Role of point defects in the growth of the oxidation-induced stacking faults in silicon

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(Received 27 April 1977)

A new mechanism, describing the growth of the oxidation-induced stacking faults (OISF) in silicon has been formulated. This mechanism predicts the temperature, time, and oxygen-pressure dependences of the length of the faults in agreement with experimental measurements. The formulation of the mechanism and the derivation of an equation for the length is based on the following assumptions. (a) The growth of the stacking faults at the heterogeneous nucleation sites is analogous to the crystalline growth at the surface kinks. (b) There is an excess of silicon atoms at the SiO_2-Si interface. The concentration of the excess silicon atoms depends on the partial pressure of oxygen during oxidation and on the concentration of the charged vacancies in the adjacent bulk of the silicon. (c) The self-diffusion in silicon occurs by the formation and migration of the charged vacancies. The resultant derivation and comparison with experiment strongly support the new mechanism. (i) The equation describing the length of OISF has been derived to be $L = K'P_{O_2}^m t^n \exp(-Q/kT)$, which is exactly the same as borne out of experimental findings reported earlier. (ii) Values of m and n have been derived and were found to be in good agreement with previously measured values. (iii) Expressions for K' and Q have been obtained. Using these expressions and available data from literature, K' and Q were calculated and were found to be in excellent agreement with experiment. (iv) Two different sets of values of m, K', and Q for lower and higher temperature ranges have been obtained. This is in agreement with experimental observation which clearly indicated existence of two temperature ranges (one $\leq$ 1150°C and the other $\geq$ 1200°C).

I. INTRODUCTION

Thermal oxidation of silicon is a most frequently encountered high-temperature processing step in the fabrication of any device on silicon. Such oxidations have been known[1-15] to produce stacking faults in the silicon near the oxide-silicon interface. The length (L) of these faults (we shall hence forth call them OISF, i.e., oxidation induced stacking fault) in (100) silicon wafers has been found to be dependent on time (t) and temperature T °K of oxidation and has been given as[15]

$$L \propto t^n \exp(-Q/kT), \tag{1}$$

where Q is the activation energy and n is a number exponent. More recently this author[16] has, for the first time, demonstrated that such an expression is incomplete. The complete equation was given as

$$L = K'P_{O_2}^m t^n \exp(-Q/kT), \tag{2}$$

where K' is a constant approximately equal to 3.8×10^8 μm/min$^{0.82}$, P_{O_2} is the partial pressure of oxygen in the oxidizing ambient and m is a number exponent.

There are several other important characteristics of OISF: (a) *Orientation dependence*. The growth rate of the faults is lower (by nearly a factor of 3) in (111) oriented wafers as compared to that in (100) wafers. In addition there appears[17] to be none or very little oxygen partial pressure dependence of the length of faults in (111) wafers. The growth rate is also lower in wafers which are only a few degrees off (100) orientation.[14,18,19] (b) *The temperature dependence* of the length has always been found to be the same irrespective of the orientation[14] or partial pressure of the oxidizing ambient,[16] the activation energy Q being 2.3 eV. (c) *Retrogrowth*. At very high oxidation temperatures,[14] OISFs do not grow, instead they shrink. If the temperature of oxidation is high enough no faults would form. Let us call this temperature, above which no growth occurs, as T_R. T_R varies depending on type of oxidation and the substrate orientation.[14] $T_R \approx 1240$ °C for dry 100% oxygen oxidations and $T_R \approx 1300$ °C for steam oxidation, both for (100) silicon wafers. T_R is lower for (111) and off orientation wafers. (d) In the presence of *chlorine-containing species* (HCl or C_2HCl_3) in oxygen, T_R decreases with increasing HCl or C_2HCl_3 content.[20-23] Thus by use of either HCl or C_2HCl_3 the oxidation of silicon without the formation of OISF has become possible even at temperatures as low as 1000 °C.

Several attempts[16,24-27] have been made to formulate a mechanism to explain the above characteristics of OISF. Although no complete understanding has evolved, the consensus of all these studies has been an agreement on two fronts: (i) During oxidation of silicon the stacking faults are heterogeneously nucleated by coalescence of excess silicon atoms at the nucleation centers which could be impurity contaminants, surface or bulk inhomogeneities as has been shown in several transmission electron microscopic studies of such faults.[25,28] (ii) The growth of the faults during oxidation is related to the presence of an excess of unoxidized

