Diffusion Fundamentals
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Formation Mechanism of Plateau, Rapid Fall and Tail in Phosphorus Diffusion Profile in Silicon Based on the Pair Diffusion Models of Vacancy Mechanism and Interstitial Mechanism

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Abstract

P diffuses predominantly by the interstitial mechanism in Si. Assuming that there is a strong binding energy between P and I, therefore, the basic process of P diffusion is the diffusion of (PI), where I and (PI) represent self-interstitials and P-I pairs, respectively. In the high-P-concentration region, excess I is generated by the dissociation of (PI) and the limiting process of P diffusion depends on whether or not excess I is controlled. That is, if the concentration of excess I decreases relatively to the equilibrium I concentration due to the effect of the decrease in quasi self-interstitial formation energy, or if excess I is removed by the recombination with vacancies, P diffuses fast and the plateau is formed; if not, P diffuses slowly and the rapid fall is formed. In the tail region, the P concentration is low and the limiting process of P diffusion is the basic process of P diffusion, that is, the diffusion of (PI). Excess I generated in the high-P-concentration region diffuses into the low-P-concentration region, and I is supersaturated there. Therefore, the concentration of (PI) increases, resulting in the fast diffusion of P and the formation of the tail.

Keywords: *plateau, rapid fall, tail, control of excess self-interstitial*

(received 10 February 2005, accepted 17 February 2005)

§1. Introduction

Duffy *et al.*1) found unique features of the P diffusion profile at high P surface concentration in Si, which are called the plateau,2) kink3) and tail.4) Although several models had been proposed for these unique features, Hu5) pointed out in 1973 that none of the models were satisfactory to explain them. In the present work, "rapid fall" is used in place of "kink", as will be explained in §8.

Yoshida6) and Yoshida *et al.*7) proposed the pair diffusion model of the vacancy mechanism in 1971 and 1974. Applying the idea of the pair diffusion model to the interstitial mechanism, Yoshida and coworkers8,9) obtained the P diffusion equation on the basis of the pair diffusion models of the vacancy mechanism and the interstitial mechanism. The numerical solution was obtained from the P diffusion equation.

The numerical solution of the diffusion equation should be studied on the basis of the diffusion equation. Based on this principle, they obtained the effective P diffusion coefficient from the P diffusion equation, then proposed the limiting process of P diffusion on the basis of the effective P diffusion coefficient. They8-10) successfully explained the formation mechanism of the plateau, rapid fall and tail on the basis of the effective P diffusion coefficient and the limiting process of P diffusion. In §12 of the present work, the formation mechanism is described more clearly and concisely.

§2. Pair Diffusion Model of Vacancy Mechanism

The vacancy potential energy in the vicinity of P proposed by Watkins and Corbett[11] is shown in Fig. 1.[12] The abscissa is the P-V separation expressed by consecutively numbered sites of V^-, where V represents vacancies. $E^{\mathrm{m}}_{(\mathrm{PV})^0}$ is the migration energy of $(\mathrm{PV})^0$, where (PV) represents P-V pairs. $E^{\mathrm{m}}_{\mathrm{V}^-}$ is the migration energy of V^-, $E^{\mathrm{b}}_{\mathrm{PV}}$ is the binding energy between P^+ and V^- and $E^{\mathrm{b,i}}_{\mathrm{PV}}$ is the value of $E^{\mathrm{b}}_{\mathrm{PV}}$ in the intrinsic state. Hereafter, superscript i indicates a value in the intrinsic state.

Based on the vacancy potential energy in Fig. 1, Yoshida[6] studied the P diffusion theoretically by the Lidiard method[13] and obtained

$$E^{\mathrm{d,i}}_{\mathrm{P}} = E^{\mathrm{m}}_{(\mathrm{PV})^0} + E^{\mathrm{f,i}}_{\mathrm{V}^-} - E^{\mathrm{b,i}}_{\mathrm{PV}}, \tag{1}$$

where $E^{\mathrm{d}}_{\mathrm{P}}$ is the activation energy of P diffusion and $E^{\mathrm{f}}_{\mathrm{V}^-}$ is the formation energy of V^-. Because $E^{\mathrm{f,i}}_{\mathrm{V}^-} - E^{\mathrm{b,i}}_{\mathrm{PV}}$ is the formation energy of $(\mathrm{PV})^0$, eq. (1) shows that $E^{\mathrm{d,i}}_{\mathrm{P}}$ is given by the sum of migration and formation energies of $(\mathrm{PV})^0$. This is the pair diffusion model of the vacancy mechanism[7] which means that the diffusion of P occurs through the diffusion of (PV). In other words, the basic process of P diffusion is the diffusion of (PV). For this expression, refer to the Appendix.

Figure 1 shows that there is a strong attractive force between P^+ and V^-. By this force, $(\mathrm{PV})^0$ can diffuse a long distance without complete dissociation to P^+ and V^-. This results in the pair diffusion model of the vacancy mechanism. The vacancy potential energy in the vicinity of P in Fig. 1 is the basic condition of the pair diffusion model of the vacancy mechanism.

Now we comment on Fig. 1. Assuming that P diffuses by the vacancy mechanism, $E^{\mathrm{b,i}}_{\mathrm{PV}}$=1.9 eV was obtained from eq. (1) and then Fig. 1 was obtained.[12] It is generally accepted, however, that P diffuses predominantly by the interstitial mechanism.[14-16] On the other hand, $E^{\mathrm{b,i}}_{\mathrm{PV}}$=1.8 eV was theoretically obtained.[17] Therefore it is unnecessary to correct Fig. 1.

Yoshida[6] obtained eq. (1) in 1971. Flynn[18] obtained it in 1972 and Hu[19] in 1973. Hu[5,19] also reported that Johnson[20] obtained it qualitatively in the study of impurity diffusion in

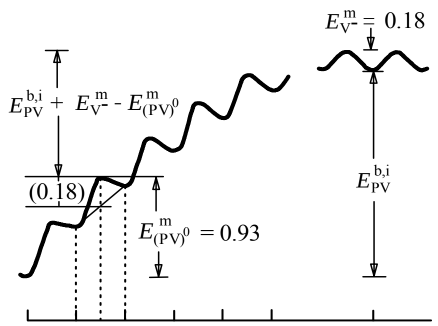

Fig. 1. Vacancy potential energy in eV in the vicinity of P atom.

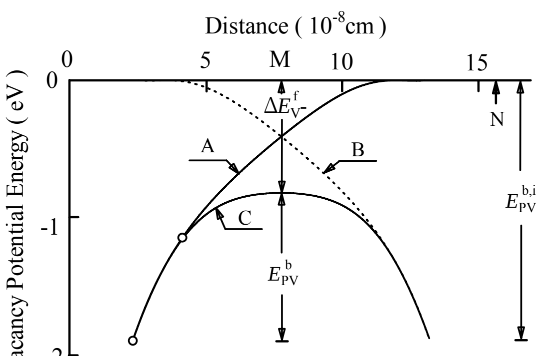

Fig. 2. Decrease in quasi vacancy formation energy.

metals in 1939. Doyama[21)] adopted the single vacancy-impurity atom complexes or the impurity-vacancy pairs in the diffusion equations for the study of quenching of metals containing impurity.

§3. Decrease in Quasi Vacancy Formation Energy

Formation-dissociation of $(\mathrm{PV})^0$ is given by

$$\mathrm{P}^+ + \mathrm{V}^- \underset{k^{\mathrm{b}}_{\mathrm{P/V}}}{\overset{k^{\mathrm{f}}_{\mathrm{P/V}}}{\rightleftarrows}} (\mathrm{PV})^0, \tag{2}$$

where $k^{\mathrm{f}}_{\mathrm{P/V}}$ and $k^{\mathrm{b}}_{\mathrm{P/V}}$ are rate constants. V^- in reaction (2) is defined as a vacancy which is located far from P^+ and is free from the effect of P^+. At low $C_{\mathrm{P}+}$, where C_{R} is the concentration of component R, this condition is satisfied and V^- is defined as a vacancy located at ∞ in Fig. 1. The formation energy of V^- in the intrinsic state is defined under this condition. At high $C_{\mathrm{P}+}$, where the unique diffusion of P occurs, however, the decrease in quasi vacancy formation energy[22-24)] occurs due to the interaction between two P^+ ions and one V^- ion, because the interaction between P^+ and V^- is long ranging as seen in Fig. 1. This is explained in Fig. 2.

