radius, $r$, of solute atoms for the coordination number 12 (28). Figure 8 shows the plot of $|\delta g|$ versus $r$ for each group in the periodic table of elements. It is noted that for the elements of the group IVb (Si, Ge and Sn), $|\delta g|$ increases linearly with increase of $r$. The atomic radius of solutes $r$ for Si, Ge and Sn is larger than that of Cu, $r_{Cu}$, thus, $|\delta g|$ increases with increase of $r-r_{Cu}$. This suggests that the lattice is strained around the solute atom and the atomic size is a factor significant in the Gibbs free energy of binding between a vacancy and a solute atom in Cu. Although for solutes of the other groups, available data on $\delta g$ are a few, it is apparent that the atomic size is effective in $\delta g$ for the solutes of all the groups, as shown by the broken lines in Fig. 8 for each group. It may be reasonable to take all the lines parallel to the line for the group IVb, then it is recognized that the broken line shifts upwards with increase of the group number of the solute element. This suggests that the valence of solute may be also an important factor on the Gibbs free energy of binding $\delta g$.

V. Conclusion

From the experimental values of the first order enhancement factor for solvent diffusivity and the vacancy flow factor for interdiffusion, appropriate numerical values of the correlation factor and the three jump frequency ratios for the impurity diffusion of Si in Cu have been determined. From the first and second order enhancement factors for solvent diffusivity, the Gibbs free energy of binding between a vacancy and a silicon atom in the copper matrix has been estimated to be $-11.8$ kJ mol$^{-1}$ at 1130 K. By combining these experimental data, all the five jump frequencies in the five jump mechanism of impurity diffusion of Si in Cu have been evaluated. These results indicate that the interaction between a vacancy and a silicon atom in copper is weak.

Acknowledgment

The present authors wish to thank Mr. Y. Murakami, former Graduate Student of Tohoku University and now in SONY Co., for his assistance in the experiments and Dr. S. Ushino of Tohoku University for production of the radioisotope $^{65}$Cu.

REFERENCES
