Modeling of field- and time-dependent resistance change phenomena under electrical stresses in Fe–O films

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An electrical stress-induced resistance change in an Fe–O film was studied in detail. Under constant voltage stress (CVS) and constant current injection, the resistance of the Fe–O film abruptly increased. The observed time-to-resistance increase (t_r) was found to depend on the applied voltage as well as on the injected current density. The total input energy until t_r also depended on the applied voltage. From these observations, the mechanisms of resistance change are considered to obey a field-enhanced reaction, and this resistance increase is attributed to a high-resistive Fe–O layer formation at the interface between the anode electrode and the low-resistive Fe–O layer. We proposed a simplified two-step model for the time evolution of the current under CVS [$I_{CVS}(t)$]. The predicted $I_{CVS}(t)$ showed a good agreement with experimental results. The model also explained the field dependence of t_r . © 2010 American Institute of Physics. [doi:10.1063/1.3273405]

I. INTRODUCTION

In accordance with successful advancements of shrinking microelectronic devices, there has been an increasing demand for new memory devices with high speed and reliable operations. Resistive random access memories (ReRAMs)^{1,2} have become one of the most promising candidates replacing present-day nonvolatile memories. Various binary-oxide materials such as TiO₂,³ NiO,⁴⁻⁶ CoO,⁷ ZrO,⁸ FeO,^{9,10} TaO,¹¹ and HfO₂ (Ref. 12) have been extensively investigated for ReRAM applications. The resistive switching behaviors in the above materials were reported, and the switching mechanisms have been studied from various aspects.^{4-6,10,11,13,14} In addition to data retention and endurance characteristics, the quality (reliability) of materials used for thin resistive layers is believed to be one of the critical concerns. Recently, in order to understand the basics of resistivity change, the timedependent behavior was studied for Fe-O films by using a constant voltage stress (CVS) technique.¹⁵ It was experimentally observed that the time-to-resistance increase (t_r) depended on the stress voltage, i.e., field dependent. From the polarity and field dependences of t_r , it was also suggested that the resistance change obeyed a thermochemical reaction mechanism associated with the redox reaction.¹⁰ However, the measurement of t_r was not enough in order to understand dynamic behavior (time-dependent resistance behavior) as well as the basic mechanisms, which are extremely important to assess a long-term reliability of the materials.

With regard to a time-dependent dielectric breakdown of SiO_2 (gate dielectric material)^{16,17} in metal-oxidesemiconductor field-effect transistors, a charge trapping behavior plays a key role for the reliability of SiO_2 , i.e., the long-term reliability. The charge trapping process has been studied by monitoring the time evolution of leakage current under an electrical stress.^{18,19} This time-dependent behavior is widely believed to determine the basic degradation process. Therefore, an evaluation of the time-dependent resistance change behavior is extremely important to understand the reliability of resistive films.

In this paper, field-enhanced and time-dependent resistance change phenomena under various electrical stresses are modeled for Fe–O-based films. We propose a simplified twostep model to describe the electrical stress-induced resistance change and apply the model to simulate the time evolutions of the current under CVS. In this model, the resistance increase is discussed by considering two stages of structural change: an areal increase in the high-resistive sites and the thickness growth of a high-resistive layer.