In Fig. 2, the abscissa is the distance from P^+ located at 0 and line A is obtained by smoothly connecting the points of minimum vacancy potential energy in Fig. 1. The two circles on line A will be explained later. At $C_{\mathrm{P}+} = 5\times10^{20}\ \mathrm{cm}^{-3}$, the mean distance between two adjoining P^+ ions is 15.6×10^{-8} cm and is denoted by point N. Line B is the vacancy potential energy caused by P^+ ion at point N. The total vacancy potential energy caused by two P^+ ions at points 0 and N is given by line C. Line C shows that every V^- ion is under the influence of P^+ ion. Now the problem of how to define V^- in reaction (2) in this situation arises. We define it as a vacancy located at a middle point M between points 0 and N. Based on this definition, it is seen in Fig. 2 that $E^{\mathrm{f,i}}_{\mathrm{V}^-}$ at ∞ decreases by $\Delta E^{\mathrm{f}}_{\mathrm{V}-}$ at M and we have

$$E^{\mathrm{f}}_{\mathrm{V}^-} = E^{\mathrm{f,i}}_{\mathrm{V}^-} - \Delta E^{\mathrm{f}}_{\mathrm{V}^-}. \tag{3}$$

$\Delta E^{\mathrm{f}}_{\mathrm{V}-}$ is referred to as the decrease in quasi vacancy formation energy and is defined as the difference in the vacancy potential energy between ∞ and M. Basically, the vacancy formation energy is defined under the non-influence of impurities and/or lattice defects. In the present case, V^- is under the influence of two P^+ ions. To emphasize this, “quasi” is used.[24)]

In Fig. 2, the position of point N changes with changing $C_{\mathrm{P}+}$ and a new value of $\Delta E^{\mathrm{f}}_{\mathrm{V}-}$ is obtained. In this way, we have[22)]

$$\Delta E^{\mathrm{f}}_{\mathrm{V}-} = (B_{\mathrm{V}} C_{\mathrm{P}+})^2,\ \ B_{\mathrm{V}} = 2\times10^{-21}\ \mathrm{eV}^{1/2}\cdot\mathrm{cm}^3. \tag{4}$$

In the practical calculation of the simulation, B_V is used as a fitting parameter. Sometimes we denote the decrease in quasi vacancy formation energy by B_V.

It was mentioned in §2 that the vacancy potential energy in the vicinity of P in Fig. 1 is the basic condition of the pair diffusion model of the vacancy mechanism. It is also seen in Fig. 2 that the vacancy potential energy in the vicinity of P is the basic condition of $\Delta E^{\mathrm{f}}_{\mathrm{V}^-}$. Therefore $\Delta E^{\mathrm{f}}_{\mathrm{V}^-}$ should also be adopted if the pair diffusion model of the vacancy mechanism is adopted.[23,24]

The two circles on line A in Fig. 2 show the first nearest site of P^+, $2.35\times10^{-8}\,\mathrm{cm}$, and the middle point between the second and third nearest sites of P^+, $4.17\times10^{-8}\,\mathrm{cm}$. When $(\mathrm{PV})^0$ is formed, V^- is located at the first nearest site of P^+. For the migration of $(\mathrm{PV})^0$, it is necessary for V^- to overcome the energy barrier height at the middle point between the second and third nearest sites of P^+. In Fig. 2, line B has no influence on the two circles and $E^{\mathrm{b,i}}_{\mathrm{PV}}$ at ∞ decreases by $\Delta E^{\mathrm{f}}_{\mathrm{V}^-}$ at M. Therefore we have

$$E^{\mathrm{b}}_{\mathrm{PV}} = E^{\mathrm{b,i}}_{\mathrm{PV}} - \Delta E^{\mathrm{f}}_{\mathrm{V}^-}. \qquad (5)$$

Because both $E^{\mathrm{f}}_{\mathrm{V}^-}$ and $E^{\mathrm{b}}_{\mathrm{PV}}$ decrease by $\Delta E^{\mathrm{f}}_{\mathrm{V}^-}$ as seen in eqs. (3) and (5), respectively, $\Delta E^{\mathrm{f}}_{\mathrm{V}^-}$ has no effect on $(\mathrm{PV})^0$.

§4. Application to Interstitial Mechanism

Although it is generally accepted that P diffuses predominantly by the interstitial mechanism,[14-16] an isolated self-interstitial and its pair with P have not yet been found experimentally. Therefore, replacing V and (PV) in §2 and §3 with I and (PI), where I represents self-interstitials and (PI) represents P-I pairs, it is assumed that there is a strong attractive force between P and I. Based on this assumption, we obtain the pair diffusion model of the interstitial mechanism[8,9] which means that the diffusion of P occurs through the diffusion of (PI). In other words, the basic process of P diffusion is the diffusion of (PI). And as in the case of the vacancy mechanism, the decrease in quasi self-interstitial formation energy should also be adopted if the pair diffusion model of the interstitial mechanism is adopted.[23,24] It should be noted that I and (PI) probably migrate by the interstitialcy mechanism.[25]

Corresponding to reaction (2) and eqs. $(3)-(5)$, we have

$$\mathrm{P}^+ + \mathrm{I}^- \underset{k^{\mathrm{b}}_{\mathrm{P/I}}}{\overset{k^{\mathrm{f}}_{\mathrm{P/I}}}{\rightleftarrows}} (\mathrm{PI})^0, \qquad (6)$$

where $k^{\mathrm{f}}_{\mathrm{P/I}}$ and $k^{\mathrm{b}}_{\mathrm{P/I}}$ are rate constants,

$$E^{\mathrm{f}}_{\mathrm{I}^-} = E^{\mathrm{f,i}}_{\mathrm{I}^-} - \Delta E^{\mathrm{f}}_{\mathrm{I}^-}, \qquad (7)$$

$$\Delta E^{\mathrm{f}}_{\mathrm{I}^-} = (B_{\mathrm{I}} C_{\mathrm{P}+})^2, \qquad (8)$$

$$E^{\mathrm{b}}_{\mathrm{PI}} = E^{\mathrm{b,i}}_{\mathrm{PI}} - \Delta E^{\mathrm{f}}_{\mathrm{I}^-} , \tag{9}$$

where $E^{\mathrm{f}}_{\mathrm{I}^-}$ is the I^- formation energy, $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$ is the decrease in quasi self-interstitial formation energy, B_{I} is a constant and $E^{\mathrm{b}}_{\mathrm{PI}}$ is the binding energy between P^+ and I^-. Sometimes we denote the decrease in quasi self-interstitial formation energy by B_{I}.

Assuming reaction (6) to be in the near-equilibrium state, we have eq. (A·20) of ref. 9 or

$$C_{(\mathrm{PI})^0} = \left(k^{\mathrm{f}}_{\mathrm{P/I}} / k^{\mathrm{b}}_{\mathrm{P/I}}\right)^{\mathrm{i}} \exp\left(-\Delta E^{\mathrm{f}}_{\mathrm{I}^-} / kT\right) C_{\mathrm{P}^+} C_{\mathrm{I}^-} , \tag{10}$$

where k is the Boltzmann constant and T is the temperature. In eq. (10), $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$ expresses the decrease of the binding energy between P^+ and I^- shown in eq. (9). Hereafter, equations such as eq. (A·20) of ref. 9 are denoted by eq. (9,A·20), for example.

