PHYSICAL REVIEW B VOLUME 51, NUMBER 7 15 FEBRUARY 1995-I

# Generalized diffusion-reaction model for the low-field charge-buildup instability at the Si-$SiO_2$ interface

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(Received 16 May 1994)

We present a unified phenomenological model of the low-field charge-buildup phenomenon at ultrathin $SiO_2$-Si interfaces during negative-bias stresses at elevated temperatures and compare it with experiments. Based on the microscopic understanding of interfacial charges and neutral defects as trivalent silicon and its hydrogen compounds, the dissociation chemistry of hydrogen-passivated dangling silicon bonds is extensively studied by generalizing the diffusion-reaction concept to include charged as well as neutral diffusing species. The mathematical scheme consists of a detailed-balance equation for the first- or second-order chemical reaction and a diffusion equation for the charged or neutral reaction by-product whose interfacial concentration determines the reaction rate at the interface. This generalized diffusion-reaction concept is shown to provide a plausible explanation for the various dependencies of the phenomenon. The general solution of these coupled equations is characterized by its fractional-power time dependence, $\sim t^{1/4}$ for example, and the corresponding exponential dependence on the activation energy over temperature, which comes from the temperature dependence of the diffusion coefficient. For the neutral diffusing species, this scheme provides no first-principles-based information on the oxide field ($E_{ox}$) dependence. Thus the experimentally observed field dependence, such as $\sim E_{ox}^{3/2}$, can be ascribed to the nature of the fundamental electrochemical reaction at the interface. On the other hand, for charged diffusing species, this scheme provides $E_{ox}^{1}t^{1/2}$ dependence. Comparison of these mathematical predictions with experimental data leads us to conclude that the low-field charge-buildup instability of the ultrathin $SiO_2$-Si interface under negative-bias temperature stresses is successfully explained by our generalized diffusion-reaction model of neutral-diffusing (atomic or molecular) hydrogen with the boundary condition of an absorbing wall at the gate-electrode interface.

## I. INTRODUCTION

The degradation of the Si-$SiO_2$ interface affects the reliability of metal-oxide-semiconductor (MOS) devices. This degradation is observed mainly after carrier injection into $SiO_2$ caused by irradiation,[1,2] Fowler-Nordheim electron tunneling,[3-5] or the hot-carrier effect in short-channel metal-oxide-semiconductor field-effect transistors[6,7] and is marked by the appearance of positive fixed oxide charges and interface traps at the Si-$SiO_2$ interface. Considerable progress has been made in understanding the mechanism responsible for their generation with the introduction of the concept of hot-carrier-induced degradation.[8-12]

This fundamental concept has prompted many experimental[13-16] and theoretical[17,18] studies on electron heating in Si and subsequent electron injection into $SiO_2$ and reheating in $SiO_2$ from the standpoint of high-field transport and related fundamental processes, such as impact ionization in Si (Refs. 19 and 20) or $SiO_2$ (Ref. 21) and surface-plasmon intervention electron-hole pair creation.[22] However, this valuable concept cannot be applied to the problem of low-field charge-buildup phenomena at the Si-$SiO_2$ interface.[23-30] The distinction between high and low fields in MOS systems is conventionally drawn at about the oxide field of $6\times10^6$ V/cm for $SiO_2$.[31] At fields in the range of $(6-12)\times10^6$ V/cm, Fowler-Nordheim electron tunneling through the gate oxide of the MOS structure is observable.[31] By low fields, we mean fields whose strengths are less than 6 MV/cm where carrier injection is suppressed and subsequently no direct observable current flows through the oxide.

This low-field instability is similarly characterized by the creation of interface traps and concurrent fixed oxide charges at the Si-$SiO_2$ interface,[23-30] except their generation becomes observable only after long-term (usually a few hours or more) stresses at elevated temperatures with constant low negative gate voltages[23-26,30] or positive ones.[27-29] Although the amount of generated interface traps and fixed oxide charges are strongly dependent on fabrication processes such as oxidation and/or annealing,[24,28] this charge-buildup phenomenon is reported to be universal,[23] irrespective of the gate materials, such as Al or polycrystalline silicon, for all wet,[23,24,28,29] dry,[23-28,30] or pyrogenic[28] oxide layers of the Si-$SiO_2$ systems. It has also been reported that the stress under negative gate fields leads to higher generation of oxide charges and interface traps than that under positive gate fields.[27-29] In addition to this field-direction-induced asymmetry, the instability has a fractional power-law dependence on time. The value of the exponent is most likely $\frac{1}{4}$ (Refs. 26 and 28) or less.[24,27-29] Therefore, this long-term, low-field charge-buildup instability is of serious technological concern and has been studied as the

0163-1829/95/51(7)/4218(13)/$06.00

problem of negative-bias temperature (BT) instability of silicon-based electron devices for a long time.

On the other hand, recent extensive studies using physical,[32] electrical,[33] and theoretical methods[34–37] have considerably advanced our understanding of the microscopic nature of interface traps and fixed oxide charges at the Si-$SiO_2$ interface. The generally accepted model of the interface trap is a trivalently bonded silicon atom with an unpaired electron.[38] Interface traps are passivated when they react with hydrogen. This annealing is done at the end of the device-fabrication process by heating the silicon wafers in a hydrogen ambient.

From this microscopic understanding of the interface defects, the low-field instability is considered to be closely related to the dissociation chemistry (the reverse of passivation[39]) of hydrogen from hydrogen-passivated dangling Si bonds. However, the above-mentioned $t^{1/4}$-like time evolution implies this chemistry is not determined by the first- or second-order kinetics only.[40] From this, it can be concluded that the generation rate of these defects is strongly related to the rate at which the released hydrogen is consumed through diffusion into the $SiO_2$. This diffusion-reaction concept was originally proposed by Jeppson and Svensson[26,41] to explain the negative BT instability for a simple and ideal case where the assumptions make the mathematics easy.

In this paper, we have generalized this concept from an axiomatic approach to include the charged diffusing species as well as neutral diffusing ones and have constructed a general mathematical scheme to understand the low-field instability. Through an extensive mathematical analysis of this phenomenological model, including short-term and long-term asymptotic behaviors, compared with the experimental results published in the literature, we have obtained detailed information of this instability.

Support for this phenomenological model comes also from the fact that it provides plausible explanations of various experimentally observed dependencies. Especially, its validity is strongly supported by the oxide thickness dependence of the charge buildup observed in ultrathin $SiO_2$-Si interfaces during negative-bias temperature stress whose experimental details will be soon published elsewhere.[42]

This paper is organized as follows. In the next section, the phenomenological modeling with related equations is presented. These equations are solved in Secs. III and IV for two different boundary conditions. One is suitable for thick gate oxides, the other is for ultrathin ones. After briefly discussing the validity of the boundary condition at the gate-electrode-oxide interface in Sec. V, we compare the derived results with experimentally obtained empirical equations in Sec. VI. Section VII concludes this paper.

## II. A GENERALIZED DIFFUSION-REACTION MODEL FOR THE GENERATION OF INTERFACE TRAPS AND FIXED OXIDE CHARGES

In this section, we will present a comprehensive and complete description of the equations and boundary conditions used to evaluate the increase of the interface traps and the corresponding fixed oxide charges at the Si-$SiO_2$ interface during low-field stress at elevated temperatures.

The original diffusion-reaction model proposed by Jeppson and Svensson[26,41] is based on a detailed microscopic structural model of Si-$SiO_2$ interface defects including the trivalent silicon and its hydrogen compounds. However, we will attack this instability problem from a more axiomatic and abstract approach. As a result, the general conclusion drawn from this model is not at all dependent on the details of chemical reactions occurring at the interface. We will concentrate only on the mathematical scheme of the model and its deductive resultants.

In the following, we will first review the diffusion-reaction concept briefly, then we will generalize the concept by considering two points: (1) the charging state of diffusing species, and (2) the importance of the consuming process of the diffusing species at the gate-electrode-oxide interface, which provides the boundary condition at the interface.

In the Svensson model,[41] an interface trap is identified as an interfacial trivalent silicon atom with an unsaturated electron (a dangling bond, represented below by a dot) at the Si-$SiO_2$ interface. The expression $Si_3\equiv Si^{\cdot}$ denotes an active interface trap. A positive fixed oxide charge ($Qf^{+}$) is also created as a by-product trivalent silicon defect in the oxide, i.e., $O_3\equiv Si^{+}$. At the actual interface, there exists a large number of hydrogen-terminated trivalent Si bonds, $Si_3\equiv Si$—H, which are electrically inactive in this form. However, when the terminated hydrogen is released from the $Si_3\equiv Si$—H bond by some controversial dissociation mechanism, which is not discussed here in detail, the remaining interface trivalent silicon dangling bond acts as an interface trap.

