Defect Chemistry and Resistance Degradation in Fe-doped SrTiO₃ Single Crystal

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Defect chemistry and transport in Fe-doped SrTiO₃ single crystal are studied to understand its resistance degradation mechanism. The temporal evolution of electric conductivity under a voltage stress was obtained computationally by solving the transport equations for ionic and electronic defects coupled with the defect reaction equilibrium equations. The computational results are compared to the corresponding experimental measurement under similar conditions. It is shown that the local electron and hole concentrations are controlled by the local electronic defect equilibria rather than by their quasi-steady state diffusional transport. It is the electric field-induced migration of oxygen vacancies and the subsequent instantaneous reestablishment of the local defect equilibria that lead to the resistance degradation. The resistance degradation behavior and the defect distributions under a long-term voltage stress are strongly influenced by the sample-annealing oxygen partial pressure, degrading electric field, and temperature. The present study contributes to the understanding of resistance degradation mechanism and provides guidance to improve the lifetime and reliability of wide band-gap semiconducting capacitors.

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1. Introduction

The resistance random access memories (ReRAMs) have received considerable attentions due to their potential applications in microelectronics [1-5]. The core element of a ReRAM is a capacitor composed of insulating or semiconducting transition metal oxides such as SrTiO₃, BaTiO₃, and TiO₂, etc. The reliability and lifetime of semiconducting capacitors are limited by the voltage-induced resistance degradation process.

The resistance degradation process of both dielectric/ferroelectric ceramics and single crystals has been extensively studied [6-21]. For example, Waser *et al.* investigated the resistance degradation rates for SrTiO₃ ceramics [8] and single crystals [9] and their dependence on the dopant concentration, temperature, and the applied dc voltage. They found that the electromigration and a concentration polarization of oxygen vacancies between the cathode and anode caused the degradation [8,9]. Yang *et al.* explored the microchemical and microstructural origins of the resistance degradation in BaTiO₃-based commercial capacitors using the complementary impedance spectroscopy and analytical transmission electron microscopy. They showed that the oxygen vacancy concentration increased across the dielectric layers towards the cathode while decreased toward the anode region [14,15]. By employing the electron microscopy, diffraction and spectroscopy, Moballegh *et al.* investigated the local interface microstructure and microchemistry evolution during degradation of a TiO₂ single crystal, and they confirmed an accumulation of substoichiometric point defects at the cathode electrode [21]. It was commonly accepted that the redistributions of defects, in particular the oxygen vacancies play an important role in the resistance degradation process.

In contrast to the experimental studies, there have been very few theoretical studies on resistance degradation [22-26] or bipolar switching behaviors [27-29] of semiconducting capacitors. A common characteristic in the existing models is that a drift-diffusion equation for oxygen vacancy was solved in a time domain by treating the ionic flux across the interface as a boundary condition within the dilute solution approximation [22-26]. However, there has been no consensus as to the description of electronic defect evolution during a resistance degradation processes. For example, by obtaining the electron and hole concentrations assuming of local (herein and hereafter ‘local’ means each spatial position in the sample) ionization and electronic generation/recombination equilibria in Fe-doped SrTiO₃ single crystals, Baiatu *et al.* reported that under a dc voltage a charge depletion layer forms, and the effective resistance changes up to several orders of magnitude with the actual magnitude dependent on the ionization energy of defects [22]. However, by solving the steady-state equations to obtain the local electron and hole concentrations, Meyer [23] and Cao [24] *et al.*’s did not observe the formation of a charge depletion layer, and the effective resistance changes are relative small, within a range of at most one order of magnitude, during a degradation process. These two treatments of electronic defects, namely, local defect reaction equilibrium and steady state defect transport, represent the two limits for determining the local concentrations of electrons and holes.

In practice, for instance in an Fe-doped SrTiO₃, the doubly ionized oxygen vacancy is one of the main ionic defects that migrate under external voltage. The voltage-induced redistribution of the oxygen vacancies changes the local electronic equilibria and the effective resistance. This resistance degradation process is complicated and depends on many factors

such as sample preparation and working conditions, e.g., dopant concentration, annealing temperature, annealing oxygen partial pressure, working temperature, and working electric field. Exploring effects of these conditions on the defect equilibria and transports using computational simulation is expect to contribute to the understanding of the degradation mechanism and improvement of the capacitor reliability.

In this work, we first studied defect concentrations and conductivities based on defect chemistry during sample annealing and quenching processes (Section 2). We then obtained the temporal evolution of electric conductivity/resistance of an Fe-doped SrTiO₃ single crystal under a dc voltage using computer simulations by assuming reaction equilibria or diffusional steady state of electrons and holes (Section 3). The results are compared to the corresponding experimentally measured temporal evolution of conductivity/resistance. We then studied the effects of sample preparation and working conditions on the degradation process (Section 4). In section 5, we discussed the possible effects of polarons.

2. High-Temperature Annealing

2.1 Defect Chemistry

In SrTiO₃, the intrinsic disorder was Schottky-type in which cation and anion vacancies are simultaneously created to maintain electrical charge neutrality as well as chemical stoichiometry [30,31]. The predominant cation vacancies are strontium vacancies V_{Sr}'' [32-34], and the complete formation reaction of V_{Sr}'' and oxygen vacancies $V_{\text{O}}^{\bullet\bullet}$ is [12,35-37]

where the Kröger-Vink notation is used. At temperature below 1500K, the mobility of V_{Sr}'' is so low that the reaction R1 can be regarded as frozen-in such that the dominant ionic conduction originates from oxygen vacancies [3,38-40]. The concentration of oxygen vacancies $V_O^{\bullet\bullet}$ is controlled by the reduction reaction at the solid/gas interface

the reaction rates of which strongly depends on the oxygen partial pressure and temperature. According to Chan, Sharma, and Smith's discussion, the oxygen vacancies are mostly double ionized over the whole range of laboratory-achievable oxygen partial pressure, which had subsequently been verified in many experimental findings [41,42]. Therefore, in this work we only consider doubly ionized oxygen vacancies.

