MODELING FOR COMPUTER SIMULATION ON SILICON OXIDATION

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ABSTRACT -- A new model using dynamic concept to study the oxidation kinetics has been developed. Oxidation of silicon in dry oxygen and steam ambients has been studied in detail. Having been characterized the related dynamic constants, this developed model provides good computer simulation results for low-pressure dry oxygen oxidation and steam oxidation.

1. INTRODUCTION

The linear-parabolic oxidation model developed by Deal and Grove(1) has been widely used for reference in IC manufacturing since 1965. However, there still exist the unknown kinetic problems for silicon oxidations. Computer simulation for silicon oxidations consequently should be empirically modified in some thickness ranges(2).

In this paper, a new model based on a dynamic equilibrium concept to replace the Henry's law assumption has been developed. According to this model, silicon oxidations in dry oxygen and steam ambients have been studied in detail. Meanwhile, the related dynamic constants have been characterized. It is observed that this model provides good computer simulation results for low-pressure dry oxygen oxidation and steam oxidation.

2. DYNAMIC VIEW OF HENRY'S LAW

Consider in a gas-solution (solid or liquid) equilibrium system, Henry's law is assumed that the concentration of a specified vaporous solute in a solution (solid or liquid) is proportional to its partial pressure in gas mixture. However dynamically for a phase equilibrium of gas-solution dissolvation system (Fig.1) or a chemical equilibrium of gas-reactant reaction system, it can be expressed chemically as,

$$\text{gas}\begin{matrix}(H_2O,O_2)\\(H_2O)\end{matrix} + \begin{matrix}\text{solvent(solid or liquid)}\\\text{reactant}(SiO_2)\end{matrix} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{matrix}\text{solution(solid or liquid)}\\\text{product}(\geqslant Si\text{-}OH,H_2\ \ldots\text{etc.})\end{matrix} \cdots\cdots\cdots \begin{matrix}\text{dissolvation}\\\text{chemical reaction}\end{matrix} \text{---------------}(1)$$

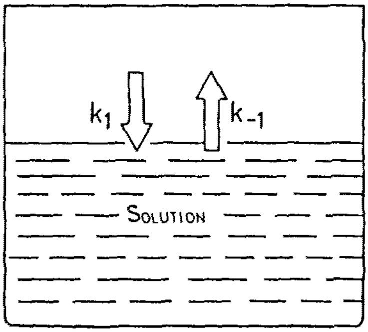

Fig. 1 Schematic representation of dynamic equilibrium in a gas-solution dissolvation system. The solution can be solid or liquid.

where k_1 is the forward dissolution (or forward reaction)rate constant, and k_{-1} is the reverse evolution (or reverse reaction) rate constant. For silicon dry oxygen oxidation, the molecular diffusion of oxygen molecule in oxide layer has been well-concluded(1,3,4). For silicon steam oxidation, both the molecular diffusion and the chemical reaction exist virtually in oxide layer as illustrated in previous investigations(4-6). However, since the molecular diffusion of steam (H_2O) molecule has been thought as the dominant contribution to silicon steam oxidation(4,7), only the dissolvation is interested here. Based on the above considerations, if the dissolvation system is in equilibrium, Eq.(1) implies that

$$H = \frac{k_1}{k_{-1}} = \frac{C^*_{solution}}{p_{gas}} \text{-------------------------------}(2)$$

However, since the silicon oxidation system is not in equilibrium but at a steady state, $k_1$and k_{-1} contribute unequally and should be weighed respectively. The concentration profile of dissolved oxidant species consequently is not kept at a constant value throughout the growing oxide layer. If we assume that only a thin layer on the surface of growing oxide in which Henry's law may be legitimately conducted keeps a constant solubility of oxidant as shown in Fig.2