As mentioned in the preceding section, the essence of the diffusion-reaction model is that the rate at which the reaction causing the generation of interface traps takes place is controlled by the diffusion of hydrogen that has been released from hydrogen-passivated defect sites previously. As a result, we would theoretically expect the fractional-power law of interface-trap generation as observed in many experimental studies.[25–29]

Although there is no doubt of the relevance of this hydrogen-depassivation reaction, i.e., $Si_3\equiv Si\text{—H} \rightarrow Si_3\equiv Si^{\cdot}+H$, for example, to the charge buildup, there still remains some controversy and debate about the chemical species involved in this dissociation reaction.[26,30,39–41,43–53] As possible diffusing species, interstitial atomic hydrogen,[40,41,43–47] molecular hydrogen,[39,48] and the hydroxyl (OH) group[26,41] including the hydronium ($H_3O^{+}$) (Refs. 30 and 53) and the hydroxide ($OH^{-}$) ions have been proposed. Each of these is strongly dependent on details of the assumed dissociation process. For example, interstitial atomic hydrogen is proposed as the species in accordance with the atomic hydrogen attack model: $Si_3\equiv Si\text{—H}+H \rightarrow Si_3\equiv Si+H_2$.[40,41,43–47] Furthermore, recently the involvement of ionic hydrogen transport in the reaction has also been proposed.[49–52]

Therefore, we have to generalize the original diffusion-reaction concept to include the charged diffusing species as well as the neutral-diffusing ones, and have to ignore details of the dissociation reaction. We should, however, stress here that any of these depassivation reactions may occur under the low-field stress (less than 6 MV/cm) because the activation energy required to break an Si—H bond is estimated to be about 0.3 eV.[43]

Consider a surface where $x=0$, as is schematically shown in Fig. 1, at which an interface trap generating chemical reaction takes place. Since the diffusing state of released hydrogen, (i.e., whether it is atomic or molecular, or ionic or neutral) has not been identified yet, we denote it by the symbol $X$. It is schematically expressed as

$$\begin{aligned}(\text{interface defects}) \leftrightarrow (\text{fixed oxide charge})^{+} & \\ &+(\text{interface trap}) \\ &+X_{\text{interface}} \\ &+e^{-}(\text{to the silicon})\ ,\end{aligned}$$

and

$$X_{\text{interface}} \overset{\text{diffusion}}{\leftrightarrow} X_{\text{bulk}}\ .$$

When the interface defect ($\mathrm{Si_3{\equiv}Si{-}H}$) is electrically activated, the diffusing species leaves a defect site at the Si-SiO$_2$ interface where an interface trap and a positive fixed oxide charge are left. This model agrees with observations that equal numbers of interface traps and fixed oxide charges are produced. Furthermore, this process is field dependent since a transfer of charge takes place.

The rate of interface-trap generation may then be expressed by the detailed-balance equation

$$\frac{\partial N_{\text{it}}(t)}{\partial t}=G\{N_D-N_{\text{it}}(t)\}-S[N_{\text{it}}(t)]^{1/a}[C_{Xi}(t)]^{1/b}\ , \tag{1}$$

where $N_{\text{it}}(t)=[\mathrm{Si_3{\equiv}Si^{\bullet}}]$ is the concentration of the interface traps, $N_D=[\mathrm{Si_3{\equiv}Si{-}H}]$ is the initial concentration of interface defects, $C_{Xi}(t)$ is the concentration of diffusing species $X$ at the interface, $G$ and $S$ are field-dependent rate constants, and the exponents $a$ and $b$ are related to the reaction coefficients, which are determined by the details of the reaction. Here, [ ] indicates the concentration. The first term on the right-hand side of Eq. (1) comes from the dissociation of $\mathrm{Si_3{\equiv}Si{-}H}$ into $\mathrm{Si_3{\equiv}Si^{\bullet}}$, and the second term comes from the competing passivation of $\mathrm{Si_3{\equiv}Si^{\bullet}}$ by released hydrogen-related species, which has a suppressing effect. If this process is diffusion-limited rather than reaction-rate limited, the interface reaction will be in quasiequilibrium, i.e., $\partial N_{\text{it}}(t)/\partial t=0$, giving

$$[N_{\text{it}}(t)]^{1/a}[C_{Xi}(t)]^{1/b}\approx(G/S)N_D\ . \tag{2}$$

Here $N_D$ may be considered constant if we assume that the reaction is always far from saturation ($N_{\text{it}} \ll N_D$).

Diffusion control means that the generation rate of $N_{\text{it}}$ is controlled by the diffusion of $X$ away from the interface, i.e.,

$$\frac{\partial N_{\text{it}}(t)}{\partial t}=\Psi_X(t)\ . \tag{3}$$

Here, $\Psi_X$ is the flow rate of the species at the interface ($x=0$) by diffusion from the interface into the oxide, i.e.,

$$\Psi_X(t)\equiv -D_X\left.\frac{\partial C_X(x,t)}{\partial x}\right|_{x=0}\ , \tag{4}$$

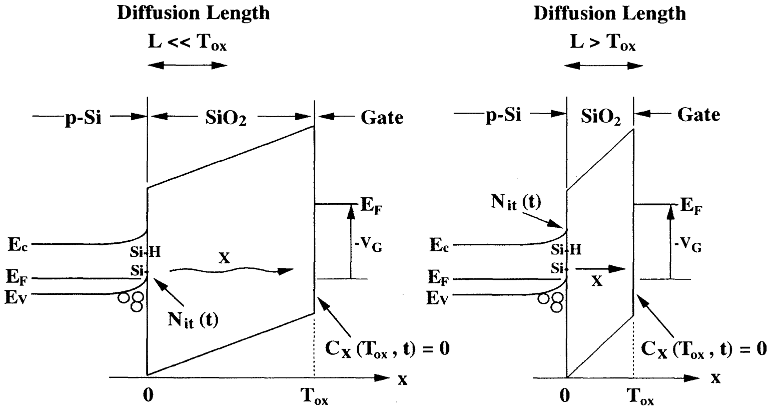
where $D_X$ is the diffusion constant of $X$ and $\partial C_X(x,t)/\partial x$ is the concentration gradient of $X$ in the oxide at a distance $x$ from the interface.

For neutral-diffusing species, as previously considered by Jeppson and Svensson,[26] the electric field has no effect on its transport. Thus, the diffusion rate is given by the ordinary diffusion equation

$$\frac{\partial C_X(x,t)}{\partial t}=D_X\frac{\partial^2 C_X(x,t)}{\partial x^2}\ , \tag{5}$$

where $C_x(x,t)$ is the concentration of $X[C_{Xi}(t)=C_X(0,t)]$.

On the other hand, for charged diffusing species, the external field strongly affects transport across the oxide



(a) Thick Gate Oxides (b) Thin Gate Oxides

FIG. 1. Schematic diagram showing the geometrical configuration considering the diffusion-reaction kinetics for (a) thick gate oxides and (b) thin oxides. $X$ may be interstitial atomic hydrogen, molecular hydrogen, or a hydroxyl group (OH).

so the polarity of the field can be expected to cause asymmetrical results, as observed in the low-field instability under negative and positive gate biases at elevated temperatures. Therefore, we assume the charged species diffusing through the oxide follows the drift-diffusion current model[54] of the form

$$J_X(x,t)=-D_X\frac{\partial C_X(x,t)}{\partial x}\pm\mu E_{\mathrm{ox}}C_X(x,t)\ , \qquad (6)$$

where $\mu$ is the mobility of the positively charged diffuser in the oxide, and the ± sign corresponds to the oxide-field direction. The second term is required to provide the above field-induced asymmetry. In this case, the diffusion of charged species in an external uniform oxide field $E_{\mathrm{ox}}$ is described by the generalized equation

$$\frac{\partial C_X(x,t)}{\partial t}=D_X\frac{\partial^2 C_X(x,t)}{\partial x^2}\pm\mu E_{\mathrm{ox}}\frac{\partial C_X(x,t)}{\partial x}\ , \qquad (7)$$

where the plus sign corresponds to drift diffusion under positive-bias-temperature (+BT) stress, and the negative sign to that under negative-bias-temperature (−BT) stress.

If the diffusion process in Eqs. (5) or (7) coupled with the detailed-balance reaction in Eq. (1) can be ignored, and the whole reaction occurs uniformly similar to the way it does in the liquid phase, the problem is a trivial one, which is discussed in textbooks on basic electrochemistry. However, when the reaction is in the solid-state phase, such as in Si-SiO$_2$ systems, we can no longer ignore the diffusion process, which makes the solution difficult to derive, and we have to take into account the importance of the geometrical boundary condition, which makes the mathematics more complicated.

