Fraction of Interstitialcy Mechanism in Impurity Diffusion in Silicon

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Diffusions of impurities in silicon under oxidizing ambient have been analysed by developing the Hu's model. General expression of diffusion coefficient, which include both the vacancy and interstitialcy mechanisms, is used. The temperature dependences of a fraction of interstitialcy mechanism for arsenic, phosphorus and boron are obtained from the data of oxidation enhanced diffusion and oxidation induced stacking faults. Diffusion coefficients of impurities via interstitialcy mechanism and via vacancy mechanism are determined, respectively.

1. Introduction

It is well known that the diffusion coefficients of impurities such as boron, phosphorus and arsenic are enhanced under oxidizing ambient, depending upon crystal orientation of surface plain. It is also known that stacking faults grow during thermal oxidation of silicon. The similarity between the phenomenon of oxidation enhanced diffusion(OED) and that of oxidation induced stacking faults(OSF) has been pointed out by Hu. 1) He proposed the model based on the generation of silicon self-interstitials at the Si-SiO2 interface due to the incomplete oxidation of silicon. OED is considered to be attributed to these excess silicon self-interstitials because impurities diffuse via both vacancies and interstitials, i.e., dual mechanism.

In this work, we will try to apply the general equation of the diffusion coefficient in the dual mechanism for arsenic, phosphorus and boron diffusions under oxidizing ambient by developing the Hu's model. From the data of OED and OSF, the temperature dependences of the fraction of interstitialcy mechanism for these impurities are determined. Diffusion coefficients of these impurities via interstitialcy mechanism and via vacancy mechanism are obtained, respectively.

2. Calculation of Silicon Self-Interstitial Concentration

We assume that impurities diffuse via both vacancies and silicon self-interstitials as proposed by Hu.¹⁾ In such case, the flux of impurity can be expressed by the superposition of vacancy and interstitialcy mechanism.²⁾ Thus, the intrinsic diffusion coefficient of impurity, D*, is given by

$$D^* = D_{IV} + D_{II}, \qquad (1)$$

where D_{IV} and D_{II} are the diffusion coefficients of impurity related to vacancy and interstitialcy mechanisms, respectively. Generally, the diffusion coefficient, D, can be written by,³⁾

$$D/D* = (1 - f)C_v/C_v + fC_i/C_i$$
, (2)

where C_v and C_i are the concentrations of wacancy and silicon self-interstitial, respectively, C_{vo} and C_{io} are the concentrations of them at thermal equilibrium and f is given by D_{II}/D^* . We will apply Eq. (2) for the calculation of time dependence of OED.

According to the Hu's model, the generation rate of silicon self-interstitials, R_{gen} , is a fraction θ of the silicon atoms oxidized, that is,

$$R_{gen} = \theta(dx/dt)/v, \qquad (3)$$

where v is the molecular volume of SiO_2 and x is the thickness of SiO_2 . As pointed out by Hu,⁴⁾ the linear relationship between the generation rate of self-interstitials and the oxidation rate cannot explain the experimental results of time dependence of stacking faults. It is necessary to introduce the non-linear relationship to rationalize the experimental results. Taking account of works of Lin et al.⁵⁾ and Tan et al.⁶⁾, we will use the relationship of $(dx/dt)^{0.5}$ in Eq. (3), instead of (dx/dt). Thus, we have

$$R_{gen} = \Theta g(dx/dt)^{0.5}/v , \qquad (4)$$

where g is a complex equilibrium and proportionality constant with a dimension of $(\text{cm}^{0.5}\text{s}^{-0.5})$.

The rate equation for silicon self-interstitials is given by ignoring the diffusion term¹⁾

$$w dC_{i}/dt = \theta_{g}(dx/dt)^{0.5}/v - \pi g_{aD_{i}}(C_{i}-C_{io}), \quad (5)$$

where w is the thickness of wafer, $\boldsymbol{\rho}$ is the surface density of kinks, a is the capture radius of interstitials by kinks and D_i is the diffusion coefficient of silicon self-interstitials.

