Title	Thermal generation of Frenkel pair in silicon
Sub Title	
Author	Yoshida, Masayuki(Matsumoto, Satoru) 松本, 智
Publisher	慶應義塾大学理工学部
Publication year	1987
Jtitle	Keio Science and Technology Reports Vol.40, No.2 (1987. 12) ,p.19- 25
JaLC DOI	
Abstract	A basic concept in thermodynamics states that, if an isolated system is left standing, it comes eventually to a final state which does not change. This final state is called the thermal equilibrium state. If vacancies and self-interstitials coexist, it is sure that they recombine with each other. Greatest importance is given to the basic concept in the thermodynamics mentioned above. Therefore, regardless of whether or not the thermal generation of the Frenkel pair is energetically possible, the Frenkel pair should be generated thermally as a reverse reaction of the recombination, to get the thermal equilibrium state.
Notes	
Genre	Departmental Bulletin Paper
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=KO50001004-00400002-0019

KEIO SCIENCE AND TECHNOLOGY REPORTS
VOL. 40, NO. 2, pp. 19-25, 1987, ISSN: 02864215

THERMAL GENERATION OF FRENKEL PAIR IN SILICON

Masayuki YOSHIDA*
Kyushu Institute of Design,
Shiobaru, Minami-ku, Fukuoka 815, Japan

Satoru MATSUMOTO**
Department of Electrical Engineering, Keio University,
Hiyoshi, Yokohama 223, Japan

(*Received July 2, 1987*)

ABSTRACT

A basic concept in thermodynamics states that, if an isolated system is left standing, it comes eventually to a final state which does not change. This final state is called the thermal equilibrium state. If vacancies and self-interstitials coexist, it is sure that they recombine with each other. Greatest importance is given to the basic concept in the thermodynamics mentioned above. Therefore, regardless of whether or not the thermal generation of the Frenkel pair is energetically possible, the Frenkel pair should be generated thermally as a reverse reaction of the recombination, to get the thermal equilibrium state.

1. Introduction

In silicon, only vacancies produced by irradiation of high energy particles have been observed at low temperature and self-interstitials have never been observed.[1] On the other hand, based on the experimental results of oxidation enhanced diffusion (OED) of phosphorus, oxidation retarded diffusion (ORD) of antimony and growth of the extrinsic stacking fault by oxidation (oxidation stacking fault: OSF), it is generally believed that vacancies and self-interstitials coexist at high temperature.[2,3] It should be noted that the conclusion obtained from the experimental results of OED, ORD and OSF at high temperature is not consistent with the conclusion at low temperature, that is, diffusion coefficients of these point defects at high temperature are so small that the freeze-in of them is possible.[4] The assumption, however, of their coexistence yielding this inconsistency is difficult to refute, as there are no alternative assumptions evident to explain OED et al..

After acceptance of their coexistence, the most important assumption for point defects is the thermal generation of the Frenkel pair. This assumption is necessary to get the thermal equilibrium state of vacancies and self-interstitials,[5] although

* Kyushu Institute of Design, Shiobaru, Minami-ku, Fukuoka 815, JAPAN
** Department of Electrical Engineering, Keio University, Hiyoshi, Yokohama 223, JAPAN

it is not certain whether the thermal generation of the Frenkel pair is energetically possible or not.

In the present work, problems of the thermal equilibrium state are discussed, and then the distributions of vacancies and self-interstitials are calculated in the case of non-generation of the Frenkel pair.

2. Equilibrium State

A basic concept in thermodynamics states that, if an isolated system is left standing, regardless of the complexity of its initial state, it comes eventually to a final state which does not change.[6] This final state is called the thermal equilibrium state.

The generation and annihilation of point defects are generally considered to be chemical reactions in the study of time-dependence of their concentrations.[7] Chemical reactions are reversible.[8] At the thermal equilibrium state, an elementary process of reaction is exactly balanced by its reverse reaction. This is called the principle of detailed balancing.[9]

The formation energy of vacancy, E_V, is defined by the energy necessary to displace an atom from a lattice site inside a perfect crystal to a lattice site on the surface of crystal. If we can neglect any effect due to the change in the volume of the crystal, we have

$$C_V^0 = C_0 \exp(-E_V/kT) \tag{1}$$

at temperature satisfying $E_V \gg kT$, where C_V^0 is the concentration of vacancies in the thermal equilibrium state and C_0 is the concentration of lattice sites of crystal.[10] The concentration of self-interstitials at the thermal equilibrium state, C_I^0, is obtained by similar means.