In an Fe-doped $SrTiO_3$ single crystal, the Ti atoms are partially substituted by Fe atoms and exhibit mixed oxidation states of +3 (Fe_{Ti}') and +4 ($Fe_{Ti}^{\times}$), and the Fe^{3+} acts as acceptor dopant. The defect reaction equilibrium between Fe^{3+} and Fe^{4+} is through creation of holes, i.e.,

The recombination and generation of electrons and holes are controlled by the intrinsic electronic defect reaction,

where *nil* is the thermodynamic standard state of the crystal in which all of the electronic

carriers are in their respective ground state. In the case of dilute defects, the equilibrium defect concentrations at high-temperature satisfy the mass-action law. For Fe-doped SrTiO₃, the constants in the mass-action laws had been systematically measured and summarized by Denk *et al.* and Moos *et al.* (see Table I [11,12,43]) although some constants at certain conditions had been obtained at earlier time [22,44-46].

Combining the mass action laws with the charge-neutrality condition

$$2[V_O^{\bullet}] + p = [Fe^{3+}] + n \quad (2.1)$$

and mass-conservation equation of iron

$$[Fe^{3+}] + [Fe^{4+}] = C_a, \quad (2.2)$$

where n , p , C_a are the concentrations of electrons, holes, and the Fe acceptor dopants, respectively, the equilibrium defect concentrations can be calculated at different annealing temperatures and oxygen partial pressures (P_{O_2}).

2.2 Equilibrium Defects Concentrations in Annealed Fe-doped SrTiO₃

Figs. 1a and 1b show dependence of equilibrium defect concentrations on the annealing P_{O_2} at different temperatures calculated using the mass-action constants from Table I. The weight concentration of the doped iron in our experimental sample is 100 ppm corresponding to an atomic concentration of $5.58 \times 10^{18} \text{ cm}^{-3}$. It can be seen from Fig. 1a and 1b that the type of the semiconductor is determined by the oxygen partial pressure, i.e., at low P_{O_2} region it is n -type while at high P_{O_2} region it is p -type. The oxidation state of iron atoms is Fe^{3+} when P_{O_2} is lower than 10^{-5} bar, while Fe^{4+} concentration increases until P_{O_2}

reaches 10^5 bar making Fe^{4+} predominant. The concentration of oxygen vacancies decreases with increase in p_{O_2} . This trend becomes stronger above 10^0 bar. However, it is impossible to totally eliminate the oxygen vacancies under the laboratory conditions because there is always an equilibrium concentration of intrinsic point defects at finite temperatures [47-49]. The effect of temperature on defect equilibrium concentrations is illustrated in Fig. 1a and 1b. As expected, the concentrations of the electrons and holes increase with temperature due to the enhanced thermal agitation that results in continuous excitation of electrons and holes from the valence band to the conduction band. The Fe^{3+} and Fe^{4+} concentrations increase and decrease, respectively, as a consequence of the charge neutrality requirement.

There are differences between the results calculated from Denk *et al.*'s and Moos *et al.*'s mass-action law constants. It can be seen that at high p_{O_2} region the oxygen vacancy concentration has a stronger dependence on p_{O_2} with Moos *et al.*'s constants, and the hole concentrations are lower than those using Denk *et al.*'s constants. However, the overall defect equilibria from these two sets of constants still are very similar, which will be further confirmed by the high-temperature conductivity results discussed below.

2.3 Effective Electric Conductivities of Annealed Fe-doped SrTiO_3

During annealing, the species of oxygen vacancies, electrons, and holes are mobile. With the knowledge of their concentrations as well as their mobility (see Table II), the effective specific and total conductivities as functions of sample-annealing conditions can be calculated using

$$\begin{aligned}\sigma_{V_{\text{O}}} &= 2e_0\mu_{V_{\text{O}}}[V_{\text{O}}^{\bullet\bullet}], \quad \sigma_n = e_0\mu_n n, \quad \sigma_p = e_0\mu_p p, \\ \sigma_{\text{total}} &= \sigma_{V_{\text{O}}} + \sigma_n + \sigma_p\end{aligned}\quad (2.3)$$

As shown in Fig. 2a and 2b, the conductivities of the oxygen vacancies, electrons, and holes calculated using both Denk *et al.*'s and Moos *et al.*'s mass-action constants depend strongly on the annealing p_{O_2} and temperature. Corresponding to the defects concentrations in Fig. 1a and 1b, both Fig. 2a and 2b show that the dominant contribution to the total conductivity comes from electrons at low p_{O_2} (below 10^{-20} bar) and from holes at high p_{O_2} (above 10^0 bar). In the intermediate p_{O_2} region (from 10^{-20} to 10^0 bar) the ionic conductivity is dominant. At a given p_{O_2} , the conductivities of electrons, holes, and oxygen vacancies increase with temperature as expected. The electronic conductivity increase is mainly due to the increase of electronic concentration with increasing temperature which overwhelms the negligible mobility decrease of the electronic defects. On the other hand, the increase in ionic conductivity is mainly attributed to the increase in oxygen vacancy mobility (based on Table II) as the ionic concentration is less dependent on temperature at intermediate p_{O_2} .