Equation (5) can be solved numerically. It is confirmed from the numerical calculation that the exact solution of Eq. (5) can be approximated well by the following simple form for t > 0.2 s as

$$C_{i} - C_{io} = \Theta_{g} (dx/dt)^{0.5} / \hbar g a D_{i} v.$$
 (6)

Assuming the parabolic relationship $^{7)}$ of the oxide thickness, the thickness is expressed by

$$x = (2MHPO_2 t/N)^{0.5}$$
, (7)

where M is the diffusion coefficient of oxidizing species in the oxide layer, H is the Henry's law constant, N is the number of oxidant molecules in a unit volume of oxide and PO_2 is the oxygen partial pressure in the gas phase.

Using Eq. (7), Eq. (6) can be written as

$$C_{i} - C_{io} = KPO_{2}^{0.25} t^{-0.25} / 2^{0.5} \pi gaD_{i}v,$$
 (8)

where $K = \varphi_g (2MH/N)^{0.25}$.

The rate of growth of stacking faults is given by

$$dr/dt = \pi a^2 D_i (C_i - C_{io})$$
, (9)

where r is the radius of the stacking faults. By substituting Eq. (8) into Eq. (9) and integrating, we have

$$r = 4aKP0_2^{0.25} t^{0.75}/3 2^{0.5} Pv.$$
 (10)

The value of K can be determined by comparing

Eq. (10) with the experimental data of the length of stacking faults. In this case, experimental data within the temperature region where the retrogrowth effect is negligible should be used since Eq. (9) do not include the effect of retrogrowth of stacking faults. We calculate the value of K from one set of experimental data of 80 min oxidation in 100% dry 0_2 by Murarka.⁸⁾ Thus, we have

$$K = 1.10 \times 10^{-1} \exp(-2.29/kT)$$
 (11)

In these calculations, values of $P = 10^{12} \text{ cm}^{-2}$, a=3.85x10⁻⁸ cm, v=2x10⁻²³ cm³ are taken.¹⁾ We also use the Leroy's estimation for the diffusion coefficient D_i and the equilibrium concentration of interstitials C_i. That is, D_i=2.13exp(-2.0/kT) and C_{io}=4.76x10²⁹ exp(-3.02/kT).⁹⁾ The present value of K is available for the growth of OSF in dry O₂ ambient on (100) silicon. K will generally depend on the orientation of the wafer and oxidizing ambient.

By using Eq. (10) with the now known K, the length of stacking faults can be calculated for different oxidation times and partial pressure of oxygen. An example of thus calculated results of the length of stacking faults is shown in Fig. 1 as a function of reciprocal absolute temperatures.

It is convenient to express C_i and r as an numerical form by substituting Eq. (11) into Eqs. (8) and (10), respectively. We have

$$C_{i}/C_{io} = 1 + 3.2 \times 10^{-10} \exp(2.73/kT) \times PO_{2}^{0.25} t^{-0.25}, \qquad (12)$$

$$r = 200 \exp(-2.29/kT) PO_2^{0.25} t^{0.75} .$$
(13)

Equation (12) has a same expression with that derived by Antoniadis,³⁾ though there is a difference of about factor 2 in the estimation of C_i/C_{io} . Equation (13) has also essentially same dependence of time and partial pressure with Eq. (30) of Ref. 9 except a somewhat different activation energy and the preexponential factor.

3. Time Dependence of OED

We consider the diffusion of impurity under oxidizing ambient in intrinsic conditions in which the concentration of impurity is below the intrinsic carrier concentration at the diffusion temperature.