3. Distribution of Vacancy and Self-Interstitial

If vacancies and self-interstitials coexist, it is sure that they recombine with each other. Greatest importance is given to the basic concept in the thermodynamics mentioned in section 2. Therefore, regardless of whether or not the thermal generation of the Frenkel pair is energetically possible, the Frenkel pair should be generated thermally as a reverse reaction of the recombination, to get the thermal equilibrium state.

Based on this, diffusion equations of vacancies and self-interstitials are

$$\frac{\partial C_V}{\partial t} = D_V \frac{\partial^2 C_V}{\partial x^2} + G_{VI} - k_{VI} C_V C_I, \tag{2}$$

$$\frac{\partial C_I}{\partial t} = D_I \frac{\partial^2 C_I}{\partial x^2} + G_{VI} - k_{VI} C_V C_I, \tag{3}$$

where C_V, D_V, C_I and D_I are the concentrations and the diffusion coefficients of vacancy and self-interstitial, and G_{VI} and k_{VI} are the rate constants for the generation of the Frenkel pair and for the recombination of a vacancy and a self-interstitial, respectively. D_V et al. are related to the self-diffusion coefficient, D_{sd}, by

$$d_I^{sd} = f_I^{sd} D_I C_I^0 / D_{sd} C_0, \tag{4}$$

$$1 - d_I^{sd} = f_V^{sd} D_V C_V^0 / D_{sd} C_0, \tag{5}$$

where d_I^{sd} is the fractional component of the interstitialcy mechanism for self-diffusion and f_I^{sd} and f_V^{sd} are the correlation factors for self-diffusion by interstitialcy and vacancy mechanisms, respectively. The value of Mayer, Mehrer and Maier,[11] $1460 \exp(-5.02/kT)\,\mathrm{cm}^2 s^{-1}$, is adopted as D_{sd}. In eqs. (2) and (3), the effect of dislocations upon generation and annihilation of vacancies and self-interstitials are neglected for simplicity. We write k_{VI} as

$$k_{VI} = 4\pi r_{VI} (D_V + D_I) f_{VI}, \tag{6}$$

where r_{VI} is the capture radius for recombination of a vacancy and a self-interstitial with no interaction between them and is assumed to be one atomic distance 3.37×10^{-8} cm, and f_{VI} is the calibration factor for the interaction. To get the thermal equilibrium state mentioned in section 2, we have

$$G_{VI} = k_{VI} C_V^0 C_I^0. \tag{7}$$

Solving Eqs. (2) and (3) under the conditions of

$$C_V = C_V^0 \text{ and } C_I = C_I^0 \text{ for } x=0 \text{ and } l,\ t \geqslant 0, \tag{8}$$

$$C_V = 0 \text{ and } C_I = 0 \text{ for } 0 < x < l,\ t = 0, \tag{9}$$

where l is the thickness of the specimen, we have

$$C_V=C_V^0 \text{ and } C_I=C_V^0 \tag{10}$$

for $0 \leqslant x \leqslant l$ at steady state, if Eq. (7) is taken into account. Equation (10) is the result which should be satisfied thermodynamically, as mentioned in section 2.