In the Jeppson and Svensson model,[26] the oxide was assumed to be infinitely thick so that the effect of gate-electrode-oxide interface could be completely ignored. This treatment was suitable for thick oxides at that time. However, for the ultrathin gate oxides that will be used in future technology, we can no longer ignore the gate-electrode effect for the interface-trap generation at the Si-SiO$_2$ interface, i.e., we should take into account the effect of the finite thickness of the oxide. For the concentration $C_X$ of diffusing species $X$ at the electrode-SiO$_2$ interface, two possible boundary conditions are considered:

(i) The gate electrode acts as a perfect reflector of species $X$. In this case, the flow $J_X$ species $X$ across the interface is completely blocked by the gate:

$$J_X(x,t)\equiv-D_X\frac{\partial C_X(x,t)}{\partial x}=0\ , \qquad (8)$$

where $x$ is at the SiO$_2$-gate-electrode interface, and $D_X$ is the diffusion constant of species $X$ in the oxide. This condition is generally not realistic because the diffusing species can always escape from the oxide to the gate material or the species may be consumed at the gate-oxide interface, both of which give finite current flow at the interface.

(ii) The second boundary condition is that the gate electrode acts as an absorbing wall at the interface. If the gate is a perfect absorber, the concentration of species $X$ is exactly zero at the interface;

$$C_X(x,t)=0\quad(t>0), \qquad (9)$$

where $x$ is at the SiO$_2$ gate electrode interface. This condition is not so unrealistic. For example, if species $X$ is atomic hydrogen, two diffusing interstitial hydrogen atoms recombine with each other at the interface to form molecular hydrogen, which is easily diffused away from the interface into the gate material.

In the next two sections, we will solve the system of Eqs. (2)–(4), and (7) for two cases. One is the same boundary condition considered by Jeppson and Svensson,[26] i.e., the oxide thickness $T_{\mathrm{ox}}$ is sufficiently larger than the characteristic diffusion length $L_D$ of the species in the oxide, defined as $L_D\equiv(4D_Xt)^{1/2}$, i.e., $T_{\mathrm{ox}}\gg L_D$. The other is our case where the oxide is too thin to ignore the geometrical confinement for the diffusing species imposed by the thin oxide and the gate electrode, which acts as an absorbing wall.

## III. SOLUTION FOR INFINITELY THICK OXIDES (REFS. 55 AND 56)

The boundary-value problem for the concentration $C_X(x,t)$ is as follows:

$$\frac{\partial C_X(x,t)}{\partial t}=D_X\frac{\partial^2 C_X(x,t)}{\partial x^2}\pm\mu E_{\mathrm{ox}}\frac{\partial C_X(x,t)}{\partial x}$$
$$(0<x<\infty)\ , \qquad (7a)$$

$$C_X(x,0)=0\quad\text{(initial condition)}\ , \qquad (7b)$$

$$-D_X\left.\frac{\partial C_X(x,t)}{\partial x}\right|_{x=0}=\Psi_X(t)\quad(\text{at } x=0)\ , \qquad (7c)$$

and

$$C_X(\infty,t)=0\quad(t>0)\ . \qquad (7d)$$

The problem in the Laplace transform of $C_X(x,t)$ is then

$$sC_X(x,s)-D_XC_{X,xx}(x,s)$$
$$\pm\mu E_{\mathrm{ox}}C_{X,x}(x,s)=0\quad(0<x<\infty)\ , \qquad (10)$$

with $C_X(0,s)=C_{Xi}(s)$ and $\lim_{x\to\infty}C_X(x,s)=0$, where ,$x$ and ,$xx$ mean the first and second derivatives with respect to $x$, i.e., $d/dx$ and $d^2/dx^2$, respectively. The solution of ordinary differential Eq. (10) is

$$C_X(x,s)=\exp(\pm\beta x)(C_1\exp\{-[(s+\gamma^2)/D_X]^{1/2}x\}$$
$$+C_2\exp\{+[(s+\gamma^2)/D_X]^{1/2}x\})\ , \qquad (11)$$

with $\beta=\mu E_{\mathrm{ox}}/2D_x$, $\gamma=(D_x)^{1/2}\beta$, and $C_X(x,t)=0$ for $t\le 0$. Using the condition $C_X(\infty,t)=0$, we obtain $C_2=0$ and $C_1=C_X(0,s)=C_{Xi}(s)$. Note that this assumption is valid only if the oxide may be considered infinitely thick, i.e., if $T_{\mathrm{ox}}^2/4D_Xt\gg 1$ where $T_{\mathrm{ox}}$ is the oxide thickness. Thus, Eq. (11) becomes

$$C_X(x,s)=C_{Xi}(s)\exp(\pm\beta x)\exp\{-[(s+\gamma^2)/D_X]^{1/2}x\}\ , \tag{12}$$

with the Laplace inversion in the form

$$C_X(x,t)=\int_{x/\{2(D_X t)^{1/2}\}}^{\infty} d\lambda\, C_{Xi}\left[t-\frac{x^2}{4D_X\lambda^2}\right] \times\exp\left\{-\left[\lambda\pm\frac{\beta x}{2\lambda}\right]^2\right\}\frac{2}{\sqrt{\pi}}\ . \tag{13}$$

The Laplace transform of the flow of $X$ from the interface is obtained from Eqs. (4) and (12) as

$$\Psi_X(s)=(D_X)^{1/2}C_{Xi}(s)\{(s+\gamma^2)^{1/2}\mp\gamma\} \times\exp(\pm\beta x)\exp\{-[(s+\gamma^2)/D_X]^{1/2}x\}_{x=0}\ . \tag{14}$$

For neutral species, $\beta=\gamma=0$. Therefore, Eq. (14) gives

$$\Psi_X(s)=\sqrt{D_X}sC_{Xi}(s)/\sqrt{s}\ .$$

Since $s^{-1/2}=L\{(\pi t)^{-1/2}\}$ and $sC_{Xi}(s)=L\{C'_{Xi}(t)\}+C_{Xi}(+0)$, assuming that $C_{Xi}(t)$ is a continuous function, then the Bromwich integral (i.e., the inverse Laplace transform) with the aid of the convolution is easily obtained as

$$\Psi_X(t)=(D_X/\pi)^{1/2}\left[C_{Xi}(+0)/\sqrt{t} + \int_0^t d\tau\, C'_{Xi}(t-\tau)/\sqrt{\tau}\right]\ .$$

The Laplace transform of Eq. (3) with Eq. (12) gives

$$\begin{aligned}N_{\mathrm{it}}(s)&=\Psi_X(s)/s\\ &=\sqrt{D_X}C_{Xi}(s)\frac{1}{\{(s+\gamma^2)^{1/2}\mp\gamma\}}\exp(\pm\beta x)\exp\{-[(s+\gamma^2)/D_X]^{1/2}x\}_{x=0}\\ &=(D_X)^{1/2}C_{Xi}(s)L\left\{\frac{1}{\sqrt{\pi t}}\exp\left[-\left[\frac{x}{2\sqrt{D_X t}}\mp\gamma\sqrt{t}\right]^2\right]\pm\gamma\ \mathrm{erfc}\left[\frac{x}{2\sqrt{D_X t}}\mp\gamma\sqrt{t}\right]\right\}_{x=0}\\ &=C_{Xi}(s)L\{(D_X/t)^{1/2}\Phi_1(\mp\gamma\sqrt{t})\}\ ,\end{aligned} \tag{15}$$

where

$$\Phi_1(x)\equiv\int_x^\infty d\eta\,\mathrm{erfc}(\eta)=\frac{1}{\sqrt{\pi}}\exp(-x^2)-x\,\mathrm{erfc}(x)\ ,$$

with the definition of the complementary error function

$$\mathrm{erfc}(x)=1-\mathrm{erf}(x)=\frac{2}{\sqrt{\pi}}\int_x^\infty dt\exp(-t^2)\ .$$

Thus, the Laplace inversion gives the time evolution of $N_{\mathrm{it}}(t)$ as

$$N_{\mathrm{it}}(t)=(D_X)^{1/2}\int_0^t d\tau\, C_{Xi}(t-\tau)\frac{\Phi_1(\pm\gamma\sqrt{\tau})}{\sqrt{\tau}}\ , \tag{16}$$

where the negative (positive) sign corresponds to negative (positive) low-field bias-temperature instability.

When the diffusing species are electrically neutral, the analytical expression for $N_{\mathrm{it}}(t)$ can be easily obtained by noting the relation

$$\lim_{\gamma\to 0}\Phi_1(\pm\gamma\sqrt{\tau})=1/\sqrt{\pi}\ .$$

Assuming the power law for the flow rate of species $X$ at the interface, $C_{Xi}(t)=At^p$, the time evolution of interface-trap density $N_{\mathrm{it}}(t)$ is

$$N_{\mathrm{it}}(t)=A\sqrt{D_X}\left[t^{p+1/2}\frac{\Gamma(p+1)}{\Gamma(p+3/2)}{}_1F_1(\tfrac{1}{2},p+\tfrac{3}{2};-\gamma^2 t)\pm\gamma\frac{t^{p+1}}{p+1}+\gamma^2 t^{p+3/2}\frac{\Gamma(p+1)}{\sqrt{\pi}} \times\sum_{k=0}^{\infty}\frac{(-\gamma^2 t)^k}{k!(k+1/2)}\frac{\Gamma(k+3/2)}{\Gamma(k+5/2+p)}\right]\ , \tag{17}$$

where ${}_1F_1(\alpha,\beta;z)$ denotes the confluent hypergeometric function of argument $z$ and parameters $\alpha$ and $\beta$, $\Gamma$ is the gamma function, and the plus (minus) sign correspond to the negative (positive) bias-temperature instability.