II. EXPERIMENTAL PROCEDURE

An Fe-O film with a thickness of 100 nm was deposited by rf magnetron sputtering process at 400 (denoted as "film A") and 490 °C (denoted as "film B") under a pressure of 2.0 Pa using an Fe₃O₄ target. As-deposited initial films were identified as a stoichiometric Fe₃O₄-containing film from a Fourier transform infrared spectrum.¹⁰ Also an Fe-O-based film with a multilayer structure (Fe₃O₄/Fe₂O₃/Fe₃O₄ =47.5/5.0/47.5 nm) (denoted as "film C") was prepared by the same magnetron sputtering process chamber at 400 °C. Those Fe-O films were sandwiched between the top and bottom Pt electrodes with a thickness of 100 nm. The area of the Fe–O film was $0.5 \times 0.5 \ \mu m^2$. Details of the fabrication process and test structure were reported elsewhere.¹⁰ In order to investigate a time-dependent resistance change, we applied a constant voltage (V_{st}) stress and injected a constant current (I_{st}) with different polarities; i.e., positive V_{st} and I_{st} correspond to the electron injection from the bottom electrode and negative $V_{\rm st}$ and $I_{\rm st}$ to that from the top electrode, respectively. All the electrical measurements were performed at room temperature. Samples without the electroforming process were used in this study in order to investigate the fun-

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FIG. 1. Examples of time evolution of (a) applied voltage under constant current injection [$V_{\text{CCS}}(t)$, upper figure] and (b) injected current under CVS [$I_{\text{CVS}}(t)$, lower figure] for different stress polarities. Time-to-resistance change (t_r) is judged as the changes in $V_{\text{CCS}}(t)$ and $I_{\text{CVS}}(t)$ as indicated, respectively.

damental characteristics.¹⁵ By monitoring an injected current under CVS $[I_{CVS}(t)]$, the time-to-resistance increase (t_r) was judged as a sudden change in resistance $[R(t)]:\Delta I_{CVS}/I_{CVS}$ >50%. With regard to the constant current stress (CCS) test, the time-to-resistance increase (t_r) was judged as a sudden increase in applied voltage $(|V_{CCS}(t)| > 0.5 \text{ V})$. Note that the higher V_{st} was found to induce the larger resistance increase.

III. RESULTS AND DISCUSSION

A. Field-enhanced time-to-resistance increase

Figures 1(a) and 1(b) show the time evolutions of $V_{\rm CCS}(t)$ and $I_{\rm CVS}(t)$ for film A under CCS and CVS, respectively. One can see the abrupt increase in the resistance resulting from the increase in $V_{\text{CCS}}(t)$ and the decrease in $I_{\text{CVS}}(t)$, respectively. One can also find that t_{r} under CCS is dependent on the injected current [Fig. 1(a)] and that under CVS is dependent on the applied voltage [Fig. 1(b)]. This is attributed to γ -Fe₂O₃ layer formation^{9,10,15} (higher resistance layer compared to Fe₃O₄ layer) by electrical stresses. Figures 2(a) and 2(b) show the obtained t_r as a function of I_{st} and V_{st} , respectively, for different stress polarities (film A). The solid lines are obtained by a least-squares fit. From these figures, one can confirm that the observed time-dependent resistance changes are field enhanced (i.e., functions of I_{st} and V_{st}), regardless of the stress configurations, CCS or CVS, and the stress polarities. The calculated slopes of t_r versus I_{st} and V_{st} are close to each other for both polarities, respectively. These findings indicate that the resistance increase is governed by the same fundamental mechanism, i.e., a thermochemical model. Since the time-to-resistance increase (t_r) is associated



FIG. 2. Time-to-resistance increase (t_r) as a function of (a) stress current (I_{st}) and stress voltage (V_{st}) for different stress polarities, respectively (positive stress: open circles; negative stress: closed circles). The solid lines are obtained by a least-squares fit.

with the oxygen ion diffusion and reaction process, 10,15 this process is described by the reaction rate constant k; $k \propto \exp(-\Delta H/k_BT)$, where k_B is Boltzmann's constant, T is the temperature, and ΔH is the enthalpy for the reaction usually referred to as activation energy depending on test structures, materials, and electric field. In particular, the dependence of enthalpy on the electric field was derived from the thermochemical model.^{15,17} Details will be discussed in Sec. III B.