In §3, it was mentioned that $\Delta E^{\mathrm{f}}_{\mathrm{V}^-}$ has no effect on $(\mathrm{PV})^0$. Applying this to the interstitial mechanism, we have "$\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$ has no effect on $(\mathrm{PI})^0$". This will be quoted in §9.

Because vacancies and self-interstitials coexist, recombination-generation of the Frenkel pair,

$$\mathrm{I}^- + \mathrm{V}^- \rightleftarrows 2\,\mathrm{e}^- , \tag{11}$$

is taken into account, where e^- is an electron. Assuming reaction (11) to be in the near-equilibrium state, we have eq. (9,A·21) or

$$C_{\mathrm{I}^-} C_{\mathrm{V}^-} = C^{\mathrm{eq}}_{\mathrm{I}^-} C^{\mathrm{eq}}_{\mathrm{V}^-} . \tag{12}$$

In eq. (12), $C^{\mathrm{eq}}_{\mathrm{I}^-}$ and $C^{\mathrm{eq}}_{\mathrm{V}^-}$ are equilibrium concentrations of I^- and V^-, respectively, and are given by

$$C^{\mathrm{eq}}_{\mathrm{I}^-} = C^{\mathrm{eq,i}}_{\mathrm{I}^-} \exp[(\Delta E^{\mathrm{f}}_{\mathrm{I}^-} / kT) + \eta - \eta^{\mathrm{i}}], \tag{13}$$

$$C^{\mathrm{eq}}_{\mathrm{V}^-} = C^{\mathrm{eq,i}}_{\mathrm{V}^-} \exp[(\Delta E^{\mathrm{f}}_{\mathrm{V}^-} / kT) + \eta - \eta^{\mathrm{i}}]. \tag{14}$$

In eqs. (13) and (14), $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$ and $\Delta E^{\mathrm{f}}_{\mathrm{V}^-}$ express the decrease of the formation energies of I^- and V^- shown in eqs. (7) and (3), respectively, and η is defined as

$$\eta = (e_{\mathrm{f}} - e_{\mathrm{c}}) / k\,T , \tag{15}$$

where e_{f} is the Fermi level and e_{c} is the energy at the bottom of the conduction band. It is assumed that e_{f} depends only on C_{P^+} because concentrations of other components are much lower than $C_{\mathrm{P}+}$ and that e_{f} is obtained from the Boltzmann statistics. Therefore we have

$$\exp\eta = \left(C_{\mathrm{P}+} + \sqrt{C_{\mathrm{P}+}^{2} + 4n_{\mathrm{i}}^{2}}\right) \Big/ 2N_{\mathrm{c}}, \tag{16}$$

where n_{i} is the intrinsic carrier concentration and N_{c} is the effective density of states in the conduction band. At 900℃, $n_{\mathrm{i}} = 3.80\times10^{18}\ \mathrm{cm}^{-3}$ and $N_{\mathrm{c}} = 2.20\times10^{20}\ \mathrm{cm}^{-3}$.

Substituting $\Delta E_{\mathrm{I}^-}^{\mathrm{f}}$ and η of eqs. (8) and (16) into eq. (13), it is seen that $C_{\mathrm{I}^-}^{\mathrm{eq}}$ depends on $C_{\mathrm{P}+}$. Therefore $C_{\mathrm{I}^-}^{\mathrm{eq}}$ is referred to as "the equilibrium value of C_{I^-} corresponding to $C_{\mathrm{P}+}$". In the present work, "equilibrium" means "equilibrium corresponding to $C_{\mathrm{P}+}$" and superscript eq indicates a value in the equilibrium state corresponding to $C_{\mathrm{P}+}$.

§5. Simulation of P Diffusion Profile

Yoshida *et al.*,[7] Matsumoto *et al.*[26] and Matsumoto and Niimi[27] measured P diffusion profiles systematically by changing diffusion time, diffusion temperature and P surface concentration under an inert atmosphere. Many researchers[28-33] adopted these profiles for the study of P diffusion, mainly on the basis of the pair diffusion models of the vacancy mechanism and the interstitial mechanism.

For the simulation in ref. 9, six experimental P diffusion profiles[7,27] of P surface concentration $C_{\mathrm{P}+}^{\mathrm{s}}$ from 3×10^{20} to $2.5\times10^{18}\ \mathrm{cm}^{-3}$ at the diffusion temperature of 900℃ were used. In Fig. 3, the experimental P diffusion profile of $C_{\mathrm{P}+}^{\mathrm{s}} = 3\times10^{20}\ \mathrm{cm}^{-3}$ is shown.[7] Because P diffusion profiles at a constant P surface concentration are a function of

$$x/\sqrt{t} = \lambda, \tag{17}$$

where x is the distance from the specimen surface and t is the diffusion time,[7,26,27] the abscissa is λ. The profile exhibits the unique features of the plateau, rapid fall and tail.

The eleven components of P^+, I^0, I^-, $\mathrm{I}^=$, $(\mathrm{PI})^0$, $(\mathrm{PI})^-$, V^0, V^-, $\mathrm{V}^=$, $(\mathrm{PV})^0$ and $(\mathrm{PV})^-$ were adopted. The diffusion equations of total P and total point defects of eqs. $(9,\mathrm{A}\cdot1)$ and $(9,\mathrm{A}\cdot2)$ were obtained on the basis of the pair diffusion models of the vacancy mechanism and the interstitial mechanism. Because the P diffusion profiles used for the simulation were a function of λ, the independent variable of the diffusion equations was λ. Equations $(9,\mathrm{A}\cdot1)$ and $(9,\mathrm{A}\cdot2)$ were solved simultaneously with eqs. $(9,\mathrm{A}\cdot13)-(9,\mathrm{A}\cdot21)$, in which eqs. (10) and (12) are included. In the simulation of profiles of different $C_{\mathrm{P}+}^{\mathrm{s}}$ at the same diffusion temperature, only $C_{\mathrm{P}+}^{\mathrm{s}}$ should be changed with other fitting parameters kept constant. Based on this principle, the diffusion equations were solved to simulate them. In the simulation, the experimental fraction of interstitial component $f_{\mathrm{I}}^{\mathrm{i}}$ = 0.96 of P diffusion in the intrinsic state at 900℃[16] was adopted. The definition of $f_{\mathrm{I}}^{\mathrm{i}}$ will be shown in eq. (21). For details of the mathematical procedure and the simulation, refer to ref. 9.

The three models in ref. 9 are listed in Table I. The reason why these models were selected

Table I. Values of main parameters. B_I in $10^{-21}\,\mathrm{eV}^{1/2}\cdot\mathrm{cm}^3$.

Model	Constituent	f_I^i	B_I	$\varphi_{(PV)}$
61	(PI) I B_I	1.00	2.2	0
61 $B_I = 0$	(PI) I B_I	1.00	0	0
64	(PI) (PV) I V B_I B_V	0.96	2.0	0.01
71	(PI) (PV) I V	0.96	0	0.45

will be described in the end of §9. Model 61 is a pure interstitial model with $f_I^i = 1$, in which the components are P^+, I^0, I^-, $I^=$, $(PI)^0$ and $(PI)^-$ and B_I or $\Delta E_{I^-}^f$ of eq. (8) is adopted. Under the "Constituent" column of Table I, these are listed as (PI) I B_I. In models 64 and 71, all components are adopted. In model 64, B_I and B_V of eq. (4) are adopted under the condition of $B_I = B_V$. In model 71, they are not adopted. In models 61 and 64, the

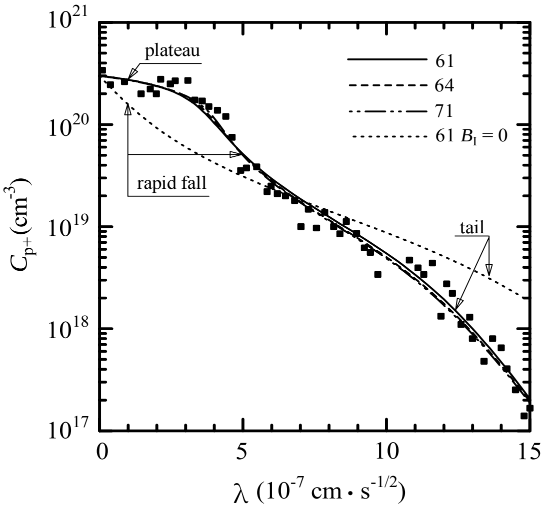

Fig. 3. Experimental P diffusion profile and C_{p^+} solution.