For neutral species, it is easy to obtain a closed analytical expression for $N_{\mathrm{it}}(t)$, since the second and third terms in the right-hand side of Eq. (17) vanish. Therefore, we obtain by noting that ${}_1F_1(\frac{1}{2},p+\frac{3}{2},0)=1$,

$$N_{\mathrm{it}}(t)=A(D_X/\pi)^{1/2}B(\tfrac{1}{2},p+1)t^{p+1/2}\ , \tag{18}$$

where

$$B(m+1,n+1)\equiv\int_0^1 dt\, t^m(1-t)^n$$
$$=\Gamma(m)\Gamma(n)/\Gamma(m+n)$$

is the beta function. The quasiequilibrium condition of Eq. (2) imposes the constraint for the power $p$;

$$[N_{\mathrm{it}}(t)]^{1/a}[C_{Xi}(t)]^{1/b}\approx t^{\{(p+1/2)/a+p/b\}}$$
$$\approx \mathrm{const}\ . \tag{19}$$

For the first-order reaction kinetics with coefficients $a=b=1$, the power exponent $p$ is determined to be $p=-\frac{1}{4}$. Hence, the time dependence of $N_{\mathrm{it}}(t)$ is

$$N_{\mathrm{it}}(t)=(D_X)^{1/4}t^{1/4}\left\{\frac{G}{S}N_D\frac{\Gamma(3/4)}{\Gamma(5/4)}\right\}^{1/2}, \tag{20}$$

which is nothing but the $t^{1/4}$ dependence.

On the other hand, for the charged species, it is no longer possible to obtain a closed analytical solution. Instead we have to treat the asymptotic behavior of Eq. (17) for small and large $t$.

For small $t$, the expression in Eq. (17) can be approximated by Eq. (18), since the field-dependent (second and third) terms are negligibly small. Therefore, the asymptotic behavior of Eq. (17), which satisfies the quasiequilibrium condition of Eq. (2), for small $t$ is the same as Eq. (20), i.e., $t^{1/4}$ dependence.

For large $t$ or large $\gamma$, we must examine the asymptotic behavior of each term. Noting the functional relation[58,59]

$${}_1F_1(\alpha,\beta;z)=e^z{}_1F_1(\beta-\alpha,\beta;-z)\ ,$$

and the asymptotic representation of ${}_1F_1(\alpha,\beta;z)$

$${}_1F_1(\alpha,\beta;z)\sim\frac{\Gamma(\beta)}{\Gamma(\beta-\alpha)}e^{\pm\alpha\pi i}z^{-\alpha}\left[\sum_{k=0}^{\infty}\frac{(-1)^k(\alpha)_k(\alpha-\beta+1)_k}{k!}z^{-k}+O(|z|^{-n-1})\right]$$
$$+\frac{\Gamma(\beta)}{\Gamma(\alpha)}e^z z^{-(\beta-\alpha)}\left[\sum_{\kappa=0}^{\infty}\frac{(\beta-\alpha)_k(1-\alpha)_k}{k!}z^{-k}+O(|z|^{-n-1})\right],$$

where $(|\arg z|\leq\pi-\delta,\beta\neq0,-1,-2,\ldots,)$. The first term of Eq. (17) behaves as $\exp(-\gamma^2 t)\gamma^{-2(p+1)}t^{-1/2}$, which converges to zero for sufficiently large $t$ or $\gamma$. Furthermore, the third term in Eq. (17) can also be proved to converge to zero for large $t$,[59] by noting the inequality

$$\sum_{k=0}^{\infty}\frac{(-\gamma^2 t)^k}{k!(k+1/2)}\frac{\Gamma(k+3/2)}{\Gamma(k+5/2+p)}\ll\sum_{k=0}^{\infty}\frac{(-\gamma^2 t)^k}{k!}=\exp(-\gamma^2 t)\ .$$

Therefore, for large $t$, $N_{\mathrm{it}}(t)$ evolves asymptotically as

$$N_{\mathrm{it}}(t)\sim\pm\gamma A(D_X)^{1/2}t^{p+1}/(p+1)\ , \tag{21}$$

where the plus (minus) sign corresponds to the negative- (positive-) bias-temperature instability. Since $N_{\mathrm{it}}(t)$ is the amount of generated interface-trap density, the minus evolution can be interpreted as no generation. Thus, this model naturally provides asymmetrical behavior under positive- and negative-BT stress aging.

With the same argument leading to Eq. (20), the quasiequilibrium condition of Eq. (2) imposes a constraint on the power as $p=-\frac{1}{2}$. In the case of charged-diffusing species, the time dependence of $N_{\mathrm{it}}(t)$ is

$$N_{\mathrm{it}}(t)\sim\begin{cases}\gamma(D_X)^{1/4}t^{1/2}\left\{\frac{G}{S}N_D\frac{\Gamma(3/4)}{\Gamma(5/4)}\right\}^{1/2} & \text{for } -\text{BT aging}\\ 0\ \text{ for } +\text{BT aging}\ ,\end{cases} \tag{22}$$

which predicts the $E_{\mathrm{ox}}^1 t^{1/2}$ dependence of $N_{\mathrm{it}}$ generation under negative low fields at elevated temperatures when the diffusing species are positively charged.

## IV. SOLUTION FOR FINITE OXIDE THICKNESS: $T_{\mathrm{ox}}<\infty$ (REFS. 56 AND 57)

If the oxide thickness $T_{\mathrm{ox}}$ is not thick enough to ignore the gate-electrode effect where species $X$ is absorbed, we can no longer impose the infinite thickness boundary condition of Eq. (7d). In this case, the boundary value problem in $C_X(x,t)$ is almost the same as that expressed in Eqs. (7a)–(7c), except for Eq. (7d). Instead, we impose the boundary condition

$$C_X(T_{\mathrm{ox}},t)=0\quad(t>0)\ . \tag{7e}$$

The solution of the ordinary differential equation, i.e., Eq. (7), that satisfies the conditions (7b) and (7e) is

$$C_X(x,s)=C_{Xi}(s)\exp(\pm\beta x)\frac{\sinh\{(T_{\mathrm{ox}}-x)[(s+\gamma^2)/D_X]^{1/2}\}}{\sinh\{T_{\mathrm{ox}}[(s+\gamma^2)/D_X]^{1/2}\}}\ . \tag{23}$$

Correspondingly, the Laplace transform of the flow rate $\Psi_X(t)$ is

$$\Psi_X(s)=C_{Xi}(s)(D_X)^{1/2}\left\{(s+\gamma^2)^{1/2}\frac{\cosh\{(T_{\rm ox}-x)[(s+\gamma^2)/D_X]^{1/2}\}}{\sinh\{T_{\rm ox}[(s+\gamma^2)/D_X]^{1/2}\}}\mp\gamma\frac{\sinh\{(T_{\rm ox}-x)[(s+\gamma^2)/D_X]^{1/2}\}}{\sinh\{T_{\rm ox}[(s+\gamma^2)/D_X]^{1/2}\}}\right\}\exp(\pm\beta x)\bigg|_{x=0} . \tag{24}$$

Hence, from Eq. (3), the Laplace transform of $N_{\rm it}(t)$ becomes

$$N_{\rm it}(s)=C_{Xi}(s)(D_X)^{1/2}\left\{\left[1+\frac{\gamma^2}{s}\right]\frac{\cosh\{(T_{\rm ox}-x)[(s+\gamma^2)/D_X]^{1/2}\}}{(s+\gamma^2)^{1/2}\sinh\{T_{\rm ox}[(s+\gamma^2)/D_X]^{1/2}\}}\mp\frac{\gamma}{s}\frac{\sinh\{(T_{\rm ox}-x)[(s+\gamma^2)/D_X]^{1/2}\}}{\sinh\{T_{\rm ox}[(s+\gamma^2)/D_X]^{1/2}\}}\right\}\exp(\pm\beta x)\bigg|_{x=0} . \tag{25}$$