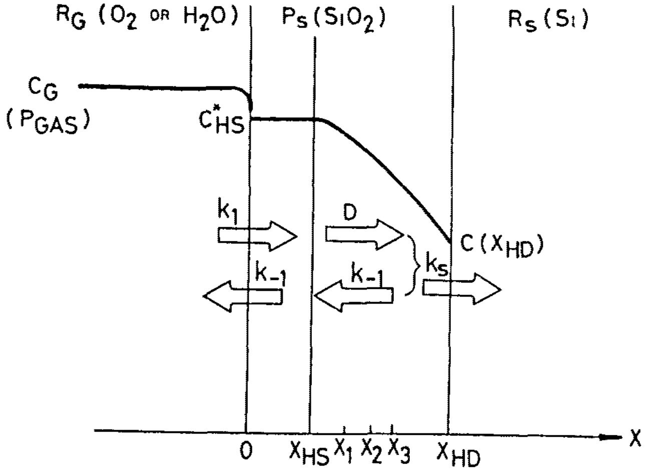

Fig . 2 Schematic representation of reactant transport through static Henry's layer $0<X<X_{HS}$ & dyamic Henry's layer $X_{HS}<X<X_{HD}$.

from $x=0$ to x_{HS}. This thin layer is defined as "static Henry's layer". The other part of growing oxide from $x=x_{HS}$ to x_{HD} in which the oxidant concentration profile varies with the thickness is defined as "dynamic Henry's layer".

3. REACTANT TRANSPORT PHENOMENA AND KINETIC MODELING

As shown in Fig.2 (example as in dry oxygen oxidation), the dissolved oxidant diffuses across the deeper "dynamic Henry's layer" and finally reacts with the substrate Si in the interface region to form the new oxide. The reaction process can be expressed chemically as the following formulas,

$$O_2(g) + Si(s) \xrightarrow{k_1} SiO_2(s) \text{.....initial reaction------(3)}$$

initially, a thin SiO_2 layer thus is formed on Si surface and then the further reactions proceed to occur

$$O_2(g) + SiO_2(s) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2(SiO_2) \text{..dissolvation reaction--}$$
$$\text{--(4)}$$

$$O_2(SiO_2) \xrightarrow{D} O_2(SiO_2 - Si) \text{.....diffusion-------------(5)}$$

$$O_2(SiO_2 - Si) + 2 \geqslant Si - Si \leqslant \xrightarrow{k_s} 2 \geqslant Si - O - Si \leqslant$$
$$\text{.........surface reaction} \text{------------------------------} (6)$$

where k_i is the rate constant of initial reaction, $O_2(SiO_2)$ means the dissolved oxygen molecule in SiO_2 layer, $O_2(SiO_2\text{-}Si)$ means the dissolved oxygen molecule in $SiO_2\text{-}Si$ interface region.

In dissolvation reaction, Eq.(4), the reaction rate R_1 can be expressed by

$$R_1 = k_1 P_{O_2} - k_{-1} C^*_{HS} \text{ ----------------------------------} (7)$$

where P_{O_2} is the partial pressure of oxygen and C^*_{HS} is the saturated concentration or solubility of oxygen in static Henry's layer.

However, in dynamic Henry's layer the oxygen concentration is a function of x. At steady state, based on the chemical potential consideration(8), the evolution flux from the dynamic Henry's layer can be expressed by

$$k_{-1}C^*_{HS} = k_{-1}(x_1)C(x_1) = k_{-1}(x_2)C(x_2) = k_{-1}(x_3)C(x_3) = \dots$$
$$\dots\dots = k_{-1}(x_i)C(x_i) = \dots \equiv k_{-1}(x)C(x) \text{ -------------} (8)$$

where $k_{-1}(x_i)$ is the evolution rate constant at x_i , and $C(x_i)$ is the concentration of oxidant at x_i. If we assume that $k_{-1}(x_i)$ varies negligibly small with position, by taking this 1st order approximation, $k_{-1}(x_i) \approx k_{-1}$, Eq.(7) then becomes

$$R_1 = k_1 P_{O_2} - k_{-1} C(x) \text{ -------------------------------} (9)$$

Next, the diffusion rate R_2 can be expressed by

$$R_2 = \frac{dC(x,t)}{dt} = \frac{\partial C(x,t)}{\partial t} - D\frac{\partial^2 C(x)}{\partial x^2} \text{ ---------------} (10)$$

where C(x,t) is the concentration of oxygen molecules.