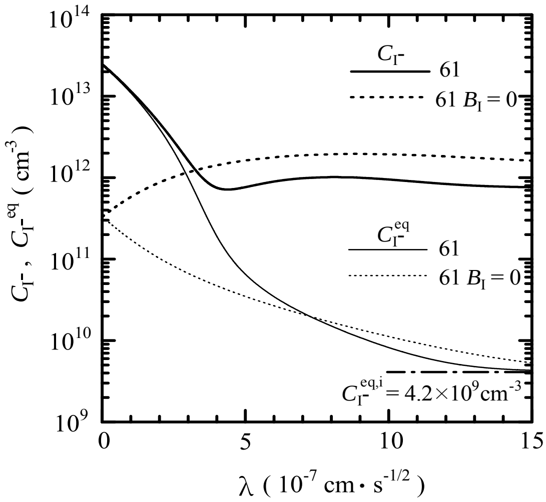

Fig. 4(a). C_{I^-} solution of models 61 and 61 $B_I = 0$.

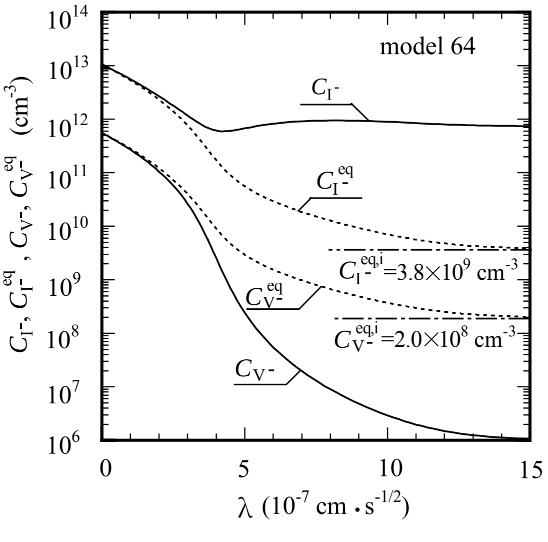

Fig. 4(b). C_{I^-} and C_{V^-} solutions of model 64.

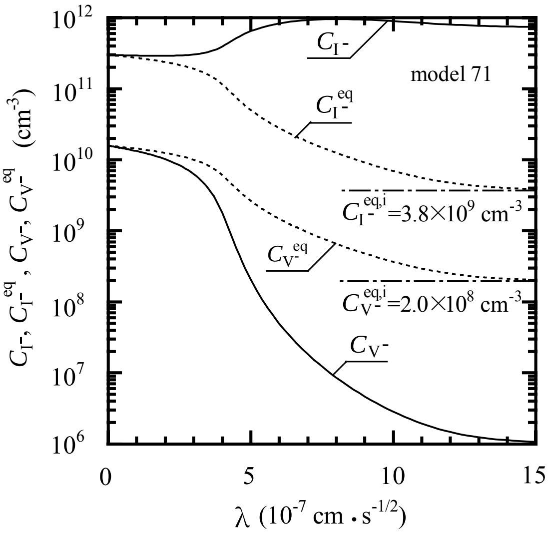

Fig. 4(c). C_{I^-} and C_{V^-} solutions of model 71.

main fitting parameter is $B_{\rm I}$. In model 71, it is $\varphi_{\rm (PV)}$ defined as

$$\varphi_{\rm (PV)} = D_{\rm (PV)^-} / D_{\rm (PV)^0}, \tag{18}$$

where $D_{\rm R}$ is the diffusion coefficient of component R. To study the formation mechanism of the plateau, rapid fall and tail, model 61 at $B_{\rm I} = 0$ is also listed in Table I. Hereafter, model 61 at $B_{\rm I} = 0$ is denoted by model 61 $B_{\rm I} = 0$. Values of the main fitting parameters for these models are listed in Table I. The problem of the main fitting parameters will be discussed in §10.

The $C_{\rm P^+}$ solution of the diffusion equations, or the result of simulation, of models 61, 64 and 71 at $C_{\rm P^+}^{\rm s} = 3\times10^{20}\,{\rm cm}^{-3}$ are shown in Fig. 3. It is seen in Fig. 3 that the P diffusion profile is simulated well. The $C_{\rm P^+}$ solution of model 61 $B_{\rm I} = 0$ is also shown in Fig. 3.

In Fig. 4(a), the $C_{\rm I^-}$ solution, $C_{\rm I^-}^{\rm eq}$ of eq. (13) and $C_{\rm I^-}^{\rm eq,i}$ of models 61 and 61 $B_{\rm I} = 0$ are shown. In Figs. 4(b) and 4(c), the $C_{\rm I^-}$ and $C_{\rm V^-}$ solutions, $C_{\rm I^-}^{\rm eq}$ and $C_{\rm V^-}^{\rm eq}$ of eq. (14), and $C_{\rm I^-}^{\rm eq,i}$ and $C_{\rm V^-}^{\rm eq,i}$ of models 64 and 71 are shown. It is seen in Figs. 4(a), 4(b) and 4(c) that I is supersaturated over the entire range of λ for all models. It is also seen in Figs. 4(b) and 4(c) that V is undersaturated over the entire range of λ for models 64 and 71. This is a consequence of eq. (12).

§6. Effective P Diffusion Coefficient

In Fig. 3, the experimental P diffusion profile is a function of λ of eq. (17). Therefore the P diffusion coefficient can be obtained experimentally by the Boltzmann-Matano method.[7,34] If a diffusion equation does not have a chemical reaction term, independent variables of x and t can be changed to λ and an effective diffusion coefficient can be obtained from the diffusion equation.[35] Concerning this, Hu[5] pointed out that a diffusion coefficient can be obtained from a diffusion equation only when the diffusion equation does not have a chemical reaction term.

The diffusion equation of total P of eq. $(9,{\rm A}\cdot1)$ does not have a chemical reaction term. Therefore the effective P diffusion coefficient can be obtained from it. The effective P diffusion coefficient and its interstitial and vacancy components obtained from the diffusion equation of total P are shown in eqs. $(9,{\rm A}\cdot28) - (9,{\rm A}\cdot42)$.

The fraction of the interstitial component of P diffusion is defined as

$$f_{\rm I} = D_{\rm P^+,I}^{\rm eff} \Big/ D_{\rm P^+}^{\rm eff}, \tag{19}$$

$$D_{\rm P^+}^{\rm eff} = D_{\rm P^+,I}^{\rm eff} + D_{\rm P^+,V}^{\rm eff}, \tag{20}$$

where $f_{\rm I}$ is the fraction of the interstitial component of P diffusion, $D_{\rm P^+}^{\rm eff}$ is the effective P diffusion coefficient, and $D_{\rm P^+,I}^{\rm eff}$ and $D_{\rm P^+,V}^{\rm eff}$ are its interstitial and vacancy components, respectively. $f_{\rm I}^{\rm i}$ in §5 is defined as

$$f_{\rm I}^{\rm i} = D_{\rm P^+,I}^{\rm eff,i} \Big/ D_{\rm P^+}^{\rm eff,i}, \tag{21}$$

where $D_{\rm P^+}^{\rm eff,i}$ and $D_{\rm P^+,I}^{\rm eff,i}$ are shown in eqs. $(9,{\rm A}\cdot 47)$ and $(9,{\rm A}\cdot 48)$, respectively.