We further investigate the relationship between t_r and the total input energy until the resistance change E_r . By monitoring $I_{CVS}(t)$ under CVS, E_r was calculated from

$$E_{\rm r} = \int_0^{t_{\rm r}} V_{\rm st} I_{\rm CVS}(t) dt.$$
⁽¹⁾

The results are shown in Fig. 3 for different stress polarities (film A). The longer t_r in the *x*-axis corresponds to the smaller V_{st} , i.e., lower electrical stress. Thus, Fig. 3 shows that E_r is field dependent. These findings indicate that the time-to-resistance increase depends on the electric field, rather than on the total input energy.

B. Modeling of time evolution of resistance change

Figure 4 shows the time evolution of $I_{\text{CVS}}(t)$ under CVS for films B and C. As shown in this figure, one can roughly



FIG. 3. Total input energy until the resistance change under CVS as a function of time-to-resistance increase (t_i) for various stress conditions with different polarities (positive stress: open circles; negative stress: closed circles).

see a two-step process for the time evolution of $I_{\text{CVS}}(t)$. Toward t_{r} , at first, $I_{\text{CVS}}(t)$ decreases slightly (in a low-resistive phase). Then, a steep and abrupt decrease in $I_{\text{CVS}}(t)$ is detected. (This step corresponds to the transition from low- to high-resistive phase in the present structure.) After the abrupt decrease in $I_{\text{CVS}}(t)$ at the time t_{r} , $I_{\text{CVS}}(t)$ tends to fall on the other curve exhibiting slight decrease in $I_{\text{CVS}}(t)$ or almost a constant value as seen in Fig. 4. Note that this step is in a high-resistive phase. The basic mechanism for the increase in R(t) is due to the γ -Fe₂O₃ layer formation on the anode electrode by the redox reaction of Fe₃O₄;¹⁰ 2Fe₃O₄+O²⁻ $\rightarrow 3\gamma$ -Fe₂O₃+2e⁻. In the below, we focus on this time dependence of $I_{\text{CVS}}(t)$ in detail.

Here we model the reaction process for the decrease in $I_{\text{CVS}}(t)$, i.e., R(t) increase. As illustrated in Fig. 5, we focus on the γ -Fe₂O₃-layer formation trigged by the diffusion of oxygen ions to the anode interface and the subsequent reaction. For the purpose of simplicity, two steps are now considered for the transition. (For details, see the Appendix.) The first step is the areal increase in the high-resistive γ -Fe₂O₃ site and the second the thickness growth of the high-resistive γ -Fe₂O₃ layer. The thickness of the low-



FIG. 4. Examples of time evolution of injected current under CVS $[I_{CVS}(t)]$ for various Fe–O films.



FIG. 5. Schematic illustration of the resistance change mechanism under an electrical stress for an Fe–O film. On the left is shown the structure before the stressing. As illustrated in the middle, the time-to-resistance increase is induced by the increase in the area of the high-resistive Fe–O nucleus. On the right, the scenario for further resistance increase by the increase in the high-resistive film thickness is depicted.

resistive Fe₃O₄ film before electrical stresses ($t_{\text{stress}}=0$) is denoted as d_0 (=100 nm) and the resistivity as ρ_{L} . The resistance is expressed as $R = \rho_{\text{L}} d_0 / S_0$,²⁰ where S_0 is the area of the Fe₃O₄ film (=0.25 μ m²). As indicated in Fig. 5, when a stress voltage of V_{st} is applied [in this case, negative bias ($V_{\text{st}}<0$) is assumed], oxygen ions diffuse toward the bottom (anode) electrode interface. This leads to the formation of high-resistive γ -Fe₂O₃ sites (the resistivity= ρ_{H}). In the course of stress time during this stage, the total area of highresistive γ -Fe₂O₃ site [$S_{\text{H}}(t)$] increases. Thus, one can describe the time-dependent resistance R(t) as

$$R(t) = \rho_{\rm L} \frac{d_0 - d_{\rm n}}{S_0} + \rho_{\rm H} \rho_{\rm L} \frac{d_{\rm n}}{\rho_{\rm L} S_{\rm H}(t) + \rho_{\rm H} [S_0 - S_{\rm H}(t)]}, \qquad (2)$$