For steady state condition, Eq.(10) can be written as

$$R_2 = -D\frac{\partial^2 C(x)}{\partial x^2} \text{ ------------------------------------} (11)$$

Since the dissolution reaction and the diffusion are dynamically equilibrated in oxide layer, i.e., $R_1 = R_2$ and therefore

$$-D\frac{\partial^2 C(x)}{\partial x^2} = k_1 P_{O_2} - k_{-1} C(x) \text{ ----------------------} (12)$$

Assuming that static Henry's layer is negligibly thin, as shown in Fig.3, the boundary conditions at $x=0$ and $x=x_{HD}$ thus are

$$\left.\begin{aligned} C(0) &= C^*_{HS} && \text{at } x=0 \\ C(x) &= C(x_{HD}) && \text{at } x=x_{HD} \end{aligned}\right\} \text{-------------------------} (13)$$

where $C(0)$ denotes the oxidant concentration at $x=0$, and $C(x_{HD})$ is the oxidant concentration at the interface position H_{HD}.

In surface reaction, Eq.(6), the reaction rate R_3 can be written as

$$R_3 = k_s C(x_{HD}) \text{ ------------------------------------} (14)$$

However, since the surface reaction rate is equilibrated with the oxidant flux F from oxide to silicon, the following continuity condition must be satisfied:

$$\left.\begin{aligned} F &= R_3\Big|_{x=x_{HD}} \\ -D\,\frac{\partial C(x)}{\partial x}\Bigg|_{x=x_{HD}} &= k_s C(x_{HD}) \end{aligned}\right\} \text{-------------------------} (15)$$

Consequently, $C(x_{HD})$ can be calculated as

$$C(x_{HD}) = \frac{C^*_{HS}\cosh\frac{x_{HD}}{L}}{\cosh\frac{x_{HD}}{L} + \frac{k_s L}{D}\sinh\frac{x_{HD}}{L}} \text{ -------------------} (16)$$

where $L^2 = \frac{D}{k_{-1}}$ and $C^*_{HS} = \frac{k_1}{k_{-1}} P_{O_2}$, by Eqs.(12),(13) & (15).

Since the surface reaction rate equals $N\frac{dx_{HD}}{dt}$, and then

$$N\frac{dx_{HD}}{dt} = k_s C(x_{HD}) = \frac{k_s C^*_{HS}\cosh\frac{x_{HD}}{L}}{\cosh\frac{x_{HD}}{L} + \frac{LK_s}{D}\sinh\frac{x_{HD}}{L}} \text{ ----------} (17)$$

where N is the concentration of SiO_2 units (or said molecules in stoichiometric chemistry) which equals $2.2\times10^{22}/cm^3$ for dry O_2 oxidation(1).

The growth characteristics, x_{HD}-t curves, can be easily calculated by integrating Eq.(17) as

$$\left.\begin{aligned} & x_{HD} + \frac{L^2k_s}{D}\ln(\cosh\frac{x_{HD}}{L}) = k_s\frac{C^*_{HS}}{N}t \\ \text{or}\quad & x_{HD} + A\ln(\cosh Bx_{HD}) = Ct \end{aligned}\right\} \text{------------------(18)}$$

$$\text{where } A = \frac{L^2k_s}{D}\ ,\ B = \frac{1}{L}\ ,\ C = k_s\frac{C^*_{HS}}{N} = \frac{k_sk_1}{Nk_{-1}}P_{O_2} \quad \text{----------(19)}$$

Equation (18) gives a generalized delineation of silicon oxidations. The kinetic rate constants, k_1 , k_{-1} & k_s , can be obtained based on Eq.(18) if the experimental x_{HD}-t growth characteristics are developed and the literature D value is available.

In case that L is negligibly small in value and if the growing thickness $x_{HD} >> L$, the growth characteristic (Eq.(18)) becomes

$$x_{HD} + \frac{k_s}{k_{-1}}\left[x_{HD}\left(\frac{k_{-1}}{D}\right)^{1/2} - \ln 2\right] = k_s\,\frac{C^*_{HS}}{N}\,t \quad \text{------------(20)}$$

due to the fact $\frac{x_{HD}}{L} >> 1$. The x_{HD}-t growth characteristics exhibit a linear rate law with its slope equal to $(k_sC^*_{HS})/(N(1+k_s/D))$. That is, if C^*_{HS}/N is negligibly small, the reaction will be spontaneously terminated when the grown layer is thick enough that x_{HD}/L is far large compared to 1. However, if C^*_{HS}/N is not negligible, the reaction will continue linearly forever until the silicon substrate is fully reacted.

