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Temperature-dependent resistance switching in SrTiO$_3$

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Resistance switching phenomena were studied by varying temperature in SrTiO$_3$ single crystal. The resistance hysteresis loops appear at a certain temperature ranging from 340 K to 520 K. With the assistance of 375 nm ultraviolet continuous laser, the sample resistance is greatly reduced, leading to a stable effect than that in dark. These resistance switching phenomena only exist in samples with enough oxygen vacancies, which is confirmed by spherical aberration-corrected scanning transmission electron microscopy measurements, demonstrating an important role played by oxygen vacancies. At temperatures above 340 K, positively charged oxygen vacancies become mobile triggered by external electric field, and the resistance switching effect emerges. Our theoretical results based on drift-diffusion model reveal that the built-in field caused by oxygen vacancies can be altered under external electric field. Therefore, two resistance states are produced under the cooperative effect of built-in field and external field. However, the increasing mobility of oxygen vacancies caused by higher temperature promotes internal electric field to reach equilibrium states quickly, and suppresses the hysteresis loops above 420 K. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4953624]

Resistance switching (RS) effect has attracted extensive interests as one candidate of the next generation of storage devices for its non-charge-based memory feature and outstanding device performance. The reversible RS effect has been found in a large number of insulators, among which transition metal oxides have been studied intensively. However, the underlying physical mechanism of RS effect is still a controversial issue. Several microscopic mechanisms have been proposed, such as defect migration under external electric field, changes of Schottky barrier at the metal-oxide interface, formation and rupture of conducting filaments, and band bending caused Mott-metal-insulator transition at an interface.

Among transition metal oxides, SrTiO$_3$ (STO) serves as an ideal model perovskite oxide and exhibits outstanding physical properties under the control of external parameters. Oxygen vacancy, an effect self-doping element, is an important factor for affecting the physical properties of STO. Theoretical and experimental studies reveal that two theories based on the migration of oxygen vacancies are proposed for the RS progress in STO. As in the case of thermally reduced STO, the switching behavior is generated by conducting filaments, which is demonstrated by conductive-tip atomic force microscopy (C-AFM). Besides filamentary-type resistive switching, another type of resistive switching is homogeneous switching, which could be ascribed to the field-induced change of the Schottky barrier at the metal-insulator interface.

Herein, we report the resistive switching phenomena in STO by adding the effect of temperature. It was observed that from 340 K to 520 K, the resistance of metal/STO/metal planar structure can be repeatedly switched between the high state and the low state by applying external bias. A numerical model based on time dependent one-dimensional drift-diffusion (TD1DDD) model is proposed in order to gain an in-depth insight of the origin behind the temperature-dependent RS phenomena. As temperature rises, the increasing of oxygen vacancy mobility results in that hysteresis loops only appear in a certain temperature range. We hope this work can promote an understanding of the RS phenomena.

STO single crystals with a size of $10 \times 10 \times 0.5$ mm$^3$ were prepared for photoelectric measurements. Subsequently, Pt interdigital electrodes with a thickness of 100 nm were sputtered on the STO wafers after the standard ultraviolet lithography technique. Figure 1(a) shows a schematic diagram of the fabrication. The fingers of the electrode have a length of 320 $\mu$m and a width of 10 $\mu$m, and the gaps between fingers are 10 $\mu$m to receive light irradiation. During the measurements, UV continuous laser (Oxxius, wavelength of 375 nm) was applied to excite light carriers in order to obtain remarkable photocurrent signal. Our samples were fixed on a probe station with a temperature controller and measured using Keithley 2400. For electrical testing, bias voltages were applied to the platinum interdigital electrodes in dark condition, as well as under illumination of 375 nm continuous laser.

The electrical transport properties at different temperatures and illumination conditions are displayed in Figs. 1(b)–1(h). The $I$–$V$ curves were measured with bias sweeping of $+V_{\text{max}} \rightarrow 0 \rightarrow -V_{\text{max}} \rightarrow 0 \rightarrow +V_{\text{max}} \rightarrow 0$, where $V_{\text{max}}$ is 20 V. In Fig. 1(b), dark currents at different temperatures indicate a maximum value at 420 K. The maximum dark current of our device is about tens of nanoampere under 20 V. Figures 1(c)–1(g) are comparison charts for dark currents and photocurrents at various temperatures. The photocurrents in Figs. 1(c)–1(h) were measured with a light intensity of 5 mW/mm$^2$.