Because model 61 is a pure interstitial model, we have $f_{\rm I} = f_{\rm I}^{\rm i} = 1$ over the entire range of λ. At a specimen surface of $\lambda = 0$ in Fig. 3, we have $f_{\rm I} = 0.97$ for model 64 and $f_{\rm I} = 0.52$ for model 71,[9] which are listed also in Table VII(c) of ref. 36. It was ascertained that $f_{\rm I} > 0.5$ over the entire range of λ for models 64 and 71. This means that the interstitial component is dominant there. Therefore the formation mechanism of the plateau, rapid fall and tail is studied on the basis of $D_{\rm P^+,I}^{\rm eff}$. $D_{\rm P^+,I}^{\rm eff}$ consists of six terms, as shown in eq. $(9,{\rm A}\cdot 29)$, or

$$D_{\rm P^+,I}^{\rm eff} = I_{\rm (PI)^0} + II_{\rm (PI)^0} + III_{\rm (PI)^0} + I_{\rm (PI)^-} + II_{\rm (PI)^-} + III_{\rm (PI)^-}, \tag{22}$$

where $I_{\rm (PI)^0}$, $II_{\rm (PI)^0}$ and $III_{\rm (PI)^0}$ are related to the diffusion of $\rm (PI)^0$ and are shown in eqs. $(9,{\rm A}\cdot 30) - (9,{\rm A}\cdot 32)$ or

$$I_{\rm (PI)^0} = D_{\rm (PI)^0} \left(k_{\rm P/I}^{\rm f} \big/ k_{\rm P/I}^{\rm b}\right)^{\rm i} \exp\left(-\Delta E_{\rm I^-}^{\rm f} \big/ kT\right) C_{\rm I^-}, \tag{23}$$

$$II_{\rm (PI)^0} = I_{\rm (PI)^0} \frac{C_{\rm P^+}}{C_{\rm I^-}} \frac{{\rm d}C_{\rm I^-}/{\rm d}\lambda}{{\rm d}C_{\rm P^+}/{\rm d}\lambda}, \tag{24}$$

$$III_{\rm (PI)^0} = -I_{\rm (PI)^0} \frac{C_{\rm P^+}}{kT} \frac{{\rm d}\Delta E_{\rm I^-}^{\rm f}}{{\rm d}C_{\rm P^+}}. \tag{25}$$

$I_{\rm (PI)^-}$, $II_{\rm (PI)^-}$ and $III_{\rm (PI)^-}$ are related to the diffusion of $\rm (PI)^-$ and have forms similar to those of $I_{\rm (PI)^0}$, $II_{\rm (PI)^0}$ and $III_{\rm (PI)^0}$, respectively. Because $I_{\rm (PI)^0}$, $II_{\rm (PI)^0}$ and $III_{\rm (PI)^0}$ are good enough for the study of the formation mechanism of the plateau, rapid fall and tail, we take only them into account in the present work and rewrite eq. (22) as

$$D_{\rm P^+,I}^{\rm eff} = I_{\rm (PI)^0} + II_{\rm (PI)^0} + III_{\rm (PI)^0} \tag{26}$$

for the sake of convenience.

At $C_{\rm I^-} = C_{\rm I^-}^{\rm eq}$, substituting eq. (13) into eqs. $(23) - (26)$, we have

$$I_{\rm (PI)^0}^{\rm eq} = D_{\rm (PI)^0} \left(k_{\rm P/I}^{\rm f} \big/ k_{\rm P/I}^{\rm b}\right)^{\rm i} \exp(\eta - \eta^{\rm i}) C_{\rm I^-}^{\rm eq,i}, \tag{27}$$

$$A \equiv \frac{C_{\mathrm{P}^+}}{C_{\mathrm{I}^-}^{\mathrm{eq}}} \frac{\mathrm{d}C_{\mathrm{I}^-}^{\mathrm{eq}}/\mathrm{d}\lambda}{\mathrm{d}C_{\mathrm{P}^+}/\mathrm{d}\lambda} - \frac{C_{\mathrm{P}^+}}{k\,T} \frac{\mathrm{d}\Delta E_{\mathrm{I}^-}^{\mathrm{f}}}{\mathrm{d}C_{\mathrm{P}^+}}$$

$$= C_{\mathrm{P}^+} \Big/ \sqrt{C_{\mathrm{P}^+}^2 + 4n_{\mathrm{i}}^2}\,, \tag{28}$$

where η of eq. (16) is substituted into $\mathrm{d}\eta/\mathrm{d}C_{\mathrm{P}^+}$ to obtain eq. (28), and

$$II_{(\mathrm{PI})^0}^{\mathrm{eq}} + III_{(\mathrm{PI})^0}^{\mathrm{eq}} = I_{(\mathrm{PI})^0}^{\mathrm{eq}} A$$

$$= I_{(\mathrm{PI})^0}^{\mathrm{eq}} C_{\mathrm{P}^+} \Big/ \sqrt{C_{\mathrm{P}^+}^2 + 4\,n_{\mathrm{i}}^2}\,, \tag{29}$$

$$D_{\mathrm{P}^+,\mathrm{I}}^{\mathrm{eff,eq}} = I_{(\mathrm{PI})^0}^{\mathrm{eq}} + II_{(\mathrm{PI})^0}^{\mathrm{eq}} + III_{(\mathrm{PI})^0}^{\mathrm{eq}}\,. \tag{30}$$

A defined by eq. (28) gives the effect of internal electric field on impurity diffusion in a semiconductor.37) As seen in eqs. (27) and (29), $I_{(\mathrm{PI})^0}^{\mathrm{eq}}$ and $II_{(\mathrm{PI})^0}^{\mathrm{eq}} + III_{(\mathrm{PI})^0}^{\mathrm{eq}}$ do not include B_{I} or $\Delta E_{\mathrm{I}^-}^{\mathrm{f}}$. This is related to the description "$\Delta E_{\mathrm{I}^-}^{\mathrm{f}}$ has no effect on $(\mathrm{PI})^0$" in §4.

§7. Mathematical Feature of Effective P Diffusion Coefficient

$I_{(\mathrm{PI})^0}$ of eq. (23) is proportional to C_{I^-} and we always have $I_{(\mathrm{PI})^0} > 0$. A feature of the pair diffusion model appears in $II_{(\mathrm{PI})^0}$ and $III_{(\mathrm{PI})^0}$ or $II_{(\mathrm{PI})^0} + III_{(\mathrm{PI})^0}$ of eqs. (24) and (25). Because they are proportional to C_{P^+}, they affect $D_{\mathrm{P}^+,\mathrm{I}}^{\mathrm{eff}}$ at high C_{P^+}. Results of this section are summarized in Table II, together with those of §8 and §9.

First, we investigate the case of high C_{P^+}, because the plateau and rapid fall exist in the high C_{P^+} region.

7-1-1) At $B_{\mathrm{I}} = 0$, we investigate only $II_{(\mathrm{PI})^0}$ because $III_{(\mathrm{PI})^0} = 0$. $II_{(\mathrm{PI})^0}$ has $\mathrm{d}C_{\mathrm{P}^+}/\mathrm{d}\lambda$ and $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda$. Because $\mathrm{d}C_{\mathrm{P}^+}/\mathrm{d}\lambda < 0$, we have $II_{(\mathrm{PI})^0} < 0$ for $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$. This results in a small $D_{\mathrm{P}^+,\mathrm{I}}^{\mathrm{eff}}$ of eq. (26), the slow diffusion of P and the formation of the rapid fall. Near the surface of $\lambda \approx 1 \times 10^{-7}\ \mathrm{cm{\cdot}s^{-1/2}}$ in Fig. 4(a) and in Fig. 3, model 61 $B_{\mathrm{I}} = 0$ has $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ and the rapid fall. In the region of $\lambda \approx 5 \times 10^{-7}\ \mathrm{cm{\cdot}s^{-1/2}}$ in Fig. 4(c) and in Fig. 3, model 71 has $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ and the rapid fall.