silicon (or of a decreased vacancy concentration) in silicon near the oxide-silicon interface. The proof of the presence of a large excess of silicon atoms in the oxide at the oxide-silicon interface has been obtained by the careful analysis of the interface by use of the ion backscattering technique,[29] ion scattering spectrometry,[30] ESCA (electron spectroscopy for chemical analysis),[31] and x-ray photoelectron spectral analysis.[32] Such a large excess of silicon atoms in the oxide at the interface will lead to an influx of excess silicon atoms (at the interstitial sites) in the silicon lattice near the oxide-silicon interface. On the other hand, by measuring the rate of shrinkage of prismatic dislocation loops in silicon, Sanders and Dobson[13] have shown that the vacancy concentration in silicon at the oxide-silicon interface is lower than that in the equilibrium in the bulk. At 1100 °C, the ratio of vacancy concentration at the SiO_2-Si interface to that in bulk silicon was found to be 0.8. Thus, the two sets of results have been in agreement to each other since excess silicon concentration would mean lower vacancy concentration or vice versa.

The role of point defects in control of the growth of OISF has been emphasized by Hu,[33] Shiraki,[21] Mahajan *et al.*,[25] Murarka,[15,16] and many others. The formation and migration of vacancies or interstitials in silicon have been topics of discussion for almost two decades. There has been a lack of accord even on the simple phenomenon of self-diffusion in silicon. All theoretical predictions, which excel at predicting the formation and migration energies of these defects in germanium, fail to achieve even a reasonable agreement in silicon (see, for example, Hu[34]). In this paper we have invoked a concept of the involvement of the point defects in controlling the formation and growth of the OISF. We have formulated a mechanism which can explain the experimental results with reasonable success and supports the role of charged point defects in controlling diffusion in silicon. In a subsequent paper we shall make use of the concept outlined in this paper to explain other characteristics of the OISFs.

II. MECHANISM OF THE GROWTH OF THE OISF

In suggesting a mechanism of the stacking-fault growth, the time, oxygen partial pressure, and temperature dependences of the length of OISF [Eq. (2)] have been kept mind. The question raised is what is the significance of the experimental values of m, n, and Q as determined for (100) n-type silicon wafers? m was found to be nearly $\frac{1}{3}$, varying from 0.28 at 1050 °C to 0.35 at 1150 °C and 0.5 at 1200 °C. n decreased very slightly with temperature from 0.89 at 1050 °C to 0.76 at 1150 °C, and was found to increase from 0.78 to 0.84 by changing the oxygen content in the oxidizing ambient from 100 to 10% at 1119 °C. The activation energy Q was found to be 2.3 ± 0.05 eV independent of temperature in the range of 1050–1150 °C and of variations in the oxygen partial pressures from 10 to 100%. In the following we shall discuss the three factors n, m, and Q separately.

A. Growth of the faults: time dependence

We consider the growth of the stacking faults at the heterogeneous nucleation centers analogous to the growth of a crystalline phase at the kinks of its surface.[35] It is assumed that a large super saturation of excess silicon atoms (we shall henceforth call them interstitials) exists at the SiO_2-Si interface.[36] Following Kahlweit[37] one can derive an expression

$$V(t) = \tfrac{4}{3}\pi(2\overline{V}D\Delta C_S)^{3/2}t^{3/2} \quad (3)$$

for the volume V of the growing nuclei (in our case stacking fault nuclei). Here ΔC_S is the supersaturation factor giving the number of interstitial atoms per cm^3 present at the interface in excess of their bulk concentration, t is the time of the growth, D is the self-diffusion coefficient of silicon, and $\overline{V}$ is atomic volume of the diffusing species. Freeland *et al.*[26] and Patel *et al.*,[27] have recently used the similar time dependence for the volume of the growing stacking fault nuclei in bulk silicon. The volume of the stacking fault nuclei in silicon near the SiO_2-Si interface can be approximated in a similar fashion to be equal to $\pi r^2 b$, where b is the magnitude of the Burger's vector of the dislocation binding the fault. In that case, one can easily calculate the diameter of the growing fault as

$$d(t) = 2r(t) = [4/(3b)^{1/2}](2\overline{V}D\Delta C_S)^{3/4}t^{3/4}. \quad (4)$$

Now replacing d with the measured length L, we obtain[38]

$$L = [4/(3b)^{1/2}][2\overline{V}D\Delta C_S]^{3/4}t^{3/4}. \quad (5)$$

A value of 0.75 has thus been obtained for n [Eq. (2)].

B. Growth of the faults: oxygen partial pressure dependence

It is arbitrarily assumed that concentration of Si_I, the excess silicon atoms at the Si-SiO_2 interface, increases with increasing partial pressure P_{O_2} of oxygen so that

$$[Si_I] = KP_{O_2}, \quad (6)$$

where K is an appropriate constant of proportionality. In addition to this dependence, the concen-

tration of the excess silicon atoms could be related to the temperature of oxidation and to the orientation of the silicon surface being oxidized. Such dependences could be associated in the constant K, which will then be temperature and orientation dependent (see Sec. IIID). As will be shown, this assumption leads to results in reasonable agreement with experiment.