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We discovered that at temperatures above 340 K, RS phenomena gradually appear under continuous UV laser illumination and become more pronounced with a peak at 420 K. In addition, with the temperature increasing above 420 K, the resistance loops may gradually decrease and eventually disappear at 520 K. In sharp contrast with dark currents, the photocurrents are on the order of 10$^{-1}$ A at 20 V, more than three orders of magnitude larger than the dark currents. Figure 1(h) shows that the photocurrents get larger and the RS phenomena become more pronounced with increasing the light intensity from 1 mW/mm$^2$ to 5 mW/mm$^2$.

As shown by arrows in Figs. 1(b)–1(h), under forward bias sweeping from $+20\, \text{V}$ to $0\, \text{V}$, the system is in a high resistance state (HRS). The HRS can be tuned to the low resistance state (LRS) with reverse bias from $0\, \text{V}$ to $-20\, \text{V}$. Afterwards, the decrease of the reverse bias from $-20\, \text{V}$ to $0\, \text{V}$ switches the resistance from LRS to HRS. Then, increasing forward bias is applied to the system and HRS converts to LRS once again. When the temperature is higher than 420 K, voltage negative differential resistance emerges and gradually moves to the low voltage direction.

It is worth mentioning that STO samples used in above experiments have certain concentration of oxygen vacancies. In STO samples with low concentration of oxygen vacancies, hysteresis loops are hardly observed. For convenience, the STO single crystal with RS phenomena is labeled as sample I and the STO single crystal with much less oxygen vacancies is labeled as sample II. If sample II is annealed in a reduced atmosphere at $800\, \text{°C}$ for 30 min, RS phenomena also appear, which means the appearance of HRS and LRS are closely associated with oxygen vacancies. To be more convincing, spherical aberration-corrected scanning transmission electron microscopy (STEM) was employed to confirm the difference of oxygen vacancy concentration between sample I and sample II.

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It is worth mentioning that the contrast of the HAADF and ABF images, respectively, exhibit $Z^{1.7}$ and $Z^{1/3}$ dependency, wherein $Z$ represents the atomic number. Therefore, different kinds of atom columns can be distinguished. In particular, light elements such as oxygen can be clearly identified in ABF images. In HAADF and ABF images, the heaviest strontium atoms are represented by the largest contrasts, the lighter titanium atoms are indicated by weaker contrasts, and the relatively lightest oxygen atoms are denoted by the weakest contrasts. Line profiles along the vertical Ti-O-Ti atomic chains with markers as depicted in Figs. 2(b) and 2(e) are shown in Figs. 2(c) and 2(f), respectively. We can see that the valleys of oxygen line profile in sample I are deeper than those in sample II, which means there are more oxygen vacancies in sample I than those in sample II. Considering RS phenomena only appear in sample I, we can conclude that concentration of oxygen vacancies is an important factor for the RS phenomena in STO.

For resistance switching, both the redistribution of oxygen vacancies under electric field\(^23\) and charge trapping/detrapping\(^23,25\) can modulate the electric potential distribution at the interface, leading to a similar resistance change of the device. Our retention measurement showed that the current at LRS decayed only 25% during 2500 s, different from the charge trapping/detrapping dominant switching behavior in which the LRS fully turns to be HRS during 250 s.\(^25\) A short retention time in RS controlled by trapping/detrapping is ascribed to that the exposed oxygen vacancies are easily compensated by surrounding electrons.\(^25\) Thus, we can deduce that the migration of oxygen vacancies plays a major role in our RS phenomena.