7-1-2) In contrast, we have $II_{(\mathrm{PI})^0} > 0$ for $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$. This results in a large $D_{\mathrm{P}^+,\mathrm{I}}^{\mathrm{eff}}$, the fast diffusion of P and the formation of the plateau. Near the surface of $\lambda \approx 1 \times 10^{-7}\ \mathrm{cm{\cdot}s^{-1/2}}$ in Fig. 4(c) and in Fig. 3, model 71 has $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$ and the plateau.

7-2-1) At $B_{\mathrm{I}} \neq 0$, it is necessary to investigate $II_{(\mathrm{PI})^0} + III_{(\mathrm{PI})^0}$. We always have $III_{(\mathrm{PI})^0} < 0$. Therefore we have $II_{(\mathrm{PI})^0} + III_{(\mathrm{PI})^0} < 0$ for $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$. This results in a small $D_{\mathrm{P}^+,\mathrm{I}}^{\mathrm{eff}}$, the

Table II. Mathematical feature of effective P diffusion coefficient and formation mechanism of plateau, rapid fall and tail. λ in $10^{-7}\,\mathrm{cm\cdot s^{-1/2}}$.

(a) High C_{P^+}

Line	§ 7	B_{I}	$\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda$	Effective term and its sign	$D^{\mathrm{eff}}_{\mathrm{P}^+,\mathrm{I}}$	P diffusion	Feature
1	7-1-1	0	>0	$II_{(\mathrm{PI})^0} < 0$	small	slow	rapid fall
2	7-1-2	0	<0	$II_{(\mathrm{PI})^0} > 0$	large	fast	plateau
3	7-2-1	$\neq 0$	>0	$II_{(\mathrm{PI})^0} + III_{(\mathrm{PI})^0} < 0$	small	slow	rapid fall
4	7-2-2	$\neq 0$	$(C_{\mathrm{I}^-} \cong C^{\mathrm{eq}}_{\mathrm{I}^-})$ $\cong \mathrm{d}C^{\mathrm{eq}}_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$	$II_{(\mathrm{PI})^0} + III_{(\mathrm{PI})^0}$ $\cong II^{\mathrm{eq}}_{(\mathrm{PI})^0} + III^{\mathrm{eq}}_{(\mathrm{PI})^0} > 0$	large	fast	plateau

Line	§ 7	Feature	Model	λ	Excess I	Control of excess I
1	7-1-1	rapid fall	71 ($61\, B_{\mathrm{I}} = 0$	5 1)	accumulated	no control
2	7-1-2	plateau	71	1	not accumulated	by § 9-2
3	7-2-1	rapid fall	61, 64	5	accumulated	no control
4	7-2-2	plateau	61,64	1	not accumulated	by § 9-1

(b) Low C_{P^+}

Line	§ 7	Effective term	C_{I^-}	$D^{\mathrm{eff}}_{\mathrm{P}^+,\mathrm{I}}$	P diffusion	Feature	Model	λ
5	7-3	$I_{(\mathrm{PI})^0}$	$> C^{\mathrm{eq}}_{\mathrm{I}^-}$	large	fast	tail	every model	> 10

slow diffusion of P and the formation of the rapid fall. In the region of $\lambda \approx 5\times10^{-7}\ \mathrm{cm\cdot s^{-1/2}}$ in Figs. 4(a) and 4(b) and in Fig. 3, models 61 and 64 have $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ and the rapid fall.

7-2-2) Even if we have $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$ and $II_{(\mathrm{PI})^0} > 0$, however, whether $II_{(\mathrm{PI})^0} + III_{(\mathrm{PI})^0}$ is positive or negative cannot be decided because $III_{(\mathrm{PI})^0} < 0$. Therefore, we investigate the case of $C_{\mathrm{I}^-} = C^{\mathrm{eq}}_{\mathrm{I}^-}$. Because $\mathrm{d}C_{\mathrm{P}^+}/\mathrm{d}\lambda < 0$, we have $\mathrm{d}C^{\mathrm{eq}}_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$ from eqs. (8), (13) and (16) and $II^{\mathrm{eq}}_{(\mathrm{PI})^0} + III^{\mathrm{eq}}_{(\mathrm{PI})^0} > 0$ from eq. (29). This result in a large $D^{\mathrm{eff,eq}}_{\mathrm{P}^+,\mathrm{I}}$ of eq. (30) and the fast diffusion of P. For $C_{\mathrm{I}^-} \cong C^{\mathrm{eq}}_{\mathrm{I}^-}$, we probably have $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda \cong \mathrm{d}C^{\mathrm{eq}}_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$ and $II_{(\mathrm{PI})^0} + III_{(\mathrm{PI})^0} \cong II^{\mathrm{eq}}_{(\mathrm{PI})^0} + III^{\mathrm{eq}}_{(\mathrm{PI})^0} > 0$. This result in a large $D^{\mathrm{eff}}_{\mathrm{P}^+,\mathrm{I}}$, the fast diffusion of P and the formation of the plateau. Near the surface of $\lambda \approx 1\times10^{-7}\,\mathrm{cm\cdot s^{-1/2}}$ in Figs. 4(a) and 4(b) and in Fig. 3, models 61 and 64 have $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda \cong \mathrm{d}C^{\mathrm{eq}}_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$ and the plateau.

Next we investigate the case of low C_{P^+}. The tail exists in the low C_{P^+} region.

7-3) Because $II_{(\mathrm{PI})^0}$ and $III_{(\mathrm{PI})^0}$ are proportional to C_{P^+}, they are neglected and $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda$ does not affect $D^{\mathrm{eff}}_{\mathrm{P}^+,\mathrm{I}}$ at low C_{P^+}. Only $I_{(\mathrm{PI})^0}$ affects $D^{\mathrm{eff}}_{\mathrm{P}^+,\mathrm{I}}$. Because $I_{(\mathrm{PI})^0}$ or $D^{\mathrm{eff}}_{\mathrm{P}^+,\mathrm{I}}$ is proportional to C_{I^-}, we have a large $D^{\mathrm{eff}}_{\mathrm{P}^+,\mathrm{I}}$ and the fast diffusion of P for high C_{I^-}. This results in the formation of the tail. In the bulk of $\lambda > 10\times10^{-7}\,\mathrm{cm\cdot s^{-1/2}}$ in Figs. 4(a), 4(b) and 4(c) and in Fig. 3, every model has $C_{\mathrm{I}^-} > C^{\mathrm{eq}}_{\mathrm{I}^-}$ and the tail.

In Table II, lines 1 and 3 show that P diffusion is slow in the case of $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ and lines 2 and 4 show that P diffusion is fast in the case of $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$.

§8. Physical Meaning of $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ or < 0 and Limiting Process of P Diffusion

Because P diffuses predominantly by the interstitial mechanism, the P diffusion occurs through the diffusion of (PI). This means that the basic process of the P diffusion is the diffusion of (PI).

When C_{P^+} is high, $C_{(\mathrm{PI})^0}$ is also high. While $(\mathrm{PI})^0$ is diffusing to the lower $C_{(\mathrm{PI})^0}$ region, therefore, reaction (6) proceeds to the left and excess I is generated by the dissociation of $(\mathrm{PI})^0$. In this case, I on the left-hand side of reaction (6) includes a large amount of excess I and we have $C_{\mathrm{I}^-} > C_{\mathrm{I}^-}^{\mathrm{eq}}$. This results in $C_{\mathrm{V}^-} < C_{\mathrm{V}^-}^{\mathrm{eq}}$ from eq. (12). It is seen that I is supersaturated in Figs. 4(a), 4(b) and 4(c) and V is undersaturated in Figs. 4(b) and 4(c). It is also known from §7 that P diffuses slowly and the rapid fall is formed in the case of $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$, and that P diffuses fast and the plateau is formed in the case of $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$.

If excess I is accumulated in a heap and is not controlled, reaction (6) no longer proceeds to the left. Therefore $(\mathrm{PI})^0$ is accumulated and only a small amount of $(\mathrm{PI})^0$ migrates, resulting in the slow diffusion of P and the formation of the rapid fall. This corresponds to $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ and was described in §7-1-1 and §7-2-1. Regarding the control of excess I, refer to §9.