Consider now the interaction of point defects in the bulk of the silicon. We confine ourselves to the very small volume of material in Si near the SiO_2-Si interface. Any imbalance in the point-defect equilibrium in this volume is of direct concern to us, although such imbalance will affect the defect concentrations in the rest of the silicon in the usual manner, the effect decreasing with increasing distance from the interface.

The creation of interstitials and vacancies can be independently accomplished as

$$Si^0_{(s)} \rightleftharpoons Si^0_I, \quad K_1 = [Si^0_I]/[Si^0_s] \tag{7}$$

and

$$Si_{Si} \rightleftharpoons Si^0_s + V^0_{Si}, \quad K_2 = [Si^0_s][V^0_{Si}], \tag{8}$$

where subscripts s, I, and Si denote surface, interstitial, and silicon lattice positions occupied by the atom or the defect. Superscript 0 indicates a neutral defect. For convenience in the rest of the discussion we will drop the subscript Si for vacancies.

As an alternative, instead of writing two independent equations for interstitials and vacancies, one can write an equation for the combination of the two processes (Frenkel disorder):

$$Si_{(Si)} \rightleftharpoons Si^0_I + V^0, \quad K_3 = K_1K_2 = [Si^0_I][V^0]. \tag{9}$$

From Eqs. (6) and (9), then one can write the equation

$$[V^0_{Si}] = K_3/[Si^0_I] = K_3K^{-1}P^{-1}_{O_2}. \tag{10}$$

Writing of the Eqs. (9) and (10) implies interaction between the vacancies and the interstitials near the SiO_2-Si interface. A decrease in the vacancy concentration in the Si near the SiO_2-Si interface will result in the diffusion of vacancies from the bulk. Thus, such interactions will depend on the diffusion coefficient of these point defects.

Now consider the ionization of the vacancies in an n-type Si:

$$V^0 + B^0 \rightleftharpoons V^- + B^+, \quad [V^-][B^+]/[V^0][B^0] = K_4 \tag{11}$$

and

$$V^- + B^0 \rightleftharpoons V^{2-} + B^+, \quad [V^{2-}][B^+]/[V^-][B^0] = K_5, \tag{12}$$

so that

$$[V^{2-}][B^+]^2/[V^0][B^0]^2 = K_4K_5, \tag{13}$$

where B's denote the donar atoms. K's are the reaction constants. These vacancies have been assumed to act as acceptors. Proposed ionization of defects is not unlikely. Such ionization as described by reactions (11) or (12) or both are likely to occur if the position of the energy levels of these defects and of the Fermi level in the band gap are energetically favorable. Existence of ionized vacancies in silicon have been postulated by several authors. From the low-temperature electron-paramagnetic-resonance studies of electron irradiated silicon, Watkins[39] has demonstrated the existence of three charged state of vacancies namely, V^+, V^-, and V^{2-}. Van Vechten[40] proposed ionized (extended) vacancies to account for the high entropies of self-diffusion in silicon. Shaw[41] has interpreted the results of self-diffusion in silicon in terms of the simultaneous diffusion by a defect mechanism(s) involving V^0, V^+, and V^- vacancies. More recently Fair and Tsai[42] have assumed pairing of V^{2-} and V^- with phosphorous to explain in the results of the phosphorous diffusion in silicon. Further support of the negative charge on vacancies in silicon is provided by Sanders and Dobson[13] who reported higher vacancy concentration in n-type than in p-type silicon implying possible association of negatively charged vacancies with donors in n-type Si.

The final two equations to be considered are the conditions of the charge neutrality and the intrinsic electron-hole equilibrium. Several factors, for example, the nature, type, and the amount of doping of silicon, temperature, and the intrinsic point-defect equilibrium in the bulk of the silicon could influence these conditions. Since the intrinsic electron and hole concentrations are low at the temperatures of interest, the charge neutrality condition can be approximated by

$$[V^-] + 2[V^{2-}] = [B^+]. \tag{14}$$

It may be mentioned that if vacancy concentration is very low or vacancies are considered neutral, the left-hand side of the above equation has to be replaced by the electron concentration.

Which one of V^- and V^{2-} predominates will depend on the magnitudes of the constants K_4 and K_5. Thus we shall have two extreme cases.