To better understand the physical mechanism behind the experimental phenomena, we proposed an oxygen vacancies participated transport model in which the applied electric field would induce the redistribution of oxygen vacancies to form a built-in electric field, and carried out the theoretical calculations based on TD1DDD model.\(^26\) For a brief description of the mechanism of the temperature-dependent RS phenomena, only two electrodes and the crystal area between them are in considering, as shown in the inset of Fig. 3(a). The right electrode which is labeled as Electrode 2 of our device is grounded, and the left electrode (Electrode 1) is biased. Oxygen vacancies in our model are treated as +2 charged point defects, which could drift under external electric field. Computation was performed according to the finite difference numeric approach.\(^27,28\) The TD1DDD model consisting of Poisson equation and electricity continuity equations are displayed as follows:

\[
\frac{\partial}{\partial x}\left[ e \frac{\partial \phi(x,t)}{\partial x} \right] = -e [p(x,t) - n(x,t) + N_{\text{V}}(x,t)],
\]

\[
\frac{\partial n(x,t)}{\partial t} = \frac{1}{e} \frac{\partial p(x,t)}{\partial x} + G(x,t) - R(x,t),
\]

\[
\frac{\partial p(x,t)}{\partial t} = \frac{1}{e} \frac{\partial n(x,t)}{\partial x} + G(x,t) - R(x,t),
\]

where $\phi$, $n$, $p$, $j_n$, $j_p$, and $N_{\text{V}}$ represent the electrostatic potential, electron concentration, hole concentration, electron current density, hole current density, and oxygen vacancy density, respectively. $e$ and $e$ are the elementary charge and dielectric permittivity, respectively. $G$ and $R$ denote the generation and the recombination rates of electron-hole pairs, respectively. In order to simplify the model, $G$ is set to be a constant for the laser irradiation on the film surface. According to the Shockley-Read-Hall model,\(^29\) $R$ can be expressed as

\[
R = \frac{np - n^2}{\tau_p(p + n_i) + \tau_n(n + n_i)},
\]

where $n_i$, $\tau_m$, and $\tau_p$ are the intrinsic carrier density, lifetime of electrons, and lifetime of holes, respectively. Presenting in terms of drift and diffusion, the currents are expressed as

\[
j_n(x,t) = -e\mu_n n(x,t) \frac{\partial \phi(x,t)}{\partial x} + k_B T \mu_n \frac{\partial n(x,t)}{\partial x},
\]

\[
j_p(x,t) = -e\mu_p p(x,t) \frac{\partial \phi(x,t)}{\partial x} - k_B T \mu_p \frac{\partial p(x,t)}{\partial x},
\]

FIG. 2. Crystal structures of STO single crystals of different oxygen vacancies. The high-angle annular dark-field (HAADF) images and corresponding annular-bright field (ABF) images are viewed from [110] crystallographic direction. HAADF micrographs of sample I (a) and sample I (d) and ABF micrographs of sample I (b) and sample II (e) are shown, respectively. Line profiles along the O-Ti chains are shown in (c) and (f) with respect to the blue and red markers shown in (b) and (e). The Sr, Mn, and O sites are displayed by magenta, green, and orange circles, respectively.
conditions are expressed as for mobile ions. According to above settings, the boundary faces are supposed to be trap-free and completely blocking determined by the Fermi potential at the interface. The inter-

where \( j_{\text{VO}} \) is the current density of +2 charged oxygen vacancies, and satisfies the current continuity equation  

\[
j_{\text{VO}}(x, t) = -2e \mu_{\text{VO}} N_{\text{VO}}(x, t) \frac{\partial \varphi(x, t)}{\partial x} - k_B T \mu_{\text{VO}} \frac{\partial N_{\text{VO}}(x, t)}{\partial x},
\]

(7)

where \( \mu_e, \mu_p, k_B, \) and \( T \) are the mobility of electrons, mobility of holes, Boltzmann constant, and temperature, respectively; \( j_{\text{VO}} \) is the current density of +2 charged oxygen vacancies.

The amount of oxygen vacancies is assumed to remain unchanged during the entire simulation. The concentrations of electrons and holes are fixed to their equilibrium levels determined by the Fermi potential at the interface. The interfaces are supposed to be trap-free and completely blocking for mobile ions. According to above settings, the boundary conditions are expressed as

\[
\varphi(0, t) = V(t),
\]

(9)

\[
\varphi(L, t) = 0,
\]

(10)

\[
j_{n_0}(0, t) = j_{n_0}(L, t) = 0,
\]

(11)

where \( L \) is the total length of STO and \( V(t) \) is the voltage bias between two electrodes.