2.4 Quenching

In our experiment, the Fe-doped SrTiO_3 single crystals were annealed at temperature of 900 °C and p_{O_2} of 2×10^{-5} bar for 12 hours and then quenched to room temperature. The degradation process was characterized at 210 °C. At temperature lower than 700K, the oxidation/reduction reactions at the solid/gas interface becomes negligible, and the reaction R2 can be regarded as frozen-in, and thus the total amount of the oxygen vacancies in the crystal remains constant during degradation [9,22,50]. However, the ionization reaction R3

and band-band transfer reaction R4 are still active so that n , p , and the ratio of $[\text{Fe}^{3+}]/[\text{Fe}^{4+}]$ can change because of the change in band gap and the shift in Fermi energy when the temperature is changed from 900°C to 210°C.

Fig. 3a and 3b show the defect concentrations at temperatures of 900°C and 210°C calculated using Denk *et al.*'s and Moos *et al.*'s mass-action constants, respectively. It can be seen that at the low p_{O_2} region (below 10^{-13} bar) the electron concentrations before and after quenching are almost the same. The electron concentration has a sharp decrease at $p_{\text{O}_2} \approx 10^{-12}$ bar. The hole concentration drops significantly through the entire p_{O_2} region considered, but when $T=210$ °C it has a sharp jump at $p_{\text{O}_2} \approx 10^{-12}$ bar. When p_{O_2} is above 10^{-12} bar, quenching greatly decreases both electron and hole concentrations because of their recombination while the amount of Fe^{4+} remains about the same. Note that the logarithmic scale is used to show the defects concentrations. Although very low defect concentrations are not experimentally detectable, they are included to indicate their variation with oxygen partial pressure.

The conductivity differences between 900°C and 210°C are shown in Fig. 4a and 4b. At the low p_{O_2} region (below 10^{-13} bar), the total conductivity increases nearly one order at 210°C because at this region the deterministic conductivity originates from electrons for which quenching does not change the concentration (see Figs. 3a and 3b) but increase the mobility (see Table II).

On the other hand, when p_{O_2} is above 10^{-12} bar, quenching decreases the total conductivity by at least 3 orders of magnitude depending on p_{O_2} because each individual

defect conductivity is decreased. The decrease of the electronic conductivity is due to the recombination of electrons and holes during quenching, and the decrease of the ionic conductivity is mainly due to the decrease in mobility. However, quenching does not change the predominant conductivity contributions, i.e., the oxygen vacancy contribution is predominant when $10^{-11} < p_{O_2} < 10^0$ bar and the hole is predominant when $p_{O_2} \geq 10^0$ bar.

As shown above, for both defect equilibria and conductivities of annealed and quenched crystals, there is no big difference between the results calculated from Denk *et al.*'s and Moos *et al.*'s mass-action constants. Therefore, hereafter we will just use Denk *et al.*'s constants to study the defect transport properties.

3. Defect Transport

3.1 Transport Equations

As shown in Table II, at the degradation temperature of 210 °C, the mobility of the oxygen vacancy is on the order of $10^{-9} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is extremely low compared to that of electrons and holes (about $10^0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). Therefore, under an electric field, the slow migration of the oxygen vacancies dictates the long-time defect concentration evolution. The evolution of oxygen vacancies is described by the classic Nernst-Planck transport equation, i.e.,

$$\begin{aligned} J_{V_{\ddot{O}}} &= -q_{V_{\ddot{O}}} D_{V_{\ddot{O}}} \nabla[V_{\ddot{O}}] + q_{V_{\ddot{O}}} \mu_{V_{\ddot{O}}} [V_{\ddot{O}}] E, \\ \frac{\partial[V_{\ddot{O}}]}{\partial t} &= -\frac{1}{q_{V_{\ddot{O}}}} \nabla \bullet J_{V_{\ddot{O}}}, \end{aligned} \quad (3.1)$$

where $q_{V_{\ddot{O}}}$, $D_{V_{\ddot{O}}}$, $\mu_{V_{\ddot{O}}}$, and $J_{V_{\ddot{O}}}$ represent the charge, diffusivity, mobility, and flux of

oxygen vacancy, respectively. $D_{V_{\text{O}}}$ relates to $\mu_{V_{\text{O}}}$ through the Nernst-Einstein equation $D_{V_{\text{O}}} = \mu_{V_{\text{O}}} k_B T / |q_{V_{\text{O}}}|$. The first term and second term of $J_{V_{\text{O}}}$ in Eq. (3.1) represent the flux contributions from diffusion $J_{V_{\text{O}}}^{\text{diff}}$ and drift $J_{V_{\text{O}}}^{\text{drift}}$, respectively. In order to solve Eq. (3.1), we adopted essentially the same method in Baiatu *et al.*'s paper [22]. A sample is partitioned into N slices with equal thickness Δx along the x axis. Then, the differential Eq. (3.1) is converted into a finite difference equation:

$$\Delta[V_{\text{O}}](i, t) = -\frac{\Delta J_{V_{\text{O}}}(i, t)}{q_{V_{\text{O}}} \Delta x} \Delta t, \quad (3.2)$$

where i represents the i th slice of the partitioned sample and $\Delta J_{V_{\text{O}}}(i, t)$ is considered to be the flux change of the i th slice at time t equaling to

$$\Delta J_{V_{\text{O}}}(i, t) = J_{V_{\text{O}}}^{\text{out}}(i, t) - J_{V_{\text{O}}}^{\text{in}}(i, t) \quad (3.3)$$

with

$$\begin{aligned} J_{V_{\text{O}}}^{\text{out}}(i, t) &= J_{V_{\text{O}}}(i, t), \\ J_{V_{\text{O}}}^{\text{in}}(i, t) &= J_{V_{\text{O}}}(i-1, t). \end{aligned} \quad (3.4)$$