Using the Bromwich contour integral method[56,57] and noting an infinite number of simple poles at $s=-n^2\pi^2$ and $s=0$, the inverse Laplace transforms of the convolution kernels in Eq. (25) are

$$L^{-1}\left\{\frac{\sinh\{(T_{\rm ox}-x)[(s+\gamma^2)/D_X]^{1/2}\}}{s\sinh\{T_{\rm ox}[(s+\gamma^2)/D_X]^{1/2}\}}\right\}=\frac{T_{\rm ox}-x}{T_{\rm ox}}+\frac{2}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi(T_{\rm ox}-x)}{T_{\rm ox}}\left\{\frac{T_{\rm ox}^2\gamma^2}{T_{\rm ox}^2\gamma^2+n^2\pi^2D_X}+\frac{n^2\pi^2D_X}{T_{\rm ox}^2\gamma^2+n^2\pi^2D_X}\exp(-\gamma^2t-n^2\pi^2D_Xt/T_{\rm ox}^2)\right\} , \tag{26}$$

and

$$L^{-1}\left\{\left[1+\frac{\gamma^2}{s}\right]\frac{\cosh\{(T_{\rm ox}-x)[(s+\gamma^2)/D_X]^{1/2}\}}{(s+\gamma^2)^{1/2}\sinh\{T_{\rm ox}[(s+\gamma^2)/D_X]^{1/2}\}}\right\}=\frac{\sqrt{D_X}}{T_{\rm ox}}\left\{1+2\sum_{n=1}^{\infty}(-1)^n\cos\frac{n\pi(T_{\rm ox}-x)}{T_{\rm ox}}\left[\frac{T_{\rm ox}^2\gamma^2}{T_{\rm ox}^2\gamma^2+n^2\pi^2D_X}+\frac{n^2\pi^2D_X}{T_{\rm ox}^2\gamma^2+n^2\pi^2D_X}\exp(-\gamma^2t-n^2\pi^2D_Xt/T_{\rm ox}^2)\right]\right\} . \tag{27}$$

Therefore, $N_{\rm it}(t)$ is expressed as

$$N_{\rm it}(t)=\frac{D_X}{T_{\rm ox}}\int_0^t d\tau\, C_{Xi}(t-\tau)\left\{\frac{T_{\rm ox}\gamma}{\sqrt{D_X}}\coth\frac{T_{\rm ox}\gamma}{\sqrt{D_X}}\pm\frac{T_{\rm ox}\gamma}{\sqrt{D_X}}+2\sum_{n=1}^{\infty}\frac{n^2\pi^2D_X}{T_{\rm ox}^2\gamma^2+n^2\pi^2D_X}\exp(-\gamma^2\tau-n^2\pi^2D_X\tau/T_{\rm ox}^2)\right\} , \tag{28}$$

where the plus (minus) sign corresponds to the negative- (positive-) bias-temperature instability.

For neutral species, with vanishing field-dependent terms including $\gamma$, and noting the relation

$$\lim_{z\to 0} z\coth z=1 ,$$

Eq. (28) can be reduced to

$$N_{\rm it}(t)=\frac{D_X}{T_{\rm ox}}\int_0^t d\tau\, C_{Xi}(t-\tau)\left\{1+2\sum_{n=1}^{\infty}\exp(-n^2\pi^2D_X\tau/T_{\rm ox}^2)\right\} . \tag{29}$$

Note both Eqs. (28) and (29), except for the second term in Eq. (28), explicitly include the geometrical scaling factor $T_{\rm ox}$. Hence, we conclude that the absorbing wall at the $\rm SiO_2$-gate electrode leads to the inverse proportional law of the oxide thickness for $N_{\rm it}$ generation.

The series expansion in the above expressions is rapidly convergent if $\pi(D_X\tau)^{1/2}/T_{\rm ox}$ is moderate; if it is 1, the second exponential in the sum is $e^{-4}=0.018$, and the next $e^{-9}=0.0001$. If $\pi(D_X\tau)^{1/2}/T_{\rm ox}$ is small, the convergence is slow. In this case, we can use the relation

$$1+2\sum_{n=1}^{\infty}\exp(-n^2\pi^2D_Xt/T_{\rm ox}^2)\cos\frac{n\pi x}{T_{\rm ox}}=\frac{T_{\rm ox}}{\sqrt{\pi D_Xt}}\exp\{-x^2/(4D_Xt)\}\left\{1+2\sum_{m=1}^{\infty}\exp(-T_{\rm ox}^2m^2/D_Xt)\cosh\frac{mxT_{\rm ox}}{D_XT}\right\} . \tag{30}$$

[This relation is easily proven by noting the transformation property of Jacobi's elliptic theta function[55]

$$\vartheta_3(z:\sigma)=1+\sum_{n=1}^{\infty}\exp(-\pi\sigma n^2)\cos(2nz)$$
$$=\sigma^{-1/2}\exp(-z^2/\pi\sigma)\vartheta_3(iz/\sigma:1/\sigma)\ ,$$

and putting $2z=\pi x/T_{\mathrm{ox}}$, $\sigma=\pi D_X t/T_{\mathrm{ox}}^2$.] Thus, for small $\pi(D_X\tau)^{1/2}/T_{\mathrm{ox}}$, the series expansion in Eq. (29) can be approximated by the first term in Eq. (30).

Assuming the power law for the flow rate at the interface, i.e., $C_{Xi}(t)=At^p$, and using Eq. (30) as an asymptotic approximation of Eq. (29) for small $t$, the time evolution of Eq. (29) can be expressed as

$$N_{\mathrm{it}}(t)=A(D_X/\pi)^{1/2}\left\{B(\tfrac{1}{2},p+1)t^{p+1/2}+2\Gamma(p+1)t^{p+3/4}\frac{(D_X)^{1/4}}{\sqrt{T_{\mathrm{ox}}}}\sum_{n=1}^{\infty}\frac{1}{\sqrt{n}}\exp\left[-\frac{n^2T_{\mathrm{ox}}^2}{2D_Xt}\right]W_{-p/2-1/4,1/4}\left[\frac{n^2T_{\mathrm{ox}}^2}{D_Xt}\right]\right\},$$

where $W_{\mu,\nu}(z)$ is the Whittaker confluent hypergeometric function of argument $z$ and parameters $\mu$ and $\nu$. Here, the first term is the same as Eq. (18). Therefore, the time evolution of $N_{\mathrm{it}}(t)$ follows the $t^{1/4}$ law, as previously shown.

For charged species with $C_{Xi}(t)=At^p$, Eq. (28) becomes

$$N_{\mathrm{it}}(t)=\frac{D_X}{T_{\mathrm{ox}}}AB(1,p+1)t^{p+1}\left\{\frac{T_{\mathrm{ox}}\gamma}{\sqrt{D_X}}\coth\frac{T_{\mathrm{ox}}\gamma}{\sqrt{D_X}}\pm\frac{T_{\mathrm{ox}}\gamma}{\sqrt{D_X}}+2\sum_{n=1}^{\infty}\frac{n^2\pi^2D_X}{T_{\mathrm{ox}}^2\gamma^2+n^2\pi^2D_X}\times{}_1F_1\left[1,p+2;-\gamma^2t-\frac{n^2\pi^2D_X}{T_{\mathrm{ox}}^2}t\right]\right\}\ . \quad (31)$$

Thus, in this case, for large $t$ or $\gamma$, the second term in Eq. (31) becomes the leading term, which gives the same field and time dependence as in Eqs. (21) and (22), i.e., $E_{\mathrm{ox}}^1t^{1/2}$, without the explicit $T_{\mathrm{ox}}^{-1}$ dependence.

## V. THE VALIDITY OF THE ABSORBING BOUNDARY CONDITION

In this section, we discuss the validity of the absorbing boundary condition at the gate-electrode-$SiO_2$ interface.

In the preceding two sections, for the sake of mathematical simplicity we assumed the concentration of diffusing species at the gate-$SiO_2$ interface is zero. In general, if the diffusion constants of species $X$ are $D_1$ and $D_2$ in the oxide and the gate material, respectively, the boundary condition for the concentration of $X$ diffusing in the two-phase region without any loss due to annihilation of species at the interface is given by

$$C_1=kC_2,\ \text{ and }\ D_1\partial C_1/\partial x|_{\mathrm{interface}}=D_2\partial C_2/\partial x|_{\mathrm{interface}}\ , \quad (32)$$

where $C_1$ and $C_2$ are the concentrations of species $X$ in the oxide and the gate, respectively. This condition makes the mathematics for analytical solutions very complicated. The problem is to determine what condition makes it possible to simplify Eq. (32) to $C_{\mathrm{interface}}=0$. Here, factor $k$ is the ratio of equilibrium concentrations $C_1$ and $C_2$, which is related to the square root of the ratio of $D_1$ to $D_2$. Thus, if $k$ is sufficiently large, $C_2$ can be considered to be negligibly small.