where d_n is the thickness of the high-resistive γ -Fe₂O₃ nucleus (d_n =1 nm in this study). Since the increasing rate of the total area of the high-resistive site [$dS_H(t)/dt$] is considered to be in proportion to the flux of ions [\propto electric field (= V_{st}/d_0)], the time dependence of the total high-resistive area $S_H(t)$ is given by

$$S_{\rm H}(t) = \zeta(V_{\rm st}, T) \left(\mu \frac{V_{\rm st}}{d_0}\right) n_{\rm O} t^{\alpha},\tag{3}$$

where μ is the effective mobility of oxygen ion under an electric field. n_0 is the volume density of mobile oxygen ions. $\zeta(V_{\rm st}, T)$ is a field- and temperature-dependent reaction constant, at the anode. The $\zeta(V_{\rm st}, T)$ corresponds to the reaction constant *k* as mentioned in Sec. III A. α (=1) is a power-law component. For charged hydrogen-related species in SiO₂, the time dependence of the SiO₂–Si interface state generation was determined by α =1/2 from a diffusion-reaction model with the competing hydrogen release and passivation process.²¹ (See the Appendix.) From Eqs. (2) and (3), the time evolution of current $I_{\rm CVS}(t)$ can be calculated by using $I_{\rm CVS}(t) = V_{\rm st}/R(t)$.

At the second step, the thickness of the high-resistive γ -Fe₂O₃ layer increases. The time-dependent resistance R(t) can be expressed as

$$R(t) = \frac{f\rho_{\rm L}d_0 + (1-f)\rho_{\rm L}d_{\rm H}(t)}{fS_0},$$
(4)

where $d_{\rm H}(t)$ is the time dependence of the thickness of the high-resistive γ -Fe₂O₃ layer as shown in Fig. 5. *f* is the ratio of $\rho_{\rm L}$ to $\rho_{\rm H}$ (= $\rho_{\rm L}/\rho_{\rm H}$). The flux of ionic species is determined

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FIG. 6. Time evolution of currents $I_{\text{CVS}}(t)$ simulated for various Fe–O films on the basis of the proposed model (broken lines). (a) Film A and (b) films B and C. The calculated results show a good agreement with the experimental data (solid lines).

by the drift and diffusion terms in a drift-diffusion model: As the thickness of the high-resistive layer increases, that of the low-resistive layer decreases. This leads to the decrease in the electric field in the low-resistive layer, resulting in the decrease in an oxygen ion flux. It is also expected that the local temperature increase by Joule heating decreases with the increase in the resistance. Therefore, we can assume the maximum thickness of the high-resistive layer (d_{max}). Then, the growth rate of $d_{\rm H}(t)$ can be described as

$$\frac{d}{dt}[d_{\rm H}(t)] = \beta(V_{\rm st}, T) \left(\mu \frac{fV_{\rm st}}{fd_0 + (1 - f)d_{\rm H}(t)} \right) n_{\rm O}[d_{\rm max} - d_{\rm H}(t)],$$
(5)

where $\beta(V_{\text{st}}, T)$ is a field- and temperature-dependent constant, at the reacting interface. In Eq. (5), $[d_{\text{max}}-d_{\text{H}}(t)]$ corresponds to the thickness of the remaining low-resistive layer. Therefore, once $d_{\text{H}}(t)$ is determined by Eq. (5), the time evolution of current $I_{\text{CVS}}(t)$ can be calculated from Eq. (4) and V_{st} .