Combining Eq. (3.2) and Eq. (3.3) we have

$$[V_{\text{O}}](i, t + \Delta t) = [V_{\text{O}}](i, t) + \frac{J_{V_{\text{O}}}^{\text{in}}(i, t) - J_{V_{\text{O}}}^{\text{out}}(i, t)}{q_{V_{\text{O}}} \Delta x} \Delta t. \quad (3.5)$$

With the knowledge of the ionic fluxes across the cathode and anode boundaries, the boundary condition of Eq. (3.5) can be directly set as

$$\begin{aligned} J_{V_{\text{O}}}^{\text{out}}(i = N) &= J_{V_{\text{O}}}^{\text{cathode}}, \\ J_{V_{\text{O}}}^{\text{in}}(i = 1) &= J_{V_{\text{O}}}^{\text{anode}}. \end{aligned} \quad (3.6)$$

As an initial condition, i.e., before applying the voltage, the defect distributions through the

whole sample are assumed to be homogeneous. Under a voltage difference, the electric field inside the sample at $t=0$ is also homogeneous and can be simply calculated using $E=U/d$ where U is the applied voltage and d is the thickness of the sample. After one-step iteration for the oxygen vacancy distribution, there are two different ways to obtain the electron and hole concentrations. The first way is to consider each local slice of the sample as a thermodynamic equilibrium [22], i.e., the local thermodynamic equilibrium condition for electronic species, and then calculate the electron and hole concentrations using the same method in Section 2. In this way, the ionization reaction R3 and electronic generation/recombination reaction R4 are regarded as fast enough to consider a full compensation from electrons and holes.

The second way is to solve the steady-state equation for electrons

$$\frac{\partial n}{\partial t} = D_n \nabla^2 n + \mu_n \nabla \cdot [n\mathbf{E}] = 0, \quad (3.7)$$

with fixed-concentration boundary conditions [23,24] by assuming constant band gap (Eq. R4) and “Fermi level pinning” effect

$$n|_{i=1,N} = N_c \exp\left(-\frac{E_c - E_{fm}}{k_B T}\right), \quad (3.8)$$

where $N_c = 3.0 \times 10^{21} \text{ cm}^{-3}$ the effective density of states of the conduction band [22], $E_c = 2.00 \text{ eV}$ the energy of the conduction band (correspondingly the energy of valence band $E_v = -1.12 \text{ eV}$), and $E_{fm} = 0.0 \text{ eV}$ the work function of the metal electrode, respectively. Once the electron and hole concentrations are obtained, the local conductivity $\sigma(i)$ and further the effective conductivity σ^{eff} of the crystal can be calculated as following

$$\sigma(i) = 2e_0\mu_{V_0}[V_0] + e_0\mu_n n + e_0\mu_p p$$

$$\sigma^{\text{eff}} = \frac{1}{\sum_{i=1}^N \frac{1/N}{\sigma(i)}} \quad , \quad (3.9)$$

where e_0 is the unit charge and N is the grid number used in the simulation.

The local electric field can be calculated according to the Maxwell equation, i.e.,

$$E(i) = \frac{J^{\text{drift}}}{\sigma(i)} \quad . \quad (3.10)$$

The local charge density is calculated according to the Poisson equation

$$\rho(i) = \varepsilon_0 \varepsilon_r \frac{\partial E}{\partial x} \quad , \quad (3.11)$$

where ε_r and ε_0 represent the relative dielectric constant of SrTiO₃ and the vacuum dielectric constant, respectively. The relative dielectric constant we measured at 210 °C is around 200. In this work we used this value and assumed that it is independent of temperature when discussing the working temperature effect on the degradation. The calculated electric field and local charge density at time t are used as inputs for the calculation at the time $t+\Delta t$. In the simulation, we found that the time interval Δt and thickness interval Δx has to satisfy $\Delta t / (\Delta x)^2 \leq 0.4 \text{ s} \cdot \text{cm}^{-2}$ to ensure the convergence of the algorithm. By solving Eq.(3.1) for a specific case with a constant electric field and comparing the numerical solution with the corresponding analytical solution, we found that the grid number N has to be greater than 1000 in order to reach a good accuracy. All the variables with reduced units according to Table III were used in the simulations.

3.2 Conductivity Evolution during Degradation: Experiment and Simulation

A SrTiO₃ single crystal with Fe dopant concentration of $5.58 \times 10^{18} \text{ cm}^{-3}$ was annealed at the temperature of 900 °C and the oxygen partial pressure of 2×10^{-5} bar in our experiment. The thickness of the sample is 0.3cm and both electrodes are platinum. The experimentally measured time-dependence of the conductivity after applying an electric field of 800V/cm is shown in Fig. 5a using four-stage measurements. As it can be seen, the initial conductivity is in an order of $10^{-8} \Omega^{-1}\text{cm}^{-1}$ at temperature of 210 °C, consistent with the defect equilibria calculation after quenching the sample (see Figs. 4a and 4b). At this time the predominant contribution to the total conductivity originates from the mobile oxygen vacancies. After 14 hours under the electric field of 800V/cm, the effective conductivity increases to values on the order of $10^{-6} \Omega^{-1}\text{cm}^{-1}$, corresponding to two orders of magnitude degradation for the resistance.