If excess I is controlled and is not accumulated, reaction (6) proceeds further to the left. Therefore $(\mathrm{PI})^0$ is dissociated and is not accumulated, $C_{(\mathrm{PI})^0}$ becomes low and a large amount of $(\mathrm{PI})^0$ migrates to compensate for the low $C_{(\mathrm{PI})^0}$, resulting in the fast diffusion of P and the formation of the plateau. This corresponds to $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$ and was described in §7-1-2 and §7-2-2.

The physical meaning of $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ is that excess I is accumulated in a heap and is not controlled, while that of $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda < 0$ is that excess I is controlled and is not accumulated. The limiting process of P diffusion at high C_{P^+} depends on whether or not excess I is controlled. For the expression of this, refer to the Appendix. If excess I is controlled, P diffuses fast and the plateau is formed. If excess I is not controlled, P diffuses slowly and the rapid fall is formed.

As described in §7-3, at low C_{P^+}, only $I_{(\mathrm{PI})^0}$ affects $D_{\mathrm{P}^+,\mathrm{I}}^{\mathrm{eff}}$. Therefore, the limiting process of P diffusion is the basic process of P diffusion, that is, the diffusion of (PI). In the bulk of $\lambda > 10 \times 10^{-7}\ \mathrm{cm{\cdot}s^{-1/2}}$ in models 61, 64 and 71, excess I is not generated because C_{P^+} is low. However a part of excess I generated in the high C_{P^+} region near the surface diffuses into the bulk and I is supersaturated there. Therefore, the concentration of (PI) increases, resulting in the fast diffusion of P and the formation of the tail.

As mentioned above, the rapid fall is formed in the P diffusion profile by the slow diffusion of P and the plateau is formed by the fast diffusion of P. Therefore "rapid fall" is used in place of "kink".[8)] The physical meaning of the rapid fall is as clear as that of the plateau.

The effect of the accumulation of excess I and $\mathrm{d}C_{\mathrm{I}^-}/\mathrm{d}\lambda > 0$ is clearly seen in model

$61\,B_{\mathrm{I}} = 0$. In Fig. 4(a), we can see that near the surface of $\lambda \approx 1\times 10^{-7}\,\mathrm{cm\cdot s^{-1/2}}$ a large amount of excess I is accumulated and we have $C_{\mathrm{I^-}} > C_{\mathrm{I^-}}^{\mathrm{eq}}$ and $\mathrm{d}C_{\mathrm{I^-}}/\mathrm{d}\lambda > 0$. If only $I_{(\mathrm{PI})^0}$ of eq. (23) is taken into account, $C_{\mathrm{I^-}} > C_{\mathrm{I^-}}^{\mathrm{eq}}$ gives a large $I_{(\mathrm{PI})^0}$ and a plateau should be formed. As seen in Fig. 3, however, model $61\,B_{\mathrm{I}} = 0$ has no plateau but the rapid fall near the surface because of the accumulation of excess I and $\mathrm{d}C_{\mathrm{I^-}}/\mathrm{d}\lambda > 0$.

§9. Control of Excess I

The concentration of excess I is defined as $C_{\mathrm{I^-}} - C_{\mathrm{I^-}}^{\mathrm{eq}}$. The relative concentration of excess I, $\delta C_{\mathrm{I^-}}$, is defined as

$$\delta C_{\mathrm{I^-}} = (C_{\mathrm{I^-}} - C_{\mathrm{I^-}}^{\mathrm{eq}})\big/C_{\mathrm{I^-}}^{\mathrm{eq}}. \tag{31}$$

$C_{(\mathrm{PI})^0}$ of eq. (10), $C_{\mathrm{I^-}} - C_{\mathrm{I^-}}^{\mathrm{eq}}$ and $\delta C_{\mathrm{I^-}}$ are shown in Figs. 5, 6 and 7, respectively. The case that excess I is accumulated or not is quantitatively defined as $\delta C_{\mathrm{I^-}} > 1$ or < 1 in the present work. $C_{\mathrm{p+}}$ is closely related to $\delta C_{\mathrm{I^-}}$ by seeing the following points. Three $C_{\mathrm{p+}}$ of models 61, 64 and 71 in Fig. 3 agree well, and three $\delta C_{\mathrm{I^-}}$ of these models in Fig. 7 also agree well, although $C_{\mathrm{p+}}$ and $\delta C_{\mathrm{I^-}}$ of model $61\,B_{\mathrm{I}} = 0$ are very different from those of the other models. It should be noted that the agreement of $C_{(\mathrm{PI})^0}$ among models 61, 64 and 71 in Fig. 5 is due to the fact that $\Delta E_{\mathrm{I^-}}^{\mathrm{f}}$ has no effect on $(\mathrm{PI})^0$. It should also be noted that $C_{\mathrm{I^-}} - C_{\mathrm{I^-}}^{\mathrm{eq}}$ of every model in Fig. 6 does not agree with each other.

There are two methods for controlling excess I and decreasing $\delta C_{\mathrm{I^-}}$.

[1] Relative decrease in the concentration of excess I to the equilibrium I concentration due

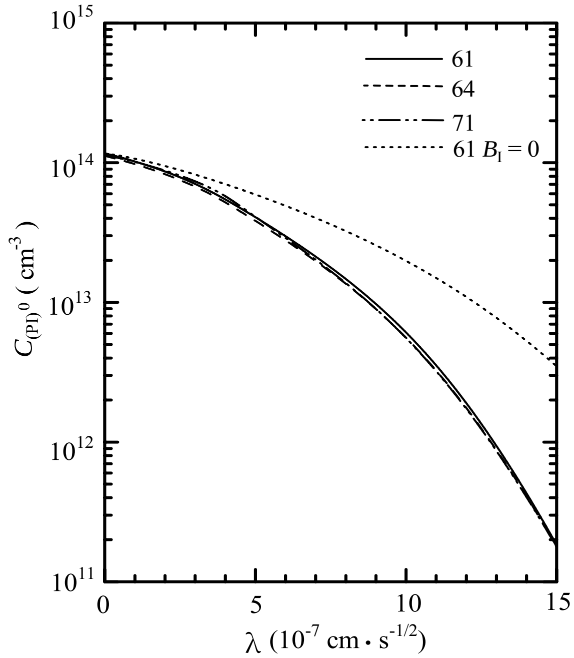

Fig. 5. Concentration of $(\mathrm{PI})^0$.

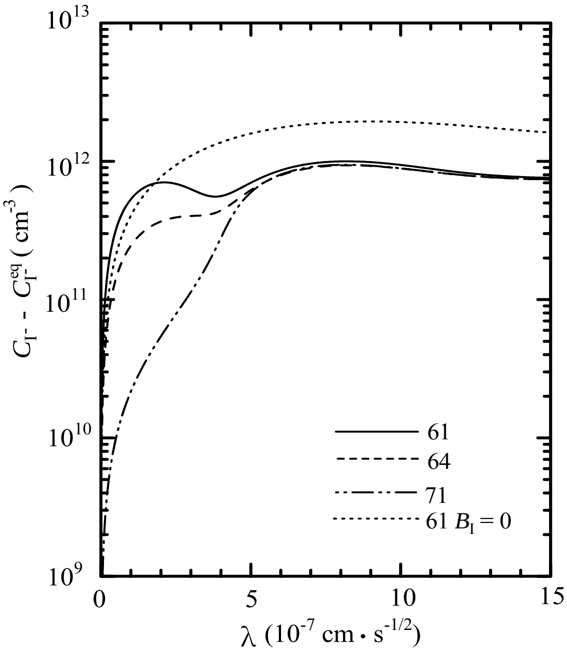

Fig. 6. Concentration of excess I.