Case I: $K_4 \gg K_5$, i.e., $[V^-] \gg [V^{2-}]$, so that

$$[V^-] \approx [B^+], \tag{15}$$

and by substitution in Eq. (14),

$$[V^-]^2 = K_4[V^0][B^0]. \tag{16}$$

Case II: $K_5 \gg K_4$ $[V^{2-}] \gg [V^-]$, so that

$$2[V^{2-}] \approx [B^+], \tag{17}$$

and by substitution in the Eq. (13),

$$[V^{2-}]^3 = \tfrac{1}{4}K_4K_5[V^0][B^0]^2 . \qquad (18)$$

In germanium Kroger,[43] using the data of Morin and Maita[44] and of Tweet,[45] has calculated a slightly larger value for the concentration of singly ionized vacancies compared to that for doubly ionized vacancies (with higher energy of formation for V^{2-} than that for V^-). No similar information is available for vacancies in silicon although Van Vechten[40] has calculated larger enthalpies for V^{2-} than that for V^- in line with the Ge results. We will therefore associate case I with low-temperature cases and case II with high-temperature cases.

It may now be noted that ionization of donors occurs relatively completely even at very low temperatures so that $[B^+]$ is unaffected in any significant manner by variations in partial pressure of oxygen or even in temperature. B^0 is, however, a minority and $[B^0]$ may not be a constant (see discussion). By substituting for $[V^0]$ from Eq. (10), we obtain *case I* for low temperatures

$$[V^-] = C_1P_{O_2}^{-1/2} ; \qquad (19)$$

and *case II* for high temperatures

$$[V^{2-}] = C_2P_{O_2}^{-1/3} , \qquad (20)$$

where various constants have been grouped into C_1 and C_2, such that

$$C_1 = [K_3K_4B^0/K]^{1/2} \qquad (21)$$

and

$$C_2 = [K_3K_4K_5B^{02}/4K]^{1/3} . \qquad (22)$$

In summary, by assuming $[\mathrm{Si}_I^0] \propto P_{O_2}$ we have shown that charged vacancy concentration can be given by Eq. (19) or (20) depending on the charge state chosen for the vacancies.

1. Diffusion coefficient D

Self-diffusion in silicon is assumed to take place by a mechanism in which charged vacancies participate. We shall consider two cases as discussed earlier to obtain Eqs. (19) and (20):

Case I: V^- mainly contributes to diffusion. The diffusion coefficient in that case will be given by

$$D' = j\nu a^2 w_{V^-}[V^-] , \qquad (23)$$

where j, ν, a, and w represent a geometrical factor, vibration frequency, the jump distance, and the migration probability of the jump in a given diffusion direction. By substitition for $[V^-]$ from Eq. (19) we get

$$D' = j\nu a^2 w_{V^-}C_1P_{O_2}^{-1/2} ,$$

and in terms of activation energy

$$D' = D_0' \exp(-Q'/kT)P_{O_2}^{-1/2} , \qquad (24)$$

where

$$D_0' = j\nu a^2(B^0/K)^{1/2} \exp(\Delta S'/k) \qquad (25)$$

and

$$Q' = \tfrac{1}{2}[\Delta H_I + \Delta H_V + \Delta H'] + \Delta H_m' . \qquad (26)$$

Here ΔS includes all ΔS terms similar to ΔH terms. ΔH_I, ΔH_V, $\Delta H'$, and $\Delta H_m'$ are the enthalpies of interstitial formation, vacancy formation, vacancy ionization (V^-), and of migration of V^-, respectively.

Case II: On the other hand if the diffusion is mainly controlled by V^{2-}, we can similarly derive equation

$$D'' = D_0'' \exp(-Q''/kT)P_{O_2}^{-1/3} , \qquad (27)$$

where

$$D_0'' = j\nu a^2[(B^0)^2/4K]^{1/3} \exp(\Delta S''/k) \qquad (28)$$

and

$$Q'' = \tfrac{1}{3}(\Delta H_I + \Delta H_V + \Delta H' + \Delta H'') + \Delta H_m'' , \qquad (29)$$

$\Delta H''$ being the enthalpy of ionization of V^{2-} as described by Eq. (12).

2. Complete equation

The complete equation for the length of the stacking faults near the SiO_2-Si surface can now be obtained by substituting for D and ΔC_{Si} from Eqs. (24) or (27) and (6), respectively.

Case I: Low temperature, V^- controls diffusion:

$$L = \frac{4.2^{3/4}(\bar{V})^{3/4}D_0'^{3/4}K^{3/4}}{\sqrt{3}\,b^{1/2}}\, t^{3/4}P_{O_2}^{3/8} \exp\left(-\frac{Q}{kT}\right), \qquad (30)$$

where $Q = \tfrac{3}{4}Q'$.