Figs. 5b and 5c show the calculated conductivity evolutions as a function of degradation time by obtaining the electron and hole concentrations either from local equilibria (Fig. 5b) or from the steady-state equation (Fig. 5c), respectively. It can be clearly seen that when electronic concentrations are calculated based on the defect equilibria conditions, the conductivity evolution increases by two orders of magnitude from $10^{-8} \Omega^{-1}\text{cm}^{-1}$ to $10^{-6} \Omega^{-1}\text{cm}^{-1}$, which is quantitatively consistent with the experimental measurement. However, if the local electron and hole concentrations are obtained by solving the steady-state diffusion equations, the increase in the conductivity is limited (much less than one order of magnitude), similar as the results in Meyer *et al.*'s [23] and Cao *et al.*'s [24] studies. Therefore, based on the comparisons between experimental measurements and calculated conductivities, we conclude that the electrons and holes can be regarded more as compensating charges and their

local concentrations are determined by the defect equilibria during degradation. Therefore, further studies on the degradation mechanism will be performed by assuming the electronic species are at local defect equilibria.

Fig. 6a-d show the calculated concentration evolutions for the oxygen vacancies, Fe^{3+} , electrons and holes as a function of time under an electric field of 800V/cm, corresponding to the conductivity evolution during degradation in Fig. 5b. It can be seen that initially all the defects are homogeneous. With time increasing, the oxygen vacancies migrate from the anode region to the cathode region, forming a depletion layer at around $x/d = 0.27$ (see Fig. 6a). The simulation shows that the position of the depletion layer stabilizes once the bulk region disappears. At the anode region, the oxygen vacancies are mainly compensated by the Fe^{3+} , thus the profile of Fe^{3+} at the anode region (see Fig. 6b) is very similar to the oxygen vacancy. The decrease of Fe^{3+} at the anode region is accompanied by an increase in the hole concentration according to the redox reaction R3 (see Fig. 6d). At the cathode region, the amount of Fe^{3+} species is not sufficient to compensate all the oxygen vacancies due to the electric field-induced pile-up although nearly all the Fe atoms exhibit an oxidation state of +3 (see Fig. 6b). Therefore, a large amount of electrons are generated (see Fig. 6c) to compensate the positive charges. The simulated electron density reaches values of up to $3.3 \times 10^{18} \text{ cm}^{-3}$ exceeding the limit for semiconductor metal transition according to Mott [51]. This issue will be addressed in the discussion section. Consequently, a *pn* junction is formed in the sample at the position of the oxygen vacancy depletion layer (see Figs. 6c-d).

The local summation of Fe^{3+} and Fe^{4+} is constant due to the mass conservation, thus a resulting profile for Fe^{4+} can be obtained according to Fig. 6b. At the anode region, the Fe^{4+}

concentration is greater than Fe^{3+} , leading to an electrocoloration front forming at the pn junction position. In the experiment, we observed an obvious electrocoloration front at a relative position of 30% toward the anode electrode (see the inset of Fig. 6f under electric field of 800V/cm), compared with a result of 27% from the simulation under electric field of 800V/cm. Evolution of the electric field profile shown in Fig. 6e indicates that the electric field concentrates at the junction position. The electric field is quite weak at the cathode region due to the high concentration of the electrons. The charge density profile after long-time degradation is shown in Fig. 6f, indicating a space charge region at the pn junction. By converting the net charge density to an ensemble of defects (D^*) using

$$\rho / e_0 = [D^*] = \left(2[V_O^{\bullet\bullet}] + p - [\text{Fe}^{3+}] - n \right), \quad (3.12)$$

the concentration order of the ensemble of defects at the junction position is 10^{13} cm^{-3} (corresponding to an interfacial concentration of 10^{11} cm^{-2}), which is much lower than the predominant defects concentrations. This comparison verifies that the assumption of temperature-independent dielectric constant is reasonable.

In order to further understand the mechanism of the resistance degradation and the formation of a pn junction, the local defect equilibria and the conductivities are calculated as a function of the oxygen vacancy concentration. These results are shown in Fig. 7a and 7b. It can be clearly seen from Fig. 7a and 7b that there is a critical value for the oxygen vacancy defining the predominant charge carriers. The critical concentration of oxygen vacancy is equal to half of the doping iron concentration, i.e., $2.79 \times 10^{18} \text{ cm}^{-3}$ in this work. When the oxygen vacancy concentration in a local position is greater than the critical value, the dominant electronic defects are electrons. On the other hand, the dominant electronic defects

are holes when a local oxygen vacancy concentration is lower than the critical value. Under a duration of an electric field, the oxygen vacancies are driven to the cathode region leading to higher local concentrations than the critical value, making the cathode region a *n*-type semiconductor. On the other hand, at the anode region, out drifting of the oxygen vacancies induces the lower local concentrations than the critical value, making the anode region a *p*-type semiconductor. This explains the formation of a *pn* junction at the depletion layer of the oxygen vacancies. Furthermore, Fig. 7b indicates that the total conductivity at both the holes-dominating anode region and the electrons-dominating cathode region are several orders higher than the initial ions-dominating bulk conductivity, thus the resistance of the sample can be decreased by several orders after degradation.