In case that L is very large in value and if the growing thickness is very thin that $x_{HD} << L$, then according to Taylor's expansion, Eq.(18) can be written as

$$x_{HD} + \frac{L^2k_s}{D}\ln\left(1 + \frac{1}{2}\frac{x^2_{HD}}{L^2} + \frac{1}{4!}\frac{x^4_{HD}}{L^4} + \frac{1}{6!}\frac{x^6_{HD}}{L^6} + \ldots\right)$$

$$= k_s \cdot \frac{C^*_{HS}}{N} \cdot t \quad \text{---------------------------------------(21)}$$

If $\frac{x_{HD}}{L}$ is so small that the higher power terms in Eq.(21) can be neglected, we have

$$x^2_{HD} + \frac{2D}{k_s}x_{HD} = \frac{2DC^*_{HS}}{N} \cdot t \quad \text{---------------------------(22)}$$

If the static Henry's layer thickness, x_{HS} , is considered as onset of occurring diffusion reaction as shown in

Fig.2, then Eq.(23) becomes

$$x_{HD}^{2} + \frac{2D}{k_s} x_{HD} = \frac{2DC_{HS}^{*}}{N}(t+\tau) \text{ ------------------------- } (23)$$

$$\text{where } \tau = \frac{N(x_{HS}^{2} + \frac{2D}{k_s} x_{HS})}{2DC_{HS}^{*}}$$

this formula is identically equal to that derived by Deal & Grove(1).

However, when the growing layer becomes thicker that x_{HD}/L is very large compared with 1, the growth characteristics also will be close to that described in Eq.(20).

On the other hand, when the growing layer thickness x_{HD} is so thick that $(x_{HD}/L)^4$, $(x_{HD}/L)^6$ terms in Eq.(21) can not be neglected and Eq.(21) then becomes

$$x_{HD} + \frac{k_s}{2D} x_{HD}^{2} + \frac{1}{24} \frac{k_s k_{-1}}{D^2} x_{HD}^{4} + \frac{k_s}{144} \frac{k_{-1}^{2} x_{HD}^{6}}{D^3} = k_s \frac{C_{HS}^{*}}{N} t \text{ ----} (24)$$

i.e., a higher power of $x_{HD}^{n} \propto t$ with $n>2$ could be observed.

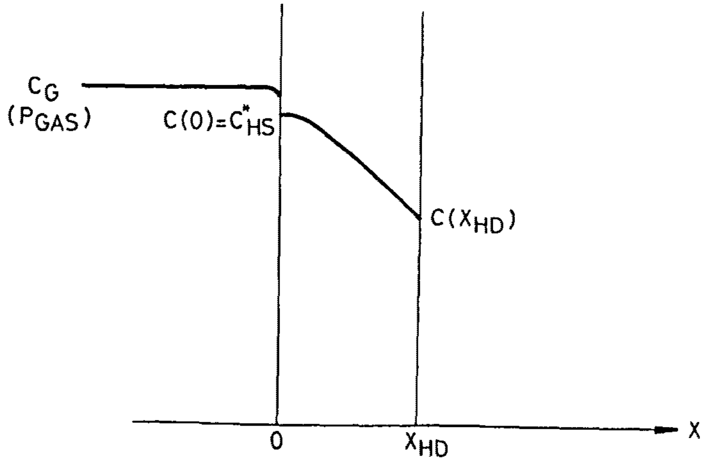

Fig. 3 Simplified growth kinetic diagram of solid silicon surface reaction.

In order to provide a clearer delineation of the relations between the kinetic constants and the x_{HD}-t growth characteristics, Table 1 is summarized. Also, Fig.4, shows the variations of x_{HD}-t characteristics schematically for a given silicon oxidation.

TABLE 1

Summary of silicon oxidation growth characteristics

CONDITION	$\frac{X_{HD}}{L}$	RATE LAW
NEGLIGIBLY SMALL L	DETECTABLE X_{HD} VALUE	LINEAR, $\frac{dX_{HD}}{dt} = \frac{k_s C^*_{HS}}{N(1+\frac{Lk_s}{D})}$
LARGE L	0 ↓ INCREASING $\frac{X_{HD}}{L}$	LINEAR, $\frac{dX_{HD}}{dt} = \frac{k_s C^*_{HS}}{N}$ ↓ PARABOLIC ↓ QUARTIC ↓ HEXATIC ↓ ⋮ ↓ LINEAR, $\frac{dX_{HD}}{dt} = \frac{k_s C^*_{HS}}{N(1+\frac{Lk_s}{D})}$