Case II: High temperature, V^{-2} controls diffusion:

$$L = \frac{4.2^{3/4}(\bar{V})^{3/4}D_0''^{3/4}K^{3/4}}{\sqrt{3}\,b^{1/2}}\, t^{3/4}P_{O_2}^{1/2} \exp\left(-\frac{Q}{kT}\right), \qquad (31)$$

where $Q = \tfrac{3}{4}Q''$.

III. COMPARISON WITH EXPERIMENTAL RESULTS

We have obtained an expression for the length of the stacking faults, which predicts the time, oxygen partial pressure, and temperature dependence.

A. Time dependence

Consider the time dependence first. Experiments show that $L \propto t^n$, with n varying from 0.76 to 0.89 for dry oxidations and approximately 0.66 for steam oxidations. Both Eqs. (30) and (31) predict $n = 0.75$, which is in reasonable agreement with

experiment. Experimentally n decreases with increasing temperature, whereas our equations predict n independent of temperature or P_{O_2}. It may be noted that this discrepancy could be attributed to the assumption made to write Eq. (6) and use of this relationship to replace ΔC_{Si} in Eq. (5). At the moment we do not have any better knowledge about the concentration of excess silicon atoms as a function of time, temperature, or P_{O_2}. The temperature and P_{O_2} dependence of n could also come from the fact that the stacking faults are growing (into silicon) at SiO_2-Si interface while it advances towards the Si phase. Thus, the experimentally measured length will be affected by the time at which faults were nucleated during oxidation and by the distance from the interface at which they were nucleated.

B. Oxygen pressure dependence

There is a satisfactory agreement between the predictions of Eq. (30) and lower temperature values of m in the equation $L \propto P_{O_2}^m$. Experimentally m varied from 0.28 ± 0.05 at 1050 °C to 0.35 ± 0.02 at 1150 °C. The values may be compared with 0.375 given by Eq. (3J). The slight temperature dependence of m could again be attributed to Eq. (6) as discussed in the Sec. III A.

For 1200 °C we have Eq. (31) predicting $m = 0.5$ exactly the number obtained in experiments. This remarkable agreement of oxygen pressure dependence of the length of OISF lends support to our derivation and predicts a change over from V^- controlled diffusion to V^{2-} controlled diffusion somewhere between the temperatures of 1150 and 1200 °C.

C. Temperature dependence

The temperature dependence of the length of OISFs is reflected to some extent in values of m and n and mainly in the single activation energy of 2.3 ± 0.05 eV.[16] Not much can be said at present about m and n, than what has been discussed in previous paragraphs. Our Eqs. (26) and (29) can be used to obtain Q' and Q'' and hence the Q in Eqs. (30) and (31).

Low-temperature range:

$$Q_{LT} = \tfrac{3}{4}Q' = \tfrac{3}{4}\left[\tfrac{1}{2}(\Delta H_I + \Delta H_V + \Delta H') + \Delta H'_m\right].$$

High-temperature range:

$$Q_{HT} = \tfrac{3}{4}Q'' = \tfrac{3}{4}\left[\tfrac{1}{3}(\Delta H_I + \Delta H_V + \Delta H' + \Delta H'') + \Delta H''_m\right].$$

One can obtain the values of H_I and H_V from several theoretical calculations made by various authors. For interstitials, $\Delta H_I = 1.09$ eV has been obtained by Bennemann.[46] For ΔH_V, we chose an average of the several values compiled by Messmer.[47] Thus $\Delta H_V = 2.57$ eV. Van Vechten[40] has plotted values of $\Delta H'$ and $\Delta H''$ for V^- and V^{2-} as a function of temperature. For our range of temperature $\Delta H' = 0.8$ eV, and $\Delta H'' = 1.3$ eV are obtained from his Fig. 3(a). There are no calculated values of $\Delta H'_m$ and H''_m available except perhaps the migration energy of the vacancies (V^-) in high-temperature transition state calculated by Van Vechten.[48] This number is 1.32 eV. Several calculations for neutral vacancies have been made and an average of these values compiled by Messmer[47] is 0.95 eV. Watkins,[39] from the low-temperature EPR data of irradiated silicon, has concluded that neutral vacancies in p-type silicon have $\Delta H_m = 0.33$ eV, whereas doubly charged negative vacancies in n-type silicon have $\Delta H''_m = 0.18$ eV. The values obtained for ΔH_m by Watkins are very low and very difficult to reconcile with results of self-diffusion in silicon and the calculated values mentioned above. In absence of any resolution between the two sets of data we shall use the value of 1.32 eV as given by Van Vechten[48] for both H'_m and H''_m although one would expect a slightly higher number for the migration energy of V^{2-}.