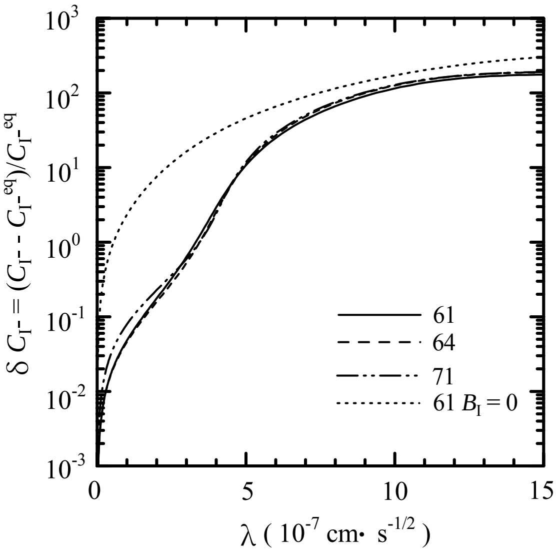

Fig. 7. Relative concentration of excess I.

to the effect of $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$ in models 61 and 64: As listed in Table I, the main fitting parameter of these models is B_{I} or $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$. Near the surface of $\lambda \approx 1 \times 10^{-7}\,\mathrm{cm \cdot s^{-1/2}}$ in Fig. 6, $C_{\mathrm{I}^-} - C^{\mathrm{eq}}_{\mathrm{I}^-}$ of model 61 is similar to that of model 61 $B_{\mathrm{I}} = 0$. In this region, model 61 has $C_{\mathrm{P}+} \approx 3 \times 10^{20}\,\mathrm{cm^{-3}}$. Therefore, $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$ is large, resulting in a high $C^{\mathrm{eq}}_{\mathrm{I}^-}$, δC_{I^-} <0.1 and the formation of the plateau. In model 61 $B_{\mathrm{I}} = 0$, on the other hand, we have $\Delta E^{\mathrm{f}}_{\mathrm{I}^-} = 0$, resulting in a low $C^{\mathrm{eq}}_{\mathrm{I}^-}$, δC_{I^-} >1 and the formation of the rapid fall. In the region of $\lambda \approx 5 \times 10^{-7}\,\mathrm{cm \cdot s^{-1/2}}$ in Fig. 3 of model 61, we have $C_{\mathrm{P}+} < 1 \times 10^{20}\,\mathrm{cm^{-3}}$. Therefore, $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$ is small, resulting in a low $C^{\mathrm{eq}}_{\mathrm{I}^-}$, δC_{I^-} >1 and the formation of the rapid fall. The characteristics of model 64 are similar to those of model 61.

[2] Removal of excess I by recombination with V in model 71: The main fitting parameter is $\varphi_{(\mathrm{PV})}$. By reaction (11), excess I recombines with V and $C_{\mathrm{I}^-} - C^{\mathrm{eq}}_{\mathrm{I}^-}$ decreases, resulting in the decrease in δC_{I^-}. Near the surface of $\lambda \approx 1 \times 10^{-7}\,\mathrm{cm \cdot s^{-1/2}}$ in Fig. 4(c), C_{V^-} is sufficiently high to remove excess I, resulting in a low $C_{\mathrm{I}^-} - C^{\mathrm{eq}}_{\mathrm{I}^-}$, δC_{I^-} <0.1 and the formation of the plateau. In the region of $\lambda \approx 5 \times 10^{-7}\,\mathrm{cm \cdot s^{-1/2}}$, C_{V^-} is low and excess I cannot be removed, resulting in a high $C_{\mathrm{I}^-} - C^{\mathrm{eq}}_{\mathrm{I}^-}$, δC_{I^-} >1 and the formation of the rapid fall.

In the simulation of P diffusion profiles of $C^{\mathrm{s}}_{\mathrm{P}+}$ from 3×10^{20} to $2.5 \times 10^{18}\,\mathrm{cm^{-3}}$ in ref. 9, it was found that excess I should not be controlled for the profiles of $C^{\mathrm{s}}_{\mathrm{P}+} \leq 1 \times 10^{20}\,\mathrm{cm^{-3}}$. Based on this, three models having the main fitting parameters of B_{I} and $\varphi_{(\mathrm{PV})}$ were selected in the present work.

§10. Discussion

In §9, two methods were described for the control of excess I. Investigating which of them really occurs is a difficult problem. As described in §4, the decrease in quasi self-interstitial formation energy, $\Delta E^{\mathrm{f}}_{\mathrm{I}^-}$, should be adopted if the pair diffusion model of the interstitial mechanism is adopted. Therefore, method [1] probably occurs. However, it is difficult to verify this experimentally.

In the simulation of the P diffusion profile of $C^{\mathrm{s}}_{\mathrm{P}+} = 3 \times 10^{20}\,\mathrm{cm^{-3}}$ under oxidation, it was found[8,9] that the $C_{\mathrm{P}+}$ solution of a model of $B_{\mathrm{I}} = 0$ shows retardation at and near the surface and enhancement in the bulk, while that of a model of $B_{\mathrm{I}} \neq 0$ shows enhancement both at and near the surface and in the bulk. It is generally accepted experimentally that the P diffusion is enhanced under oxidation (oxidation-enhanced-diffusion, OED). From a mathematical point of view, OED is a problem of a boundary condition to solve a diffusion equation. If a boundary condition under oxidation is established uniquely not only for the P diffusion but also for the diffusions of I and V, there is a possibility to investigate which of them really occurs.

§11. Comment on Paper of Uematsu

Uematsu [33] obtained the numerical solutions from his diffusion equation for simulation of the P diffusion profile,[7,27] and discussed the numerical solutions on the basis of the effective P diffusion coefficient, which was obtained from his electric circuit. Because his effective P diffusion coefficient cannot be obtained from his diffusion equation, his discussion is not based on his diffusion equation and his numerical solutions. Fortunately he published not only the numerical solution of P concentration but also those of I and V concentrations. Therefore, it was possible to study his numerical solutions on the basis of his diffusion equation. By this study, the same result as that of ref. 9 or the present work was obtained.[36]

§12. Conclusion

P diffuses predominantly by the interstitial mechanism in Si. Assuming that there is a strong binding energy between P and I, therefore, the basic process of P diffusion is the diffusion of (PI).

In the high-P-concentration region, excess I is generated by the dissociation of (PI) and the limiting process of P diffusion depends on whether or not excess I is controlled. That is, [1] if the concentration of excess I decreases relatively to the equilibrium I concentration due to the effect of the decrease in quasi self-interstitial formation energy, or [2] if excess I is removed by the recombination with vacancies, P diffuses fast and the plateau is formed; if not, P diffuses slowly and the rapid fall is formed.

In the tail region, the P concentration is low and the limiting process of P diffusion is the basic process of P diffusion, that is, the diffusion of (PI). Excess I generated in the high-P-concentration region diffuses into the low-P-concentration region, and I is supersaturated there. Therefore, the concentration of (PI) increases, resulting in the fast diffusion of P and the formation of the tail.

Two methods, [1] and [2], were described above for the control of excess I. Investigating which of them really occurs is a problem in the future.

Appendix : Correction of Previously Published Papers of Yoshida and Coworkers

It was described in ref. 9 that "the controlling process of P diffusion is how to control excess I". In this quoted sentence, "control" is used twice and the meaning of the first is different from that of the second. Moreover, "how to control" is not correct. Therefore this sentence was corrected to "the limiting process of P diffusion at high $C_{\mathrm{p}+}$ depends on whether or not excess I is controlled" in §8. Based on this correction, "the controlling process of P diffusion" in the title and other places in refs. 8 and 38 should be corrected to "the limiting process of P diffusion".

In §8, the limiting processes at high and low $C_{\mathrm{p}+}$ were distinguished. In refs. 6 and 7, however, they were not distinguished and it was described that "the diffusion of the impurity atom is limited by that of the E center"[6)] and "a limiting process of the diffusion is the diffusion of vacancy-impurity pairs"[7)] From the point of view of the present work, they should be corrected to "the basic process of diffusion of group V impurities is the diffusion of group V impurity-vacancy pairs".

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