4. Degradation Factors

In section 3, we verified the defect transport modeling by comparing the simulation conductivity behavior under the degraded electric field with the corresponding experimental measurements. We also discussed the evolutions of profiles for defects and the electric field, and the possible mechanism of degradation under a duration of the external electric field. In the following we will discuss the effects of sample-preparing and working conditions on the degradation process by simulating the conductivity behavior and the quasi-stable oxygen vacancy profile under different conditions. When referring a different sample-preparing or working condition, the other conditions are kept the same, i.e., annealed at a temperature of 900 °C, an oxygen partial pressure of 2×10^{-5} bar, and a Fe-doping concentration of $5.58 \times 10^{18} \text{ cm}^{-3}$ and degraded at a temperature of 210 °C and an electric field of 800V/cm.

4.1 Dopant Concentration Effect

Fig. 8a shows the conductivity evolutions as a function of degradation time for samples with different Fe-doping concentrations. It can be seen that with the dopant concentration increasing, the initial bulk conductivity increases because higher doping Fe concentration gives rise to higher oxygen vacancy concentration, leading to the higher initial ionic conductivity. However, the increasing magnitude of the conductivity or decreasing magnitude of the resistance after long-time degradation shows weak dependence on the dopant concentration C_a . The quasi-stable profiles for the oxygen vacancies in Fig. 8b indicate that the accumulated oxygen vacancies at the cathode region increase with the dopant concentration. However, it seems that the position of the depletion layer is not significantly affected by the dopant concentration.

4.2 Annealing Temperature Effect

As exhibited in Figs. 8c and 8d, the sample annealing temperature does not have great influence on the conductivity behavior and the quasi-stable defect profile. This can be understood from Figs. 1a and 1b wherein at $p_{O_2} = 2 \times 10^{-5}$ bar the concentrations of oxygen vacancies in samples annealed at different temperatures are almost the same, giving rise to the weak dependence of the resistance degradation on the annealing temperature.

4.3 Annealing Oxygen Partial Pressure Effect

Fig. 8e shows the conductivity behaviors as a function of time for samples annealed at different p_{O_2} . The differences among the initial conductivities can be determined according to the quenching properties shown in Figs. 4a and 4b. Basically, the higher the annealing p_{O_2} , the lower conductivity after degradation can be obtained because higher p_{O_2} induces fewer

oxygen vacancies which also need fewer electronic defects for compensation. This tendency persists until p_{O_2} is equal to 10^2 bar where there are so few oxygen vacancies, so that there is no depletion layer with the hole sample exhibiting p -type semiconductor with slightly higher conductivity than other listed cases before and after degradation.

Fig. 8f gives the quasi-stable profiles of the oxygen vacancies after long-time degradation calculated for the corresponding samples. It can be clearly seen that the position of the depletion layer depends strongly on the sample-annealing p_{O_2} . With the annealing p_{O_2} increasing from 10^{-10} bar to 10^2 bar, the depletion layer position moves towards cathode side. When the annealing p_{O_2} exceeds 10^2 bar, the depletion layer even disappears due to the low oxygen vacancy concentration. It is worth noting that the simulation on the depletion layer position or electrocoloration front not only agrees with our experimental result, but also agrees with Waser *et al.*'s experiments[9] wherein an electrocoloration front of $x/d \approx 0.75$ toward the anode electrode was observed for a Fe-doped SrTiO_3 single crystal annealed at 1073K and 1.0 bar and degraded under an electric field of 2.7 kV/cm.

4.4 Working Electric Field Effect

Fig. 9a shows the conductivity behaviors as a function of time for Fe-doped SrTiO_3 single crystals under different electric fields. With the applied electric field increasing, the conductivity after degradation increases yet the initial minimal conductivity remains the same. The working electric field also affects the characteristic time t_{ch} defined by $t_{\text{ch}} = t(\sigma^{\text{eff}} = 10\sigma^{\text{min}})$ according to Waser *et al.*'s definition[8,9]. As it can be seen from the inset of Fig. 9a, the characteristic time t_{ch} is proportional to E^n , and here $n = -0.61$. The exponent n in this

empirical law ($t_{\text{ch}} \propto E^n$) depends on the working temperature, and with temperature increasing n rises according to previous Waser *et al.*'s experiments[8,9].

Not only the characteristic time, but the position of the depletion layer are also affected by the working electric field. As exhibited in Fig. 9b, the junction position moves from $x/d \approx 0.29$ toward the anode electrode to $x/d \approx 0.51$ when the working electric field increases from 1kV/cm to 5kV/cm. However, it seems that this tendency is weakening with the electric field increasing, as seen from the inset of Fig. 9b.

4.5 Working Temperature Effect

Fig. 9c clearly shows the strong dependence of the effective conductivity on the working temperature. With the working temperature increasing, not only the minimal conductivity, but also the maximal conductivity increases. This is easy to understand because the enhanced thermal agitation results in continuous excitation of electrons and holes, generating more electronic defects. The dependence of the characteristic time t_{ch} on the working temperature is shown in the inset of Fig. 9c, where an Arrhenius-type relationship is revealed, i.e., $t_{\text{ch}} \propto \exp[W/(k_{\text{B}}T)]$ with the activation energy $W=0.84$ eV herein. The activation energy W strongly depends on the doping element and concentration. For example, with 0.31 mol% Al, 0.06 mol% Ni, and 0.15 mol% Fe as dopants, SrTiO₃ single crystals show activation energies of 0.56 eV, 0.78 eV, and 0.92 eV, respectively, according to Waser *et al.*'s experimental studies[9]. On the other hand, the position of the depletion layer (or the electrocoloration front) is less affected by the working temperature, as illustrated by Fig. 9d.