Figures 6(a) and 6(b) indicate examples of simulated results from the proposed model. The results are compared with the experimental data in Figs. 1 and 4. Figure 6(a) shows $I_{CVS}(t)$ of film A under different stress voltages, while

Fig. 6(b) shows $I_{CVS}(t)$'s of films B and C. In these calculations, d_{max} is set to be 3 nm, and other material- and structure-dependent parameters such as reaction constants are used as fitting parameters in accordance with experimental data. In Fig. 6, the resistivities of Fe₃O₄ and γ -Fe₂O₃ ($\rho_{\rm L}$ and $\rho_{\rm H}$) are determined to be (0.040, 350 Ω cm at -1.9 V), (0.0125, 0.40 $\,\Omega$ cm at -1.05 V), and (0.055, 1.2 $\,\Omega$ cm at 2.2 V) for films A, B, and C, respectively. It was reported that the film structures and process temperature strongly affect the resistance,¹⁰ and, in some cases, the resistance itself depends on the applied voltages. Thus, these differences in this study may be expected because the film structure and process temperature impacting on the resistivity are different from each other. As seen in these figures, the simulated $I_{\text{CVS}}(t)$ shows a good agreement with the experimental result, including the thickness growth step of the high-resistive γ -Fe₂O₃ layer (the second step). Thus, one can conclude that the time evolution of $I_{CVS}(t)$ observed in this study is attributed to the respective two steps for the high-resistive area increase and the thickness growth in Fe-O films.

Finally, we focus on the $V_{\rm st}$ -dependence of $t_{\rm r}$, i.e., the field-enhanced mechanism of resistance change observed in Fig. 2(a). The corresponding field-enhanced factor is expressed by $\exp(-\gamma V_{\rm st})$, where γ is a temperature-dependent constant. By taking into account the definition of $t_{\rm r}$ judgment for the transition from low- to high-resistive phase as observed in Figs. 1 and 4, the $t_{\rm r}$ can be set to be equal to the time when the abrupt decrease in $I_{\rm CVS}(t)$ occurs.

$$S_0 \approx \int_0^{t_{\rm r}} \zeta(V_{\rm st}, T) \left(\mu \frac{V_{\rm st}}{d_0} \right) \left(\frac{n_{\rm O}}{d_{\rm n}} \right) dt.$$
 (6)

Since the redox reaction obeys the so-called Arrhenius behavior, by taking into account that a field-dependent enthalpy is lowered linearly by an electric field increase affecting dipole moment,¹⁷ one can write $\zeta(V_{\rm st}, T)$ in Eq. (3) in the form of $\zeta(V_{\rm st}, T) \propto \exp(-\Delta H/k_B T)$.¹⁵ Thus, $t_{\rm r}$ is determined by

$$t_{\rm r} = \left(S_0 \frac{d_0 d_{\rm n}}{\zeta(V_{\rm st}, T) \mu V_{\rm st} n_{\rm O}}\right) \propto \frac{1}{V_{\rm st}} \exp\left(\frac{\Delta H(V_{\rm st}, T)}{k_B T}\right)$$
$$\sim \frac{1}{V_{\rm st}} \exp(-\gamma V_{\rm st}). \tag{7}$$

Since the exponential term is dominant, t_r is governed by the field-enhanced term $exp(-\gamma V_{st})$, which is deduced from the thermochemical model and observed experimentally. This explains the V_{st} -dependence of t_r as shown in Fig. 2(b) and in a previous report.¹⁵ Moreover, based on the above findings, we can suggest that an anode (electrode) interface plays a key role on determining the behavior of resistance change in Fe–O films for ReRAM applications.

IV. CONCLUSION

The dependence of time-to-resistance increase (t_r) in Fe–O films was investigated for different stress configurations, CCS and CVS. The electric stress field dependences of t_r were clarified to be the same mechanism, regardless of the stress configuration and polarity. The total input energy until t_r was found to be determined by the electric field strength. We proposed a simplified model for the time evolution of current under CVS toward the resistance change by considering the two-step structural change in the Fe–O film. The model was based on the areal increase in the high-resistive site at the anode interface as the first stage and then, the thickness increase in the layer as the second. The proposed model predicted the experimentally observed $I_{CVS}(t)$ curves with a good agreement. Moreover, it explained the field dependence of t_r . The proposed model provides an extensive understanding for resistance change phenomena as well as the reliability assessment under various operations.