With this in mind, let us consider the diffusion coefficients in the oxide and several electrode materials. In general, the diffusion coefficient $D_X$ for chemically stable species $X$ in the oxide is accurately given by

$$D=D_0\exp(-E_A/k_BT)\ , \quad (33)$$

where $E_A$ is the activation energy. By consulting data in the literature,[48,60-62] the diffusivity of hydrogen molecules, for example, is expressed by Eq. (33) with $D_0=5.64\times10^{-4}$ [cm$^2$/s] and $E_A=0.45$ eV in the oxide,[60] and with $D_0=9.4\times10^{-3}$ [cm$^2$/s] and $E_A=0.48$ eV in the crystalline silicon.[61] In the range from 150 to 290 °C, the diffusivity of $H_2$ in Si is about ten times greater than that in $SiO_2$. Thus, $k$ is about 3.2, which implies the solid solubility of $H_2$ into crystalline silicon is negligible.[39,61] Thus, the condition $C_X=0$ inside polycrystalline silicon is valid at least for molecular hydrogen as species $X$. The same argument is applicable to the aluminum gate, because $H_2$ diffusivity, expressed by Eq. (33) with $D_0=0.2-2\times10^{-2}$ [cm$^2$/s] and $E_A=0.42-0.52$ eV,[62] is also much greater than that in $SiO_2$.

## VI. DISCUSSION

### A. Comparison with experimental results

In this section, we will determine the possible mechanism of the low-field charge-building instability by comparing the above results with the experimental data on thick oxides in the literature[23-30] and our experimental results on ultrathin oxides.[42]

For sufficiently thick gate-oxide MOS samples (in the range of 40–110 nm), the $N_{\mathrm{it}}$ generation is empirically expressed as[25-29]

$$N_{\mathrm{it}}(t)=AE_{\mathrm{ox}}^mt^n\exp(-E_A/k_BT)\ , \quad (34)$$

where $m$ is the exponent to specify the power-law field dependence, $n$ is the exponent for the time dependence, and $A$ is a constant independent of the field $E_{\mathrm{ox}}$ and time $t$. The value of $m$ is reported most likely to be $\frac{3}{2}$,[29,42] and the exponent $n$ has been observed to be $\frac{1}{4}$,[26,28,42] $\frac{1}{5}$,[25,27,29] or less.[24] The value of the activation energy $E_A$ is reported to be 0.18–0.20,[29,42] 0.3,[26,27] 0.28–0.45,[28] and 0.64 eV.[25]

As shown in Sec. III, for the process controlled by the rate at which neutral species $X$ diffuses away from the interface into the infinitely thick oxide, the interface-trap density $N_{\text{it}}(t)$ is proven to increase [see Eq. (20)] as

$$N_{\text{it}}(t)=R(D_X)^{1/4}t^{1/4} . \tag{35}$$

Here, $t$ is the stress-aging time and $R$ is the field-dependent rate constant of $N_{\text{it}}$ generation reaction. Combining the diffusion coefficient $D_X$ expressed in Eq. (33), Eq. (35) yields

$$N_{\text{it}}(t)=R(E_{\text{ox}})(D_0)^{1/4}t^{1/4}\exp(-E_A/4k_BT) . \tag{35a}$$

This equation formally reproduces empirical Eq. (34) except for the oxide-field $E_{\text{ox}}$ dependence, denoted by $R(E_{\text{ox}})$.

In this scheme with neutral species, there is no first-principle-based explanation of the field-induced asymmetry between the effects under negative- and positive-bias stresses at elevated temperatures because, for neutral-diffusing species, the external field has no effect on their transport. Thus, we cannot deductively derive the functional dependence of $N_{\text{it}}$ (or the coefficient $R$) on the field $E_{\text{ox}}$. We can only infer from the experimental observation that $R(E_{\text{ox}})$ varies with the oxide field as $R=CE_{\text{ox}}^{3/2}$, where $C$ is a field-independent constant. This field dependence can be ascribed to the nature of the electrochemical reaction at the $\text{SiO}_2$-Si interface.

On the other hand, our experiments for ultrathin oxide samples[42] have provided the following simple empirical expression for various dependencies of the $N_{\text{it}}$ generation:

$$N_{\text{it}}(t)=BE_{\text{ox}}^{3/2}t^{1/4}\exp(-E_A/k_BT)/T_{\text{ox}} , \tag{36}$$

where $B$ is a field ($E_{\text{ox}}$), oxide-thickness ($T_{\text{ox}}$) independent constant.

Figure 6 of Ref. 42 shows the fractional-power time dependence of integrated interface-trap densities $N_{\text{it}}$ observed for 6.2-nm-thick oxide MOS capacitors under various stress conditions. $t^{1/4}$ dependence of $N_{\text{it}}$ generation is derived independent of the applied oxide fields ranging from $-3$ to $-5$ MV/cm. This $t^{1/4}$ relationship is also observed at 150 and 250 °C.

In Eq. (36), the $N_{\text{it}}$ generation for ultrathin oxides has an inversely proportional dependence on the oxide thickness ($T_{\text{ox}}$). This $T_{\text{ox}}^{-1}$ dependence can be easily seen in Fig. 9 of Ref. 42, which depicts the $(1/T_{\text{ox}})$ dependence of the constant $A$ in Eq. (34) applied for ultrathin oxides with the model fitting curve. The constant $A$ is obtained by normalizing the observed integrated interface-trap density ($N_{\text{it}}$) by the empirical equation $E_{\text{ox}}^{3/2} t^{1/4}\exp(-E_A/k_BT)$, i.e., Eq. (34). The experimental details on Eq. (36) and these figures will soon be published elsewhere.[42]

As discussed in Sec. IV, two simultaneous conditions on the neutral diffusing species in the oxide give formally the same dependence as in Eq. (36). The reason is twofold. First, the diffusion-limiting reaction leads to the $t^{1/4}$ law of the time evolution of $N_{\text{it}}$. Second, the geometrical boundary condition of an absorbing wall at the gate-oxide interface expressed in Eq. (7e) leads to the inversely proportional law of $N_{\text{it}}$ to $T_{\text{ox}}$, as in Eq. (29). Thus, for the finite $T_{\text{ox}}$, the diffusion-limited $N_{\text{it}}$ generation is expressed [see Eqs. (20) and (29)] as

$$N_{\text{it}}(t)=(D_X)^{1/4}R't^{1/4}/T_{\text{ox}} , \tag{37}$$

where $D_X$ is the diffusion coefficient of species $X$ in the oxide, and $R'$ is an appropriate constant that is independent of $D_X$ and the time $t$ but dependent on the ratio of the generation rate ($G$) to the suppression rate ($S$) of reaction. [See Eqs. (1) or (39) for further details.] Similar arguments as that for the thick oxide case provides the relation

$$N_{\text{it}}(t)=(D_0)^{1/4}R't^{1/4}\exp(-E_A/4k_BT)/T_{\text{ox}} , \tag{37a}$$

by combining Eq. (33) with Eq. (37). This equation also formally reproduces empirical Eq. (36) except for the oxide-field $E_{\text{ox}}$ dependence. This field dependence can also be ascribed to the nature of the electrochemical reaction.

### B. The nature of the neutral-diffusing species

The above time and oxide-thickness dependencies of the $N_{\text{it}}$ generation model including neutral diffusing species with an absorbing wall at the gate-electrode-oxide interface thus explain the experimental data in the literature[23–30] and our observations[42] very well. However, in this phenomenological scheme the actual species have not yet been identified.

From Eqs. (35a) and (37a), it turns out that the experimentally observed activation energy is one-fourth of the real activation energy, i.e., $E_A^{\text{real}}=4E_A^{\text{exp}}$. From experimentally observed values [for example, 0.20 eV (Ref. 42)], the real activation energy $E_A$ is expected to be 0.80 eV, which is almost the same value as the 0.75 eV (Ref. 40) of hydrogen atoms in the oxide. (This value is about two times larger than that of molecular hydrogen, i.e., 0.415–0.45 eV.[48,60]) This coincidence appears to support the atomic hydrogen transport model[40,41,46,47] of $N_{\text{it}}$ generation.

Unfortunately, from this kind of argument, we cannot say anything conclusive about species $X$. This is because the observed activation energy involves all fundamental processes related to $N_{\text{it}}$ formation, including the diffusion of species $X$ and the electrochemical reaction at the interface. The above argument provides a correct conclusion on species $X$ if and only if the transport process of species $X$ is dominant compared to other fundamental processes. However, this is not the case. Furthermore, the diffusion coefficient of atomic hydrogen in $\text{SiO}_2$ was estimated to have an activation energy of 0.18 eV,[48] much lower than our 0.80 eV, but certainly within the range of 0.18 (Ref. 48)–0.92 (Ref. 49) found in the literature.[40,48,49] The 0.18-eV energy is also known to be the value seen in highly damaged oxides.[40]

In order to obtain more information on the $N_{\text{it}}$ formation reaction at the Si-SiO$_2$ interface, in addition to its $E_{\rm ox}^{3/2}$ dependence,[29,42] let us consider the physical meaning of the observed $T_{\rm ox}^{-1}$ dependence.[42] The dependence implies the existence of the characteristic time $\tau$, which is defined as $\tau \equiv L_D^2/(4D_X)$ where $L_D$ is the characteristic diffusion length of the diffusing species in the oxide. The relative value of this diffusion length $L_D$ to the oxide thickness $T_{\rm ox}$ determines the boundary condition at the gate-oxide interface, i.e., for $T_{\rm ox} \gg L_D$, the infinitely thick oxide boundary condition is employed whereas the finite oxide boundary condition is applied for $T_{\rm ox} \sim L_D$. $\tau$ is the time after which the boundary condition of the absorbing wall at the gate-oxide interface starts affecting the interfacial concentration of diffusing species at the Si-SiO$_2$ interface.