5. Discussion

There are two departures from the band semiconductor conduction that are not included in the present analysis. The first is the polaron conduction. A non-adiabatic small polaron hopping conduction was observed by Liu *et al.* to be active near the cathodic interface [52]. The polaron concentration up to order of 10^{19} cm^{-3} in degraded SrTiO_3 with 1% Fe dopant observed by Liu *et al.* suggests that the large amount of electrons calculated from present simulation by considering local defect equilibria are not in free states but hopping between Ti^{3+} and Ti^{4+} or other oxygen vacancy- Ti^{3+} complexes [50]. The effective mass of the polarons in SrTiO_3 is about 16 times of the free electron [53,54,55], giving rise to a lower mobility of the hopping electron than the free electron. Nevertheless, the resistance of the cathode region is only about 1.2% and 0.04% of the anode and bulk regions, respectively, measured by Liu *et al.* for a SrTiO_3 single crystal degraded at 150 °C [56]. Therefore, the effective conductivity is still mainly determined by the bulk and anode regions. The polaron conductivity mechanism neglected in this work would not have great influence on the effective conductivity evolution during degradation, but it would affect the impedance measurement which can distinguish resistances of the bulk, anode, and cathode regions. In our future work, we will incorporate the polaron conduction mechanism into the present model for simulating the impedance evolution during degradation.

The second is the neglect of the Mott transition in this work [48,57], i.e., a transition from semiconducting to metallic behavior which should occur when the local electron concentration exceeds a critical value of $3 \times 10^{18} \text{ cm}^{-3}$ for SrTiO_3 . However, the metallic conduction behavior was not observed in experiments although it is expected at the cathode region with electron concentration up to 10^{19} cm^{-3} according to the simulation.

6. Summary

Defect concentrations and corresponding conductivities in the Fe-doped SrTiO₃ single crystal during sample annealing and after quenching are calculated as functions of the annealing oxygen partial pressure and temperature. It was found that the type of the semiconductor and the predominant conductivity can be controlled by the annealing oxygen partial pressure. The defect transport process was studied by solving a drift-diffusion equation for oxygen vacancies. By comparing the experimentally measured conductivity behavior during degradation with simulations incorporating different assumptions on the electronic defects, we found that local defect equilibria rather than the steady-state equation determine the local concentrations of electrons and holes during degradation. This implies that the electronic defects act more as charge compensating species rather than diffusional transporting species. A combination of a drift-diffusion equation for oxygen vacancies and local defect equilibria for electrons and holes was used to study the degradation mechanism as well as the factors that affect degradation. It was found that the migration of the oxygen vacancies and subsequent reestablishment of local defect equilibria caused the resistance degradation. This resistance degradation behavior and the electrocoloration front are not greatly influenced by the dopant concentration and sample-annealing temperature but are strongly dependent on the sample-annealing oxygen partial pressure.

For working conditions, the increasing working electric field decreases the characteristic time for degradation and drives the *pn* junction towards cathode side. The increasing working temperature increases both the minimal and maximal conductivities during degradation however does not affect the *pn* junction greatly.

The agreement between the experimental data and simulation results obtained assuming a homogeneous crystal also indicates that the unavoidable interfaces and dislocations in semiconducting capacitors seem to have no significant influence on the resistance degradation behavior. The present results contribute not only a further understanding on the resistance degradation mechanism but also provide some strategies to improve the lifetime and reliability of the semiconducting capacitors.

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Figure Captions

Fig. 1 Defect concentrations as a function of annealing oxygen partial pressure at different temperatures calculated from the defect equilibria using (a) Denk *et al.*'s and (b) Moos *et al.*'s measured mass-action law constants, respectively.

Fig. 2 Conductivities as a function of annealing oxygen partial pressure at different temperatures calculated from the defect equilibria using (a) Denk *et al.*'s and (b) Moos *et al.*'s measured mass-action law constants, respectively.

Fig. 3 Defects concentrations as a function of annealing oxygen partial pressure before and after quenching the sample calculated from the defect equilibria using (a) Denk *et al.*'s and (b) Moos *et al.*'s measured mass-action law constants, respectively.

Fig. 4 Conductivities as a function of annealing oxygen partial pressure before and after quenching the sample calculated from the defect equilibria using (a) Denk *et al.*'s and (b) Moos *et al.*'s measured mass-action law constants, respectively.

Fig. 5 Conductivity evolution during a degradation process at 210 °C and an electric field of 800V/cm obtained from (a) experimental measurement, (b) simulation considering local equilibria for electronic defects, and (c) simulation by solving the steady-state diffusion equation for electronic defects.

Fig. 6 Evolutions of concentration profiles for (a) oxygen vacancy, (b) Fe^{3+} , (c) electron, and (d) hole during a degradation process. (e) The electric field profile evolution during degradation. (f) The charge density profile after long-time degradation. The sample was prepared at 900 °C of annealing temperature, 2×10^{-5} bar of annealing p_{O_2} , and $5.58 \times 10^{18} \text{ cm}^{-3}$ of doping Fe concentration and degraded at the temperature of 210 °C and the electric field of 800V/cm. The inset of Fig.6f shows the experimentally measured electrocoloration image of the sample.