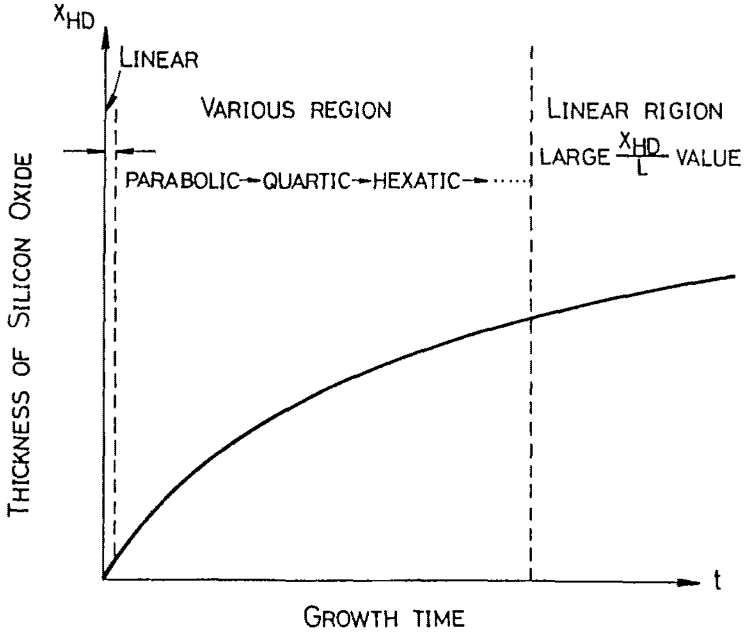

Fig. 4 Schematic representation of the growth characteristic of silicon oxidation.

4. EXPERIMENT

Silicon wafers with 4-7 Ω cm resistivity and (100) orientation were used in this investigation. The wafers had been well-cleanned by using standard acid/H_2O_2 chemical process before oxidation. Steam generated from a H_2/O_2 pyrogenic system was used for steam oxidation. Nitrogen gas was used to dilute the oxidant gas(steam or dry oxygen) with a suitable ratio to simulate the expected low-pressure condition.

5. NUMERICAL ANALYSES, EXPERIMENTAL COMPARISONS, AND COMPUTER SIMULATION

The numerical and experimental comparison of silicon oxidation at elevated temperatures both in steam and dry O_2 ambients are shown in Figs.5 & 6, and Tables 2 & 3. By referring to the literature D values(3,5,6) and utilizing Eq.(19)

for the case of 1000°C oxidation, the dynamic constants k_s, k_1, k_{-1}, and the solubility C_{HS}^* thus can be calculated as shown in Table 4 from fitting data in these two figures.

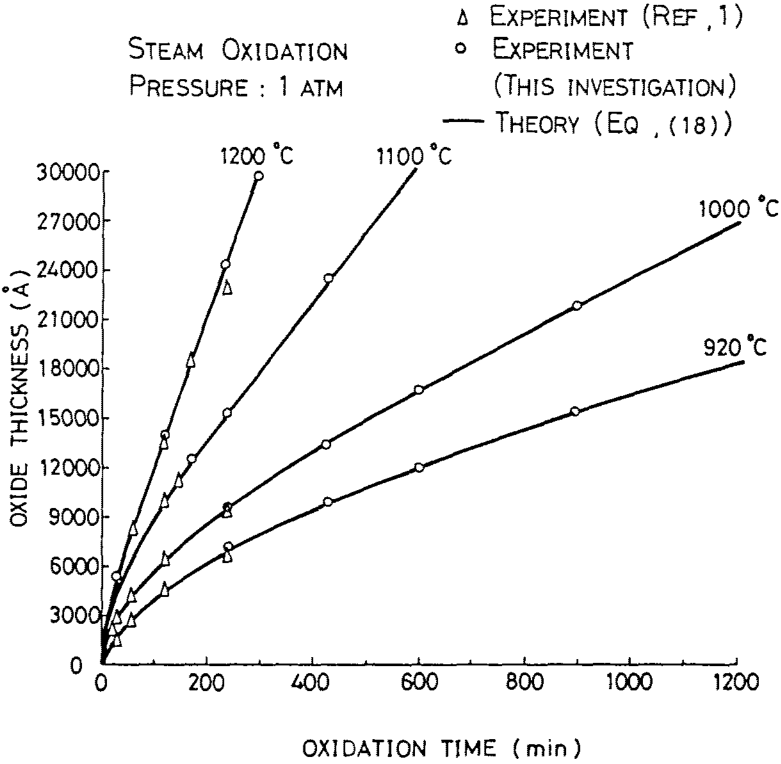

Fig. 5 Comparisons between the experiments and this developed theory , Eq . (18) , of Si steam thermal oxidation at the temperatures from 920 °C to 1200 °C .