In the diffusion-controlled reaction, this time $\tau$ also has the following physical meaning: It is the time during which the $N_{\rm it}$ formation reaction is reversible, and correspondingly the formed $N_{\rm it}$ is unstable. In other words, if the released species from the interfacial defects are sufficiently consumed by diffusion during time $\tau$, the detailed-balance reaction moves to form more $N_{\rm it}$ at the interface. On the other hand, if the species is not sufficiently consumed during $\tau$, the reverse reaction suppresses the formation of $N_{\rm it}$.

To make a rough estimate of $\tau$, we assumed a characteristic diffusion length of about 7 nm by considering the $T_{\rm ox}$ dependence shown in Fig. 9 of Ref. 42. With the values of $D_X$ in the literature,[39,40,48,60] the value of $\tau$ at room temperature is estimated to be about $1.3\times10^{-6}$ s for atomic hydrogen[48] and $7.9\times10^{-3}$ s for molecular hydrogen.[60] (See also Table 1 of Ref. 48.)

On the basis of the above findings, let us consider critically the traditional microscopic model[40,41,48] of $N_{\rm it}$ generation. This is a two-reaction model involving the atomic hydrogen dimerization and hydrogen-interface reactions

$$\mathrm{Si_3{\equiv}Si{-}H} \underset{S_1}{\overset{G_1}{\rightleftharpoons}} \mathrm{Si_3{\equiv}Si^{\cdot}} + \mathrm{H}_i\ , \tag{38a}$$

$$\mathrm{Si_3{\equiv}Si{-}H} + \mathrm{H}_i \underset{S_2}{\overset{G_2}{\rightleftharpoons}} \mathrm{Si_3{\equiv}Si^{\cdot}} + \mathrm{H_2}\ , \tag{38b}$$

$$\mathrm{H}_i + \mathrm{H}_i \overset{k}{\rightarrow} \mathrm{H_2}\ ,$$

where $\rightleftharpoons$ means a reversible process, $G$ is the generation rate, and $S$ is the suppression rate. Reaction (38c) describes dimerization of interstitial atomic hydrogen ($\mathrm{H}_i$) into H$_2$ with the rate constant $k$. Note that two species of hydrogen are involved in this model, i.e., molecular and atomic. Thus, the problem is which is the rate-limiting process characterized by $\tau$: an atomic or a molecular hydrogen involved process.

Atomic hydrogen is highly reactive and considered to be a fast diffuser in the oxide.[48] It is possible atomic hydrogen acts as the promoter of $N_{\rm it}$ formation, as in Eq. (38a) (from left to right), as well as the suppressor of $N_{\rm it}$ formation, as in Eq. (38a) (reverse direction). The released atomic hydrogen will directly attack other interfacial defect sites, as in Eq. (38b), or it will immediately form molecular hydrogen with other freed atomic hydrogen, as in Eq. (38c). On the whole, an excess of atomic hydrogen moves the detailed-balance equation, i.e., Eq. (1), to increase $N_{\rm it}$ generation. Thus, the estimated time $\tau$ is too long to characterize such a rapid atomic-hydrogen-involved reaction. Therefore, it is natural to relate $\tau$ to any one of the fundamental processes involving molecular hydrogen.

Molecular hydrogen acts as the suppressor for the $N_{\rm it}$ formation process because of the existence of the reverse reaction of Eq. (38c) (from right to left). In the reaction scheme expressed in Eqs. (38a)–(38c), interface traps may be created when there is an excess of atomic hydrogen ($\mathrm{H}_i$) and annihilated when there is an excess of molecular hydrogen (H$_2$). Thus, the consumption of excess molecular hydrogen by diffusion determines the formation rate of $N_{\rm it}$. Consequently, the characteristic time $\tau$ is naturally considered to be the time constant of the suppressing reaction $\mathrm{Si_3{\equiv}Si^{\cdot}} + \mathrm{H_2} \rightarrow \mathrm{Si_3{\equiv}Si{-}H} + \mathrm{H}_i$, i.e., it requires a time $\tau$ on the order of $10^{-3}$ s to suppress the formation of $N_{\rm it}$ by capping interface traps with H$_2$.

Actually, Brower[39] observed that molecular hydrogen (rather than interstitial atomic hydrogen) attacks dangling Si bonds to anneal them out. This means the suppressing term in the rate equation, i.e., Eq. (1), is approximated as $-S[\mathrm{Si_3{\equiv}Si^{\cdot}}][\mathrm{H_2}]_i$ where $[\,]_i$ indicates the interfacial concentration. Putting $N_D = [\mathrm{Si_3{\equiv}Si{-}H}]$, $N_{\rm it} = [\mathrm{Si_3{\equiv}Si^{\cdot}}]$, the rate equation for this model is

$$\frac{\partial}{\partial t}N_{\rm it}(t) = G\{N_D - N_{\rm it}(t)\} - SN_{\rm it}(t)[\mathrm{H_2}]_i\ , \tag{39}$$

which is the same form considered in Eq. (1). Therefore, we are naturally led to conclude the neutral-diffusing species is molecular hydrogen.

However, recently, Cartier, Stathis, and Buchanan[46] directly observed that atomic hydrogen can simultaneously passivate and depassivate silicon dangling bonds at the interface via the passivation reaction expressed in Eq. (38a) (from right to left) and the depassivation, as in Eq. (38b) (from left to right). According to Brower and Myers,[45] both reactions are exothermic with at most a very small energy barrier. If this is the case, the corresponding detailed-balance equation becomes a pair of coupled first-order nonlinear differential equations,

$$\frac{\partial}{\partial t}N_{\rm it}(t) = \{G_1 + G_2[\mathrm{H}_i]_i\}\{N_D - N_{\rm it}(t)\} - \{S_1[\mathrm{H}_i]_i + S_2[\mathrm{H_2}]_i\}N_{\rm it}(t) \tag{40a}$$

and

$$\frac{\partial}{\partial t}[\mathrm{H_2}]_{\rm bulk} = k[\mathrm{H}_i]_{\rm bulk}^2\ , \tag{40b}$$

with the corresponding diffusion equations for the concentration of interstitial atomic and molecular hydrogens, i.e., $[\mathrm{H}_i]$ and $[\mathrm{H_2}]$, respectively. Here, the suffixed square bracket $[\,]_i$ means the interfacial concentration.

For this system of equations, three cases are considered in accordance with the relative contribution of the hydrogen dimerization process in Eq. (40b).

First, if the recombination in the bulk [Eq. (38c)] is negligibly small, the most dominant diffusion is that of the atomic hydrogen because it is a fast diffuser. Therefore, we can omit the final term in Eq. (40a), i.e., $-S_2[\mathrm{H}_2]_i N_{\mathrm{it}}(t)$. In this case, the quasiequilibrium condition becomes (for $N_{\mathrm{it}} < N_D$),

$$\{G_1 + G_2 C_{Xi}(t)\} N_D \approx S_1 C_{Xi}(t) N_{\mathrm{it}}(t) , \tag{41}$$

with $C_{Xi}(t) = [\mathrm{H}_i]_i(t)$.

With this condition, the integration kernels in Eqs. (16) and (29) would provide the very complicated dependencies on time and oxide thickness of $N_{\mathrm{it}}$ formation, which are inconsistent with the experimental data found by us[42] and in the literature.[25–29]

However, if atomic hydrogen preferentially passivates dangling bonds,[46] as in Eq. (38a) (from right to left), rather than hydrogen-induced depassivation in Eq. (38b) (left to right), we can set the coefficient $G_2$ equal to zero, resulting in the same quasiequilibrium condition as Eq. (2). In this case, we find a complete parallelism between atomic and molecular hydrogen diffusion models. Both models provide phenomenologically the same dependencies on time and thickness of $N_{\mathrm{it}}$ formation.

Next, let us consider the other extreme case where hydrogen surface recombination [Eq. (38c)] is dominant because of their relative high concentration at the interface, thereby most of the diffusing species may be molecular hydrogen. In this case, the atomic hydrogen concentration becomes negligible, then the terms including $[\mathrm{H}_i]_i$ in Eq. (40a) can be omitted, resulting in the same equation as Eq. (39).

The case where recombination in the bulk is dominant is unrealistic in the case of negative-bias-temperature instability experiments, since such recombination is possible if and only if there is a large amount of atomic hydrogen in the bulk, as in the atomic-hydrogen-exposure experiment[46,47] where a lot of atomic hydrogen was constantly supplied from a remote microwave-excited hydrogen plasma. On the other hand, negative-bias-temperature instability is caused by releasing hydrogen from hydrogen-terminated interfacial dangling bonds whose number is estimated to be at most $3\times10^{14}$ cm$^{-2}$.[63]

On the basis of these findings, we can construct a model for low-field charge-building instability under negative-bias stresses at elevated temperatures that has three sequential phases.