Fig. 7 The oxygen vacancy concentration-dependent of defects: (a) concentrations, and (b) conductivities.

Fig. 8 Effects of the sample-preparing conditions on the degradation process. The conductivity evolutions (a), (c), (e), and oxygen vacancy profiles after long-time degradation (b), (d), (f) for samples prepared at (a), (b) 900 °C of annealing temperature, 2×10^{-5} bar of annealing p_{O_2} but different Fe doping concentrations, and (c), (d) 2×10^{-5} bar of annealing p_{O_2} , $5.58 \times 10^{18} \text{ cm}^{-3}$ of doping Fe concentration but different annealing temperatures, and (e), (f) 900 °C of annealing temperature, $5.58 \times 10^{18} \text{ cm}^{-3}$ of doping Fe concentration but different annealing p_{O_2} . The inset of (f) shows the comparison between the simulation results between the experimental results from present work (olive star) and the literature [9] (blue triangle).

Fig. 9 Effects of the working conditions on the degradation process. The conductivity evolutions (a), (c), and oxygen vacancy profiles after long-time degradation (b), (d) for samples working at (a), (b) temperature of 210 °C but different electric fields, and (c), (d) electric field of 800V/cm but different temperatures. All the samples were prepared at 900 °C of annealing temperature, 2×10^{-5} bar of annealing p_{O_2} , and $5.58 \times 10^{18} \text{ cm}^{-3}$ of doping Fe concentration.

Figure-1

Figure-2

Figure-3

Figure-4

Figure-5

Figure-6

Figure-7

Figure-8

Figure-9

Table I. Mass-law action constants measured by Denk *et al.* and Moos *et al.*, respectively.

The Boltzmann constant k_B is $8.617 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$. The units of temperature T , reaction-related constants K_{R2} , K_{R3} , and K_{R4} are K, $\text{cm}^{-9} \text{bar}^{1/2}$, cm^{-3} , and cm^{-6} , respectively.

Reaction-Constant Values			
Reactions	Mass-action law	Source: Denk <i>et al.</i> , Ref[11]	Source: Moos <i>et al.</i> , Ref[12]
R2	$K_{R2} = n^2 [V_{\text{O}}^{\bullet}] \sqrt{p_{\text{O}_2}}$	$1.82 \times 10^{60} \exp\left(-\frac{4.97 - 1.2 \times 10^{-3} T}{k_B T}\right)$	$5 \times 10^{71} \exp\left(-\frac{6.1}{k_B T}\right)$
R3	$K_{R3} = [\text{Fe}_{\text{Ti}}'] p / [\text{Fe}_{\text{Ti}}^{\times}]$	$2.77 \times 10^{21} \exp\left(-\frac{1.18 - 3.7 \times 10^{-4} T}{k_B T}\right)$	$3.5 \times 10^{16} T^{3/2} \exp\left(-\frac{0.94}{k_B T}\right)$
R4	$K_{R4} = np$	$7.67 \times 10^{42} \exp\left(-\frac{3.3 - 6 \times 10^{-4} T}{k_B T}\right)$	$1.44 \times 10^{32} T^3 \exp\left(-\frac{3.17 - 5.66 \times 10^{-4} T}{k_B T}\right)$

Table II. Mobility of mobile species summarized in Denk *et al.* and Moos *et al.*'s papers, respectively. In Moos *et al.*'s work, they didn't measure the mobility of the oxygen vacancy because they neglected the ionic conductivity at high temperature, so here we still used the value from Denk *et al.*'s work to make low-temperature conductivity comparison.

Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)		
Species	Source: Denk <i>et al.</i> , Ref[11]	Source: Moos <i>et al.</i> , Ref[11,12,39]
$\text{h}^{\bullet}$	$\mu_p = 8.9 \times 10^5 T^{-2.36}$	$\mu_p = 1.1 \times 10^6 T^{-2.36}$
e'	$\mu_n = 4.5 \times 10^5 T^{-2.2}$	$\mu_n = 3.95 \times 10^4 T^{-1.62}$
$V_{\text{O}}^{\bullet}$	$\mu_{V_{\text{O}}^{\bullet}} = 1.0 \times 10^4 T^{-1} \exp\left(\frac{-0.86}{k_B T}\right)$	$\mu_{V_{\text{O}}^{\bullet}} = 1.0 \times 10^4 T^{-1} \exp\left(\frac{-0.86}{k_B T}\right)$

Table III. Variables with reduced units.

$[V_{\text{O}}^{\bullet}]^*$	n^*	p^*	$[\text{Fe}^{3+}]^*$	t^*	E^*	ε_0^*	$\mu_{V_{\text{O}}^{\bullet}}^*$	σ^*	$(dx)^*$
$\frac{[V_{\text{O}}^{\bullet}]}{C_a}$	$\frac{n}{C_a}$	$\frac{p}{C_a}$	$\frac{[\text{Fe}^{3+}]}{C_a}$	$\frac{t D_{V_{\text{O}}^{\bullet}}}{(h)^2}$	$\frac{E e_0 h}{k_B T}$	$\frac{\varepsilon_0 k_B T}{(e_0 h)^2 C_a}$	$\frac{\mu_{V_{\text{O}}^{\bullet}} k_B T}{D_{V_{\text{O}}^{\bullet}} e_0}$	$\frac{\sigma k_B T}{D_{V_{\text{O}}^{\bullet}} e_0^2 C_a}$	$\frac{dx}{h}$