APPENDIX: MODEL FOR TIME EVOLUTION OF RESISTANCE

At first we define the resistivities of Fe₃O₄ and γ -Fe₂O₃ as $\rho_{\rm L}$ and $\rho_{\rm H}$, respectively. The resistances of Fe₃O₄ and γ -Fe₂O₃ are expressed,²⁰ respectively, as

$$R_i = \rho_i \frac{d_i(t)}{S_i(t)} \quad (i = \mathrm{H}, \mathrm{L}), \tag{A1}$$

where $d_i(t)$ and $S_i(t)$ (*i*=H,L) are the thicknesses and areas of the "low-" and "high-" resistive regions at the stress time *t*, respectively. As illustrated in Fig. 5, we now consider two steps as noted below.

1. First step (nucleation step)

As shown in Fig. 5, the total resistance of the film at the time t is determined from the sum of resistance. This is given by

$$R(t) = \rho_{\rm L} \frac{d_0 - d_{\rm n}}{S_0} + \rho_{\rm H} \rho_{\rm L} \frac{d_{\rm n}}{\rho_{\rm L} S_{\rm H}(t) + \rho_{\rm H} [S_0 - S_{\rm H}(t)]}, \quad (A2)$$

where d_0 and d_n are the thicknesses of the low-resistive film at t=0 and that of the high-resistive nucleus, respectively, and S_0 is the area of the anode interface. $S_H(0)$ is the total area of the high-resistive site at the time *t*. Note that $S_H(0) = 0$.

During the electrical stressing, oxygen ions diffuse from the cathode to the anode by the electric field across the film $(=V_{st}/d_0)$. The increase in $S_H(t)$ is governed by the redox reaction with the oxygen ions at the interface. The increasing rate of $S_H(t)$ is determined by an equation including the flux of oxygen ions (dependent on the electric field strength) and a reaction constant $\zeta(V_{st}, T)$. Thus, one can write the following equation as the first-order approximation:

$$\frac{dS_{\rm H}(t)}{dt} = \zeta(V_{\rm st}, T) \left(\mu \frac{V_{\rm st}}{d_0}\right) n_{\rm O},\tag{A3}$$

where μ is the effective mobility of oxygen ion under an electric field, respectively. n_0 is the volume density of mobile oxygen ions. $\zeta(V_{\rm st}, T)$ is a field- and temperature-dependent reaction constant, at the anode. This results in

$$S_{\rm H}(t) = \zeta(V_{\rm st}, T) \left(\mu \frac{V_{\rm st}}{d_0}\right) n_{\rm O} t.$$
 (A4a)

The reaction constant should obey the so-called Arrhenius behavior; thus, by taking into account that a field-dependent enthalpy is lowered linearly by an electric field increase,¹⁷ one can write $\zeta(V_{st}, T)$ in Eq. (A3) in the form of $\zeta(V_{st}, T) \propto \exp(-\Delta H/k_B T)$,¹⁵ where k_B is Boltzmann's constant, *T* is the temperature, and ΔH is the enthalpy for the reaction. As mentioned in the main text, by reviewing previous studies concerning the field-induced diffusions of hydrogen ions,^{21–23} Eq. (A4a) is described in a generalized form as

$$S_{\rm H}(t) = \zeta(V_{\rm st}, T) \left(\mu \frac{V_{\rm st}}{d_0}\right) n_{\rm O} t^{\alpha}, \tag{A4b}$$

where α (<1) is a power-law constant. For charged hydrogen-related species in SiO₂, α was determined to be 1/2, and for the neutral species, α , to be 1/4 from a diffusion-reaction model.²¹ In the present model, only oxygen ion is assumed to diffuse and the redox reaction is strongly field dependent;¹⁰ α is assumed to be unity for simplicity. Note that the power-law model expressed in Eq. (A4b) was also found to explain the characteristic $I_{\text{CVS}}(t)$ observed in Figs. 1 and 4. Then, from Eqs. (A2) and (A4a), the time evolution of current $I_{\text{CVS}}(t)$ can be calculated by using the stress voltage V_{st} as

$$I_{\rm CVS}(t) = \frac{V_{\rm st}}{R(t)}.$$
 (A5)