(1) The applied negative field dissociates interfacial $\mathrm{Si}_3{\equiv}\mathrm{Si}{-}\mathrm{H}$ bonds into interstitial hydrogen ($\mathrm{H}_i$) atoms and electrically active dangling $\mathrm{Si}_3{\equiv}\mathrm{Si}^{\cdot}$ bonds left at the Si-SiO$_2$ interface.

(2) Two diffusing hydrogen atoms recombine rapidly with each other to form molecular hydrogen, which then attacks the interfacial dangling Si bonds at the Si-SiO$_2$ interface to recover the interfacial $\mathrm{Si}_3{\equiv}\mathrm{Si}{-}\mathrm{H}$ bonds within the time period of $\tau$, or, (2′) released hydrogen atoms attack the interfacial dangling Si bonds at the Si-SiO$_2$ interface to recover the interfacial $\mathrm{Si}_3{\equiv}\mathrm{Si}{-}\mathrm{H}$ bonds.

(3) The balance of these competing processes determines the net generation of Si-SiO$_2$ interface traps by decreasing the concentration of molecular [or (3′) atomic] hydrogen by diffusing it away to the gate electrode.

In conclusion, the experimental data support a generalized diffusion-reaction mechanism of $N_{\mathrm{it}}$ formation involving neutral-diffusing species with an absorbing wall at the gate-oxide interface.

### C. The possibility of ionic hydrogen transport

Up until now, we have discussed the case of the neutral-diffusing species. However, there is a possibility of the transport of hydrogen ions[49–52] released from the interfacial Si-H bonds through the oxide during negative-bias stresses at elevated temperatures. The possible origin of the ionic hydrogen is considered to be dissociation that involves holes[30,41,43,49] ($\mathrm{Si}_3{\equiv}\mathrm{Si}{-}\mathrm{H} + h^+ \rightarrow \mathrm{Si}_3{\equiv}\mathrm{Si}^{\cdot} + \mathrm{H}^+$). This possibility is based on the observation that the released hydrogen transports in the oxide as a proton.[50,51] Protons are stable diffusing species as is neutral molecular hydrogen. The identification of the ion as H$^+$ is based on a large amount of circumstantial data in the literature suggesting a link between hydrogen ions and $N_{\mathrm{it}}$ formation.

In Secs. III and IV, we solved the system of equations consisting of a detailed-balance kinetic equation, i.e., Eq. (1); flow-rate equations, i.e., Eqs. (3) and (4); and a diffusion equation for charged species with the infinitely thick oxide boundary condition (Sec. III) and the finite oxide boundary condition (Sec. IV). The asymptotic behaviors of the analytical results for large $t$ are

$$N_{\mathrm{it}} \propto (D_X)^{3/4} E_{\mathrm{ox}}^{1} t^{1/2} \text{ for } -\text{BT aging} , \tag{42a}$$

$$\sim 0 \text{ for } +\text{BT aging} , \tag{42b}$$

irrespective of the boundary conditions of the infinite or finite oxide thickness. The numerical results are shown in Fig. 2. These results provide qualitatively the required asymmetrical behavior of the generation of $N_{\mathrm{it}}$ under positive- and negative-bias stresses at elevated temperatures.

However, Eq. (42a) does not quantitatively reproduce the functional dependence of $N_{\mathrm{it}}(t)$ on the oxide field $E_{\mathrm{ox}}$, aging time $t$, and the oxide thickness $T_{\mathrm{ox}}$ of empirical Eqs. (34) and (36). The derived $t^{1/2}$ dependence can be ascribed to the assumed constantness of the drift mobility of the charged species under the field, since this assumption inevitably leads to the ballistic transport[54] of the species in the oxide.

The actual transport of hydrogen ions in the oxide under the external fields was observed to be highly dispersive.[51,52] This property of hydrogen transport in the oxide is completely ignored in our calculation. In the analysis, for the sake of mathematical simplicity, we assumed unrealistically that the drift mobility of hydrogen ions across the oxide under the external electric field was constant. Furthermore, we have analyzed asymptotically the time dependence of $N_{\mathrm{it}}$ generation for large $t$ on the basis of the quasiequilibrium condition in Eq. (2), which holds only for a sufficiently small degree of generation,

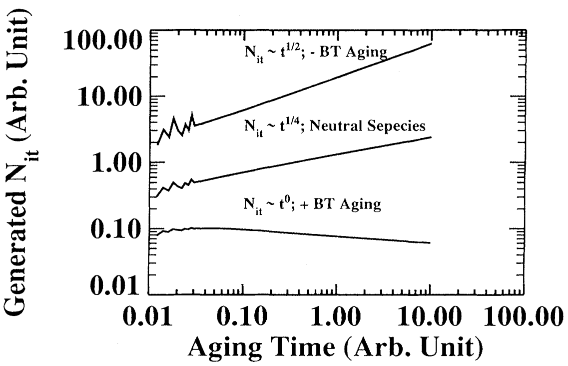


FIG. 2. Numerically calculated values of integrated interface-trap generation $N_{it}$ for positive- and negative-bias-temperature stresses for the positive ion transport model and neutral species model. The calculation is based on the diffusion-limited $N_{it}$ formation model for charged and neutral species discussed in detail in Secs. III and IV. Oscillations at the initial stage of generation are due to the numerical noise of the finite difference scheme used for numerical integration.

i.e., $N_{it} \ll N_D$. However, this condition does not hold for large $t$. Instead, for large $t$, we have to solve the nonlinear integrodifferential equation for $C_{Xi}(t)$, i.e., Eq. (1). This is because $N_{it}(t)$ solved for oxides of infinite or finite thickness, i.e., Eq. (16) or Eq. (28), respectively, contains the concentration $C_{Xi}(t)$ as a convolution integrand, if the species is assumed to be charged.

Therefore, the disagreement with the empirical expressions does not directly imply a failure of the hydrogen ion transport model, rather it can be ascribed to the inadequacy of our mathematical treatment. Showing quantitative agreement with experiments will require more elaboration.

## VII. CONCLUSIONS

In order to explain the various dependencies of the negative-bias-temperature instability at the ultrathin $SiO_2$-Si interface, we have generalized the diffusion-reaction concept to take into account the charged species as well as neutral diffusing species. The mathematical scheme consists of a detailed-balance equation for the first- or second-order chemical reaction and a diffusion equation for the reaction by-product whose interfacial concentration determines the reaction rate at the interface. The general solution of these coupled equations is characterized by its fractional-power time dependence and the corresponding exponential dependence on the activation energy over temperature, which comes from the temperature dependence of the diffusion coefficient. For the neutral-diffusing species, this scheme provides no information on the electric-field dependence. Thus, the experimentally observed field dependence can be ascribed to the nature of the fundamental electrochemical reaction. On the other hand, for charged-diffusing species, this scheme provides $E_{ox}^{1} t^{1/2}$ dependence.

Comparison of these mathematical predictions with experimental data leads us to conclude that the low-field charge-buildup instability of ultrathin $SiO_2$-Si interfaces under negative-bias temperature stresses can be successfully explained by our generalized diffusion-reaction model of diffusing molecular or atomic hydrogen with the boundary condition of an absorbing wall at the gate-electrode-oxide interface.

At this point, we would like to stress the generality of this scheme, i.e., the fact that its application is not restricted to the problem of negative-bias-temperature instability, which is of concern to the silicon-based electron-device community only. The diffusion-reaction concept can be applied to a wider range of physical phenomena, such as plasma etching and electrochemical reaction in the solid-state phase.

The physicoelectrochemistry in nanometer-range confined systems has been given less attention in spite of the recent great interest in the physics of nanometer-range electronic devices. The latter is widely studied because of characteristic "mesoscopic" phenomena, such as quantum interference and conductance fluctuation. However, the former has a close relationship to the long-term degradation of device characteristics, which consequently determines device reliability. Therefore, this problem is considered to have its own importance.

From this point of view, the investigation of the low-field instability at ultrathin $SiO_2$-Si interfaces has twofold significance: (1) The Si-$SiO_2$ interface is the most suitable system for investigating interface instability because of its reproducibility and controllability, and (2) silicon is suitable for fabricating nanometer or smaller features.

## ACKNOWLEDGMENTS

The authors are indebted to Dr. Katsutoshi Izumi, Dr. Sunao Ishihara, Dr. Atsushi Iwata, and Dr. Eisuke Arai for their advice and continuous encouragement throughout this work. The authors would like to thank Mitsuo Tsukada for several exciting and helpful discussions during the preparation of this manuscript. They also would like to thank Dr. Toshio Kobayashi, Dr. Shin-ichi Ohfuji, and Dr. Nobuyuki Sano for their kind and thoughtful suggestions for revising the original manuscript.

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