Using all these numbers, then we obtain

$$Q_{LT} = 2.66 \text{ eV}$$

and

$$Q_{HT} = 2.43 \text{ eV}.$$

These are in reasonable, though not perfect, agreement with the experiment value of $Q = 2.3 \pm 0.05$ eV. It may be pointed out that if one plots $\ln(L/t^n)$ (instead of $\ln L$) vs $1/T$ as done by Murarka and Quintana,[15] experimental values of[15] 2.55 and[16] 2.7 eV have been obtained for Q. These values are in better agreement with those predicted here.

D. Constant term

The last remaining term in the Eqs. (30) and (31) is the constant term which has to be estimated and compared with experimentally determined numbers. The constant is given by

$$C = 4 \times 2^{3/4}(\overline{V})^{3/4}(D^i)^{3/4}K^{3/4}/(3b)^{1/2},$$

where $D_0^i = D_0'$ in the low-temperature case and $D_0^i = D_0''$ in the high-temperature case.

By substituting for $\overline{V} = 2.0 \times 10^{-23}$ cm^3, $b = 1.4 \times 10^{-8}$ cm [magnitude of the Burgers vector $\frac{1}{3}a$ (1,1,1)], and

$$D_0 = j\nu a^2 \exp(\Delta S/K),$$

we obtain

$$C_{LT} = 3.2 \times 10^{-13}[D_0 K^{1/2}(B^0)^{1/2}]^{3/4}$$

and

$$C_{HT} = 3.2 \times 10^{-13}[0.63 D_0 K^{2/3}(B^0)^{2/3}]^{3/4}.$$

Let us assign some values for D_0, K, and B^0. D_0 is preexponential factor for the diffusion coefficient expression $D=D_0 \exp(-Q/kT)$. An average ($D_0=4000$) of the values given by Peart,[49] Ghostagore[50] and Fairfield and Masters[51] is chosen for present calculations and we ignore a possible small difference between ΔS values for V^- and V^{2-}.

K is the proportionality constant between $[\mathrm{Si}_I]$ and P_{O_2} as described by the Eq. (6). To the best of this author's knowledge, no temperature or P_{O_2} dependence of $[\mathrm{Si}_I]$ has been investigated. From the experimental results (a) $L \propto t^n$, (b) $L \propto P_{O_2}^m$, and (c) the phenomenon of retrogrowth it would appear that the concentration of these excess silicon atoms will increase with increasing P_{O_2} and decreasing temperature of oxidation. It has been pointed out by this author[16] that at temperatures above 1150 °C (the retrogrowth range of temperature[14]) the self-diffusion coefficient D becomes comparable to the parabolic rate constant B and in fact above 1240 °C $D > B$. One can interpret this fact in the following manner. As the self-diffusion rate increases, more and more excess silicon atoms diffuse away from the SiO_2-Si interface (or are annihilated by the vacancy flux moving towards the interface). At sufficiently high temperatures, where $D \approx B$ the concentration of excess silicon atoms decreases very sharply with temperature and above ~1240 °C, it is negligible. This picture is consistent with the temperature dependence of the length of OISF and the phenomenon of retrogrowth. The conjecture is also supported by the fact that concentration of the fixed charge (Q_{ss}) at the SiO_2-Si interface has been known[52] to decrease with increasing temperature. Deal[52] strongly supports the idea that Q_{ss} is due to unoxidized excess silicon atoms.

It is therefore assumed that (a) K is nearly constant (although slightly decreasing with temperature) at temperatures in the range of 1050–1150 °C, and (b) K decreases very sharply with temperature above 1150 °C, perhaps being zero above 1240 °C for dry oxidations. We can now calculate K for the low-temperature case. We take an indirect route to obtain K from the results of Raider and Flitsch[32] who have found that the number of excess silicon atoms in a 20-Å layer of oxide at the SiO_2-Si interface is nearly 10^{15} atoms/cm^2. The oxide was grown in a $P_{O_2}=1$ atm. This number would correspond to a concentration of ~5 $\times 10^{21}$ atoms/cm^3 in the small volume near the interface. Assuming a similar excess of interstitials in the silicon at the interface and using these numbers K can be obtained (for the case of $P_{O_2}=1$) as 5×10^{21} cm^{-3}/atm.

Finally, B^0 can be approximated by knowing the doping concentration of the wafers. Usually (at least in our experiments) the resistivity of the substrate varied from 0.5 to 10 Ω cm. We can then take a dopant concentration as 10^{15} cm^{-3}. Almost all of them are ionized. A reasonable assumption will be that ~99.9% of them are ionized having ~0.1% nonionized so that $B^0 \approx 10^{12}$ cm^{-3}.