Table 2

Growth Parameters of Steam Thermal Oxidation at Elevated Temperatures

TEMPERATURE PARAMETER	920 °C	1000 °C	1100 °C	1200 °C
A (Å)	2.0×10^5	1.6×10^5	1.37×10^5	8.94×10^4
B ($Å^{-1}$)	4.9×10^{-5}	8.1×10^{-5}	1.18×10^{-4}	2.24×10^{-4}
C ($Å\,min^{-1}$)	75	220	710	1890

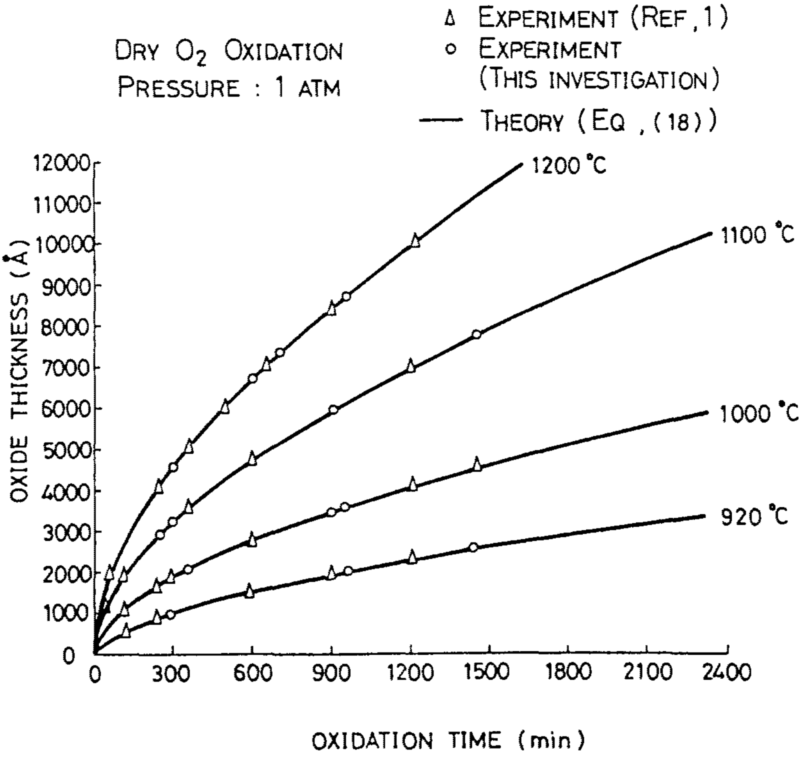

Fig.6 Comparisons between the experiments and this developed theory, Eq. (18), of Si dry oxygen thermal oxidation at the temperatures from 920°C to 1200°C.

Table 3

Growth Parameters of Dry Oxygen Thermal Oxidation at Elevated Temperature

TEMPERATURE PARAMETER	920 °C	1000 °C	1100 °C	1200 °C
A (Å)	2.5×10^{5}	2.6×10^{5}	2.65×10^{5}	2.68×10^{5}
B ($Å^{-1}$)	9.1×10^{-5}	1.05×10^{-4}	1.07×10^{-4}	1.09×10^{-4}
C ($Å\,min^{-1}$)	6.6	22.5	59	120

For a given chemical reaction, a related kinetic constant should be only a function of temperature based on the chemical kinetics theory(8), i.e., this kinetic constant will not be a function of partial pressure of reactant.

However, in using the linear-parabolic law, van der Meulen(11) reported an explicit dependence of linear rate constant on O_2 partial pressure in silicon dry O_2 oxidation. This may be due to the problem of delicacy in choosing a slope for determining the rate constant as described in previous chapters.