Moreover, the time-to-resistance change t_r is approximately equal to the time when $S_H(t) \rightarrow S_0$. Thus, from Eq. (A4b), t_r is given by

$$t_{\rm r} \approx \left(S_0 \frac{d_0 d_{\rm n}}{\zeta(V_{\rm st}, T) \mu V_{\rm st} n_{\rm O}}\right)^{1/\alpha} \propto \frac{1}{V_{\rm st}^{-1/\alpha}} \exp\left(\frac{\Delta H(V_{\rm st}, T)}{\alpha k_B T}\right).$$
(A6)

Since the exponential term is dominant, t_r is expressed by the field-enhanced term; $exp(-\gamma V_{st})$ for the case $\alpha = 1$, when considering that the enthalpy is lowered linearly by an electric field increase on the basis of the thermochemical model mentioned in the above. This is consistent with the data experimentally observed in Fig. 2 and the other data.¹⁵

2. Second step (film growth step)

At the time when the surface of the anode electrode is almost covered by the high-resistive site, i.e., $S_{\rm H}(t) \sim S_0$, the high-resistive layer growth starts (see Fig. 5). The voltages across high- and low-resistive layers can be expressed, respectively, by

$$V_{\rm H}(t) = \frac{I_{\rm CVS}(t)}{S_0} \rho_{\rm H} d_{\rm H}(t), \qquad (A7a)$$

$$V_{\rm L}(t) = \frac{I_{\rm CVS}(t)}{S_0} \rho_{\rm L} [d_0 - d_{\rm H}(t)], \qquad (A7b)$$

where $V_i(t)$ and $d_i(t)$ (*i*=H,L) are the voltage and the thickness of the layer at the time *t*, respectively. Note that $V_i(t)$ and $d_i(t)$ should hold

$$V_{\rm st} = V_{\rm L}(t) + V_{\rm H}(t), \tag{A8}$$

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$$d_0 = d_{\rm L}(t) + d_{\rm H}(t).$$
 (A9)

The flux of ionic species is determined by a drift-diffusion model. By assuming the maximum thickness of the high-resistive layer (d_{max}) , the growth rate of $d_{\text{H}}(t)$ can be described as

$$\frac{d}{dt}[d_{\rm H}(t)] = \beta(V_{\rm st}, T) \left(\mu \frac{V_{\rm L}(t)}{d_0 - d_{\rm H}(t)}\right) n_{\rm O}[d_{\rm max} - d_{\rm H}(t)]$$
$$= \beta(V_{\rm st}, T) \left(\mu \frac{fV_{\rm st}}{fd_0 + (1 - f)d_{\rm H}(t)}\right) n_{\rm O}[d_{\rm max}$$
$$- d_{\rm H}(t)], \tag{A10}$$

where $\beta(V_{st}, T)$ is a temperature-dependent reaction constant describing the redox reaction at the reacting interface, and *f* is defined by $f = \rho_{\rm L}/\rho_{\rm H}$ ($f \ll 1$). Once $d_{\rm H}(t)$ is determined, one can calculate, $I_{\rm CVS}(t)$ by solving Eqs. (A7a), (A7b), and (A8) as

$$I_{\rm CVS}(t) = \frac{fS_0}{f\rho_{\rm L}d_0 + (1-f)\rho_{\rm L}d_{\rm H}(t)} V_{\rm st}.$$
 (A11)

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