Plugging these numbers, then one obtains

$$C_{LT}=7.0\times10^2\ \mathrm{cm/sec}^{3/4} \equiv 1.5\times10^8\ \mu\mathrm{m/min}^{3/4},$$

which is in good agreement with the value of 3.8 $\times 10^8$ μm/min$^{0.82}$ obtained for the temperature range of 1050–1150 °C.

On the other hand for high temperatures, K has been assumed to decrease sharply with temperature so that C_{HT} will no longer be a constant and shall approach zero above ~1240 °C. This is consistent with the observation[14] that after the initial growth the length of the stacking faults decreases rather than increases at temperature ≈ 1200 °C or above.

IV. DISCUSSION

One can visualize the role of point defects in the growth of the oxidation induced stacking faults in a very simple manner. Oxidation of silicon results in excess silicon interstitials in silicon near the oxide silicon interface. These interstitials, in their nonequilibrium concentration, cause the growth of the faults. On the other hand these interstitials also cause a decrease in the thermal equilibrium concentration of the vacancies in this small volume of silicon near the SiO_2-Si interface. This will result in a diffusion of vacancies from the rest of the silicon towards the SiO_2-Si interface. Vacancies in effect therefore cause annihilation of that fault. Thus there are two competitive fluxes at the fault, one of the interstitials which causes the growth and the other of vacancies which causes annihilation or retrogrowth. Flux of one with respect to the other determines the growth characteristics of the fault [Eq. (9)]. At lower temperatures interstitials flux at the fault is larger and fault grows with time. At very high temperatures vacancy flux is dominating factors and faults do not grow. At some intermediate temperature there is a growth until the silicon interstitial flux, also limited by the oxide growth at the surface, becomes lower than the vacancy flux. At that point in time retrogrowth occurs and fault starts to shrink. Thus the time at which retrogrowth occurs, would depend on the temperature of oxidation and on the partial pressure of oxygen (which controls the oxide growth rate also) in the oxidizing ambient. One can predict from this discussion that higher the temperature and lower the partial pressure of oxygen, lesser will

TABLE I. Comparison of the calculated and experimental results.

	Temperature range (°C)	K' (μm/min^n)	P_{O_2} exponent m	Time exponent n	Q (eV)	Reference
Calc.	Low temperature	1.8×10^8	0.375	0.75	2.66	Present
	High temperature	a	0.5	0.75	2.43	
Expt.	1050–1150	3.8×10^8	0.28–0.35	0.89–0.76	2.3	16
	1200	a	0.5	b	b	

[a] This term cannot be uniquely calculated since K in Eq. (6) has been assumed to decrease sharply with temperature at higher temperature. This is in accordance with the experimental observation that the length of the fault decreases with temperature at $\gtrsim 1200\,^\circ$C (Ref. 14)—the so called phenomenon of retrogrowth.

[b] These terms cannot be measured becuse of the phenomenon of retrogrowth (decreasing length with temperature).

be the time at which faults start shrinking instead of growing. As pointed out earlier, the concept of the oxidation induced interstitial flux competing with the flux of the thermally generated equilibrium vacancies is very well supported by the fact that the self-diffusion coefficient D of silicon becomes comparable to the parabolic rate constant B and in fact $D > B$ at temperatures above ~1240 °C which is approximately the temperature above which faults would not form during oxidation in oxygen.[14]

In the present model, attempt has been made to incorporate the above concept on a mathematical basis. In Table I, a comparison of the calculated and experimental results has been made. It is apparent from the discussion of the previous subsections and Table I that the Eqs. (30) and (31) make reasonably correct predictions for the temperature, time, and oxygen partial pressure dependence of the length of the OISFs. The equations were derived assuming the stacking fault nuclei as spherical. Stacking faults are not spherical and the volume associated with the fault was therefore taken as $\pi r^2 b$. Justification to the use of spherical volume concept and to the replacement of this volume with $\pi r^2 b$, is difficult to find except perhaps in the following. Nucleation of OISF[25–28,33] has been considered to involve a local collapse of excess interstitials at the strain centers such as precipitates or mechanical damage. These nuclei could be envisioned to be spherical. The growth then can be considered to occur into a platelet due to the diffusion of excess silicon atoms (from a spherical volume of influence surrounding the nucleus). Patel *et al.*[27] have recently proposed a model of the growth of a precipitate and the stacking fault associated with it. They have also considered that the volume ($\frac{4}{3}\pi r^3$) of the precipitate, which is responsible for nucleation and growth of the fault, is directly related to the area of the stacking fault ($4\pi r^2$) since the interstitials generated at the particle are incorporated into the fault. Remarkable success of our model does suggest that something of this type is happening.