We assume that the dynamical equilibrium between vacancies and silicon self-interstitials is established.^{3,10,11)} That is,

$$C_{v}C_{i} = C_{v}C_{io} \quad . \tag{14}$$

Using Eq. (14), the diffusion coefficient of Eq. (2) can be written as

$$D/D^* = (1-f)C_{i0}/C_i + fC_i/C_{i0}$$
 (15)

The effective diffusion coefficient in a specified oxidation time $\langle D \rangle$ is given by

$$\langle D \rangle = \frac{1}{t} \int_{0}^{t} Ddt . \qquad (16)$$

By substituting Eqs. (8) and (15) into Eq. (16), $\langle D \rangle$ can be calculated numerically if the diffusion times and temperatures are given.

Values of f for arsenic, phosphorus and boron can be estimated by comparing Eq. (16) with the experimental data of the diffusion coefficient obtained under oxidizing ambient in intrinsic conditions with the known value of K determined in the previous section. Thus, values of f for arsenic phosphorus and boron determined from one set of experimental data for fixed diffusion time obtained by Ishikawa et al.¹²⁾ are plotted in Fig. 2 as a function of the reciprocal absolute temperatures. From the plots in Fig. 2, the temperature dependence of f for arsenic, phosphorus and boron are expressed by, respectively

f_{As}	=2.47exp(-0.184/kT)	,	(17a)
f _P	=12.9exp(-0.330/kT)	,	(17b)
fB	=7.42exp(-0.263/kT)	-13 - 1	(17c)

The contribution of interstitialcy mechanism increases as the temperature increase for all impurities in this work.

Fair¹³⁾ estimated 10-20% fraction of interstitialcy mechanism based on the Hu's model, though the diffusion coefficients were not averaged by diffusion time. Antoniadis³⁾ also obtained the fraction for phosphorus diffusion. His estimation of f at 1100°C is somewhat smaller than that of the present work.

The diffusion coefficients of arsenic, phosphorus and boron can be calculated by using Eq. (16) with values of K and f for different diffusion times. Solid curves in Fig. 3 show the calculations of the diffusion coefficients of phosphorus as a function of diffusion time with the experimental plots obtained by Ishikawa et al.¹²⁾ In this figure, data obtained by Antoniadis et al.¹³⁾ are also shown.

The different time dependence of OED for respective impurities, which has been reported by Ishikawa et al.¹²⁾, originates in the different temperature dependence of f for respective impurities.

4. Diffusion Coefficient of Impurities

Using the values of f with the intrinsic diffusion coefficient D* of arsenic, phosphorus and boron, D_{IV} and D_{II} for respective impurities can be determined. That is, D_{IV} and D_{II} are given by (1-f)D* and fD*, respectively. Figures 4, 5 and 6 show the temperature dependences of D_{IV} , D_{II} and D* for arsenic, phosphorus and boron, respectively. It should be noted that the activation energies of D_{II} for all impurities are almost about 4eV. Recently, Wada¹⁴ and Taniguchi et al.¹⁵⁾ obtained the diffusion coefficient of silicon self-interstitials independently. Their values of the activation energies of diffusion for interstitials are to be 4.4eV and 4.0eV, supporting the present estimation of D_{TT} .

5. Conclusions

General equation of the diffusion coefficient, which includes both vacancy and interstitialcy mechanism, is applied for arsenic, phosphorus and boron diffusions in oxidizing condition by developing the Hu's model. The temperature dependences of a fraction of interstitialcy mechanism for these impurities are obtained from the data of OED and OSF.

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Fig. 1 Temperature dependence of length of stacking faults in 100% oxygen



Fig. 2 Temperature dependence of a fraction of interstitialcy diffusion



Fig. 3 Enhancement of diffusion coefficient of phosphorus as a function of diffusion time



Fig. 4 Temperature dependence of D^* , D_{TV} and \mathbf{D}_{TT} of arsenic



Fig. 5 Temperature dependence of D*, D_{TV} and D_{II} of phosphorus



Fig. 6 Temperature dependence of D*, D_{IV} and D_{II} of boron