Now let us study the case in which the Frenkel pair is not generated thermally, that is, $G_{VI}=0$ in place of Eq. (7). Introducing the dimensionless parameters

$$\begin{aligned} &T_l=tD_V/l^2,\ \xi=x/l,\ \rho=D_I/D_V, \\ &k_V=k_{VI}C_I^0l^2/D_V,\ \kappa_I=k_{VI}C_V^0l^2/D_I, \end{aligned} \tag{11}$$

Eqs. (2) and (3) are written in the forms of

$$\frac{\partial}{\partial T_l}\left(\frac{C_V}{C_V^0}\right)=\frac{\partial^2}{\partial \xi^2}\left(\frac{C_V}{C_V^0}\right)-\kappa_V\frac{C_VC_I}{C_V^0C_I^0}, \tag{12}$$

$$\frac{\partial}{\rho\partial T_l}\left(\frac{C_I}{C_I^0}\right)=\frac{\partial^2}{\partial \xi^2}\left(\frac{C_I}{C_I^0}\right)-\kappa_I\frac{C_VC_I}{C_V^0C_I^0}. \tag{13}$$

Equations (12) and (13) are solved numerically under the conditions of Eqs. (8) and (9) for the two cases of $C_V/C_V^0=C_I/C_I^0$ and $C_V/C_V^0 \neq C_I/C_I^0$. $T=1100°\text{C}$ and

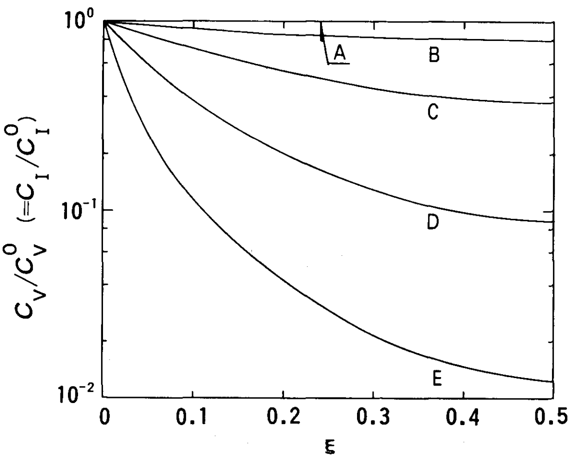

FIGURE 1. Distributions of vacancies and self-interstitials in the case of non-generation of the Frenkel pair and of $C_V/C_V^0=C_I/C_I^0$. Values of constants used are shown in TABLE I.

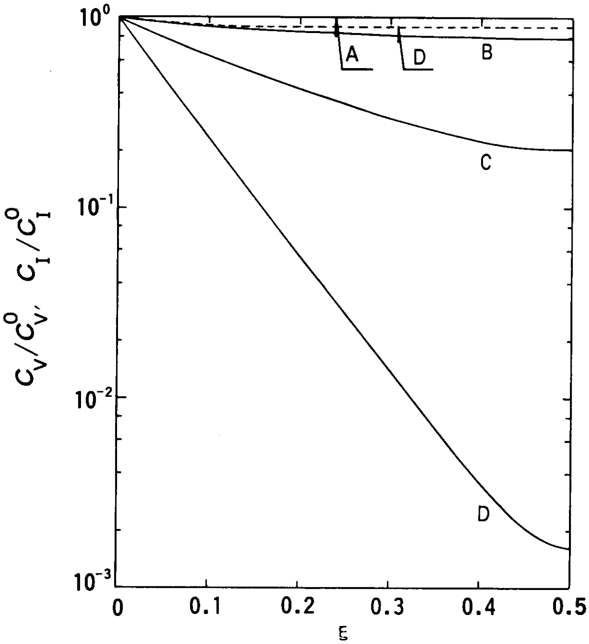

FIGURE 2. Distributions of vacancies and self-interstitials in the case of non-generation of the Frenkel pair and of $C_V/C_V^0 \neq C_I/C_I^0$. Solid lines show C_I/C_I^0 and broken line shows C_V/C_V^0. Only line *A* shows both of them as an exception. Values of constants used are shown in TABLE I.

TABLE I. Values of constants used in Figures 1 and 2.