The second assumption is the one defined in Eq. (6). It has been also assumed that K is nearly constant (although decreasing very slightly with increasing temperature) in the temperature range of 1050–1150 °C and that at higher temperatures K decreases very sharply with temperature. All experimental evidence, the phenomenon of retrogrowth, P_{O_2}, and time dependencies of the length of OISF strongly support these assumptions. As discussed earlier, several authors[29–32] have reported a large excess of silicon atoms in about 20–30 Å volume near the SiO_2-Si interface. More detailed experimentations using these surface analysis techniques are required to verify the temperature dependence of $[Si_I]$ or K.

Consider the effect of the type and concentration of the dopant on our formulations. As far as a change from n-type to p-type silicon is concerned one may consider replacing Eqs. (11) and (12) by

$$V^0 + A^0 \rightleftharpoons V^+ + A^-$$

and

$$V^+ + A^0 \rightleftharpoons V^{2+} + A^-$$

where A now denotes an acceptor atom. This way the outcome of Eqs. (30) and (31) remain unchanged by replacing B^0 with A^0. State V^+ of the vacancies have been shown to exist by Watkins.[39] Shaw[11] has considered V^+ to contribute in self-diffusion together with V^0 and V^-. No reference of V^{2+} has, however, been made. Thus at least for temperatures $\le 1150\,^\circ$C one can use Eq. (30) simply by substituting A^0 for B^0. Experimentally only n-type silicon was used for the study[16] of the oxygen partial pressure dependence of the length of the faults. Time and temperature dependence of the length was found[15] to be independent of the type of doping.

It would appear from Eqs. (24) and (27) that D is

a function of B^0 (or A^0) and that D should increase with increasing dopant concentration. Self-diffusion in silicon has indeed been reported to be enhanced by increased doping of the silicon.[51] More recently McVay and DuCharme[53] have observed the enhancement of the diffusion of Ge in silicon. D was found to increase with increasing concentration of dopant in silicon and the enhancement factor for identical increase in dopant concentration was larger for n-type silicon than that for p-type silicon. These findings clearly support the predictions of Eqs. (24) and (27). No experiments have yet been carried out to demonstrate this effect of dopant concentration on the length of the stacking fault. According to Eqs. (30) or (31) an order of magnitude change in the value of B^0 (or A^0) will change the constant term by a factor 2.4 and 3.2, respectively.

V. SUMMARY

Thermal oxidation of silicon produces stacking faults in silicon near the oxide-silicon interface. A new mechanism describing the growth of the OISF has been formulated. Growth of the faults at the heterogeneous nucleation centers has been assumed to be analogous to the growth of a crystalline phase at the surface kinks. It was assumed that a supersaturation of the excess silicon atoms, which are produced during incomplete oxidation of silicon, exists at the SiO_2-Si interface. Volume of the fault was calculated on the above basis and the length was given as

$$L = [4/(3b)^{1/2}](2\overline{V}D\Delta C_S)^{3/4}t^{3/4},$$

where b, $\overline{V}$, D, ΔC_S, and t are, respectively, the magnitude of the Burgers vector of the dislocation binding the fault, atomic volume of silicon, self-diffusion coefficient of silicon concentration of excess silicon atoms at the oxide-silicon interface, and the time of oxidation.

Concentration of the excess silicon atoms was assumed to be proportional to the oxygen partial pressure so that

$$\Delta C_S \propto P_{O_2}.$$

A vacancy mechanism, which involves self-diffusion in silicon of singly and doubly charged vacancies, has been considered. It has been then shown that for diffusion controlled by singly ionized vacancies $D \propto P_{O_2}^{-1/2}$, so that

$$L = K'P_{O_2}^{3/8}t^{3/4}\exp(-Q/kT),$$

and for diffusion controlled by doubly ionized vacancies V^{2-}, $D \propto P_{O_2}^{-1/3}$, so that

$$L = K'P_{O_2}^{1/2}t^{3/4}\exp(-Q/kT).$$

These equations have exactly the same form as obtained from the experimental observations, i.e.,

$$L = K'P_{O_2}^{m}t^{n}\exp(-Q/kT).$$

Values of m and n corresponding to V^- and V^{-2} ranges are in reasonable agreement with experimental values for two temperature ranges, one $\leq 1150\,^{\circ}C$ and the other $\geq 1200\,^{\circ}C$ (see Table I). Expressions for K' and Q have been obtained for low- and high-temperature cases. Values of K' and Q, calculated using these expressions and the available data from the literature, are also in good agreement with experimental observations. (Table I).

The mechanism has been discussed in view of the primary assumptions and applicability to all cases of silicon irrespective of the doping and its type.

ACKNOWLEDGMENTS

I would like to sincerely thank H. J. Levinstein, S. Brojdo, K. A. Jackson, and J. R. Patel for valuable discussions of the material in this paper.

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