In order to study the suitability of the generalized model developed in this investigation, the pressure dependence of x_{HD}-t characteristics for 1000°C oxidations both in steam and dry O_2 ambients is analyzed.

According to the parameters in Eq.(18), it is clearly seen that only C relates to a partial pressure dependence factor C^*_{HS}, as illustrated in Eq.(19). Therefore, if the reaction temperature is kept at constant (example as at 1000°C), then by starting from the C value obtained in the case of atmospheric pressure, the x_{HD}-t growth characteristics of lower pressure and higher pressure can be predicted. The results are shown in Figs.7 & 8 for lower pressure cases, and Figs.9 & 10 for higher pressure cases. Some experimental results are compared. It is observed that the comparison results are quite excellent for the cases of partial pressure lower than 1 atm. The discrepancy in high pressure cases may be attributed to the polymerization phenomenon, especially for steam molecule due to the hydrogen bonding(9) pheomenon in H_2O molecules.

Table 4

Dynamic Constants of Si Oxidations and C^*_{HS} Solubility of Oxidant in SiO_2 at 1000 °C

		k_S Å/MIN	k_{-1} MIN^{-1}	MOLECULES	C^*_{HS} CM^{-3}		
				k_1 MIN, CM^3, ATM	THIS WORK	OTER WORKS	
H_2O	D=1.4 x 10^8 Å^2/ MIN	1.47 x 10^5	0.92	3.0 x 10^{19}	3.3 x 10^{19}	3.0 x 10^{19}	3.4 x 10^{19} INFRARED
O_2	D=3.6 x 10^9 Å^2/MIN	7.0 x 10^6	36	1.9 x 10^{18}	5.1 x 10^{16}	5.2 x 10^{16}	5.5 x 10^{16} PERMEATION
	D=1.38 x 10^5 Å^2/ MIN	3.96 x 10^2	1.52 x 10^{-3}	1.94 x 10^{18}	1.28 x 10^{21}	1.2 x 10^{21} LAG - TIME	

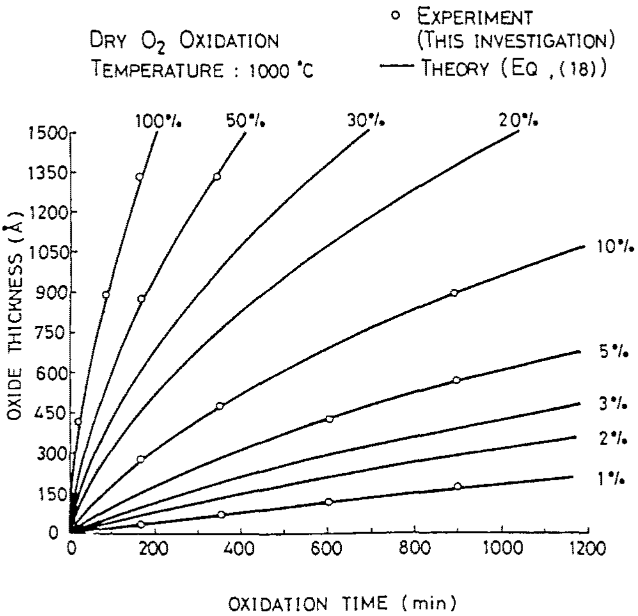

Fig.7 Computer simulation and experimental comparison of low pressure dry oxgyen silicon oxidation at 1000 °C —— The partial pressure of oxygen varies from 0.01 atm to 1 atm.

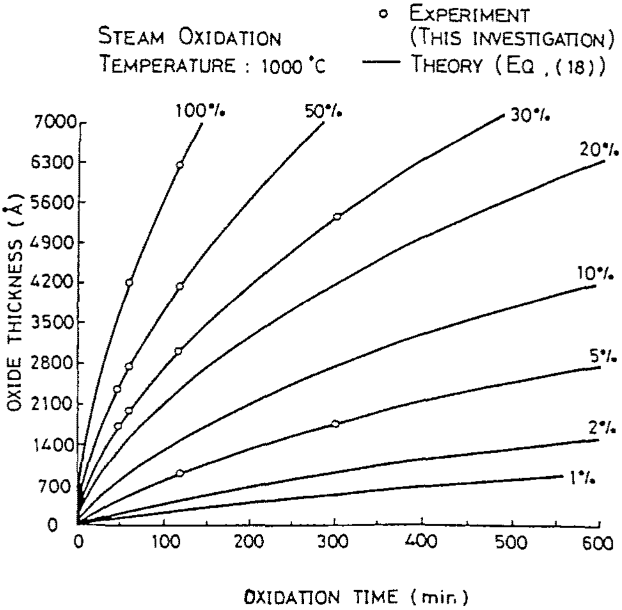

Fig.8 Computer simulation and experimental comparison of low pressure of steam silicon oxidation at 1000 °C —— The pressure of steam varies from 0.01 atm to 1 atm.