Fugure 1

Line	f_{VI}	$\kappa_V = \kappa_I$
A	0	0
B	10^{-5}	2.323×10^0
C	10^{-4}	2.323×10^1
D	10^{-3}	2.323×10^2
E	10^{-2}	2.323×10^3

Figure 2

Line	f_{VI}	κ_V	κ_I
A	0	0	0
B	10^{-5}	2.213×10^{-1}	2.233×10^0
C	10^{-4}	2.213×10^0	2.233×10^1
D	10^{-3}	2.213×10^1	2.233×10^2

$l=10^{-2}$ cm are used. For the former case $d_I^{sd}=0.5$ and $f_V^{sd}=f_I^{sd}=0.5$ are used, and $D_V=D_I=10^{-8}$ cm$^2s^{-1}$ are tentatively used.[12] For the latter case $d_I^{sd}=0.126$, $f_V^{sd}=0.5$ and $f_I^{sd}=0.7273$ are used,[13] and $D_V=10^{-8}$ cm$^2s^{-1}$ and $D_I=10^{-7}$ cm$^2s^{-1}$ are tentatively used. Distributions of C_V/C_V^0 and C_I/C_I^0 at a steady state are shown in Figures 1 and 2 for the two cases mentioned above. The parameter is f_{VI} and is shown in TABLE I, together with the relation to κ_V and κ_I. In Figure 2 C_V/C_V^0 is shown by broken line and C_I/C_I^0 are shown by solid lines. C_V/C_V^0 is equal to C_I/C_I^0 at $f_{VI}=0$ and they are shown by solid line A. Since the effect of f_{VI} upon C_V/C_V^0 is very small, only lines A and D of C_V/C_V^0 are shown for simplicity. The rest of the lines are between them.

These figures show that Eq. (10) cannot be obtained even if the interaction between a vacancy and a self-interstitial, that is, f_{VI} is very small. Comparing Figure 2 with Figure 1, it is also seen that the difference in κ_V and κ_I has a dominant effect upon C_V and C_I.

4. Conclusion

A basic concept in thermodynamics states that, if an isolated system is left standing, it comes eventually to a final state which does not change. This final state is called the thermal equilibrium state. If vacancies and self-interstitials coexist, it is sure that they recombine with each other. Greatest importance is given to the basic concept in the thermodynamics mentioned above. Therefore, regardless of whether or not the thermal generation of the Frenkel pair is energetically possible, the Frenkel pair should be generated thermally as a reverse reaction of the recombination and Eq. (7) should be satisfied, to get the thermal equlibrium state.

In Eq. (7), k_{VI} includes the effect of interaction between a vacancy and a self-interstitial and increases with increase of attraction between them. Equation (7) shows, accordingly, that the more attractive a vacancy and a self-interstitial are with each other, the more the Frenkel pairs are generated, to get the thermal equilibrium state.

This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

REFERENCES

(1) G. D. Watkins, J. R. Troxell and A. P. Chatterjee, Defects and Radiation Effects in Semiconductors 1978 (Inst. Phys., London, 1979) Conf. Ser. 46, p. 16.
(2) S. M. Hu, J. Appl. Phys. 45, 1567 (1974).
(3) S. Mizuo and H. Higuchi, Jpn. J. Appl. Phys. 20, 739 (1981).
(4) S. Mizuo and H. Higuchi, Jpn. J. Appl. Phys. 22, 12 (1983).
(5) D. Mathiot and J. C. Pfister, J. Appl. Phys. 55, 3518 (1984).
(6) R. Kubo, H. Ichimura, T. Usui and N. Hashitsume, Thermodynamics (North-Holland, Amsterdam, 1976) p. 2.
(7) A. C. Damask and G. J. Dienes, Point Defects in Metals (Gordon and Breach, New

York, 1971) p. 89.
(8) B. H. Mahan, University Chemistry (Addison-Wesley, Reading, 1975) p. 175.
(9) ibid. p. 387.
(10) R. Kubo, H. Ichimura, T. Usui and N. Hashitsume, Statistical Mechanics (North-Holland, Amsterdam, 1981) p. 61.
(11) H. J. Mayer, H. Mehrer and K. Maier, Radiation Effects in Semiconductors 1976 (Inst. Phys., London, 1977) Conf. Ser. 31, p. 186.
(12) S. Mizuo and H. Higuchi, J. Electrochem. Soc. 129, 2292 (1982).
(13) M. Yoshida, S. Matsumoto and Y. Ishikawa Jpn. J. Appl. Phys. 25, 1031 (1986).