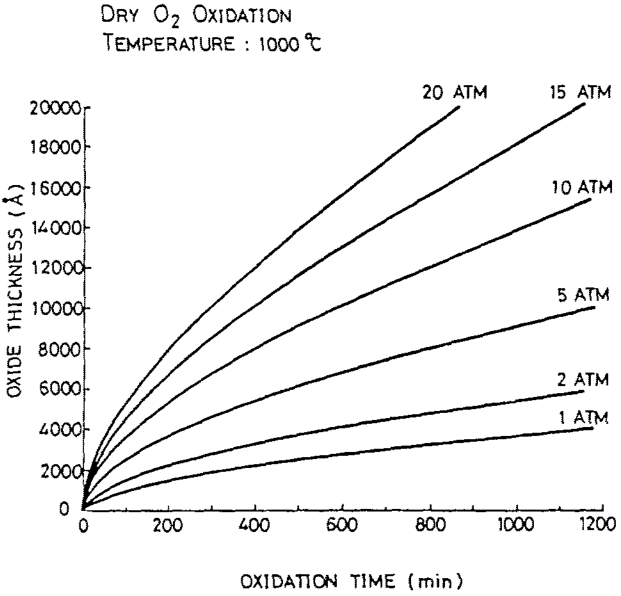

Fig. 9 Computer simulation of high pressure dry oxygen silicon at 1000 °C — The pressure of oxygen varies from 1 atm to 20 atm.

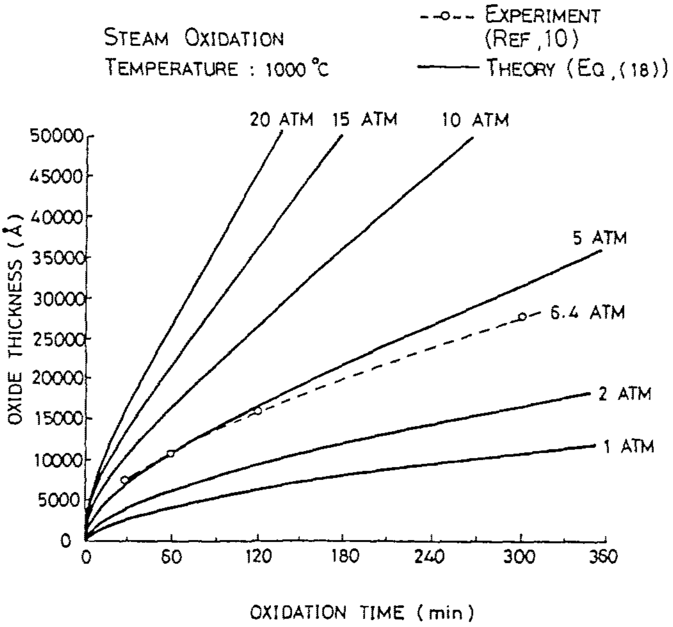

Fig. 10 Computer simulation and experimental comparison of high pressure steam silicon oxidation at 1000 °C —— The pressure of steam varies from 1 atm to 20 atm.

6. CONCLUSION:

A dynamic concept, concerning that the forward dissolution reaction and the reverse evolution reaction are not in equilibrium during silicon oxidation, is used to modify the Henry's law in delineating the kinetic picture of silicon oxidation. A new model has been developed and discussed in detail.

Silicon oxidations both in steam and dry oxygen ambients were characterized numerically and compared experimentally. The related kinetic constants thus were obtained. The made computer simulation for low-pressure silicon oxidations both in dry oxygen and steam ambients exhibits an excellent agreement with experimental results. The discrepancy in high pressure cases may be attributed to the polymerization phenomenon due to the intermolecular interactions(e.g.,hydrogen bondings of H_2O molecules).

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