In order to gain an intuitive physical picture of the influence of oxygen vacancies migration on the RS phenomena, we also calculated the built-in equivalent electric field formed by the redistribution of oxygen vacancies. The equivalent electric field \( E_{\text{ef}} \) is defined as

\[
E_{\text{ef}}(t) = -\frac{\varphi_{\text{VO}}(L, t) - \varphi_{\text{VO}}(0, t)}{L} + \text{const.},
\]

(12)

where \( \varphi_{\text{VO}}(x, t) \) is the electric potential induced only by oxygen vacancies. The constant is selected to make sure the initial state \( E_{\text{ef}}(0) = 0 \). The electric potential is calculated according to the distribution of oxygen vacancies as following equation:

\[
\nabla \cdot E_{\text{VO}}(x, t) = \frac{N_{\text{VO}}(x, t)}{e} = -\nabla^2 \varphi_{\text{VO}}(x, t).
\]

(13)

The LRS currents tend to be saturated at high voltages, which can be attributed to the drift velocity saturation effect of carriers. To represent this effect, we adjust the mobility of carriers to be voltage dependent as \( \mu_{\text{h,p}} \cdot |V| = \nu_s \cdot (1 - \exp(-|V|)) \) in our simulation, where \( \nu_s \) is the saturation velocity. For simplicity, we assume that +2 charged oxygen vacancies distribute uniformly for the initial state. The concentration of oxygen vacancies and photo-generated carriers are taken as \( 1 \times 10^{15} \text{cm}^{-3} \) and \( 5 \times 10^{16} \text{cm}^{-3} \), respectively.

A typical calculated I–V loop is shown in Fig. 3(a), which well reproduces the hysteresis curve. Corresponding \( E_{\text{ef}} \) which means the field generated by positively charged oxygen vacancies is shown in Fig. 3(b). We divide a resistive switching period into four processes \( P1-P4 \) as shown in Fig. 3(a) for convenience. If positive bias is added to electrode 1 as shown in P1 and Fig. 3(e), positively charged oxygen vacancies move toward electrode 2. With the accumulation of oxygen vacancies around electrode 2, the asymmetrical space distribution of oxygen vacancies inside STO gradually strengthens the \( E_{\text{ef}} \) whose direction is opposite to the applied external electric field. Thus, \( E_{\text{ef}} \) hinders photogenerated carriers from moving under applied bias and the device gets into the HRS. Afterwards, the positive bias becomes negative which is labeled as P2 and shown in Fig. 3(f). At this moment, oxygen vacancies are still gathering around electrode 2 with the direction of \( E_{\text{ef}} \) being the same as external field. The cooperative action of \( E_{\text{ef}} \) and external field enhances the conductivity of STO single crystal and changes the device into LRS. With the oxygen vacancies moving to electrode 1, \( E_{\text{ef}} \) is gradually reversed to the opposite direction of external field. Therefore, negative differential resistance phenomena occur at LRS. When the bias proceeds to P3 and P4, physical processes similar to P1 and P2 take place again except the bias as well as \( E_{\text{ef}} \) are in opposite
It is remarkable in Fig. 4(a) that as the temperature rises from 340 K to 420 K, the current loops expand at first, and then shrink at higher temperature. In order to investigate this temperature dependence behavior, we simulated the resistive switching effect corresponding to different temperatures in Fig. 4(b). As point defects, the mobility of oxygen vacancies in STO should become higher with the increase in temperature. When the temperature increases, larger \( E_{\text{ef}} \) is formed to enhance (reduce) the resistance in HRS (LRS). The resistance ratio of HRS from 340 K to 420 K is on the order of 10\(^{10} \). According to the calculation results, current generated by mobile oxygen vacancies at 420 K is on the order of 10\(^{-11} \) A at LRS and on the order of 10\(^{-18} \) A at HRS, which is much smaller than the current on the order of 10\(^{-5} \) A contributed by charge carriers.

In summary, temperature-dependent RS phenomena were observed in metal/STO/metal planar structure. The RS phenomena only emerge at the temperature higher than 340 K because oxygen vacancies can barely move at lower temperature. When the temperature is above 340 K, positively charged oxygen vacancies can barely move at lower temperature. The increasing mobility of oxygen vacancies caused by higher temperature promotes the built-in electric field to reach equilibrium states quickly, and restrains the hysteresis loops. The existing of competitive behaviors in the device makes the resistance hysteresis loops reach a maximum value at 420 K. It is expected that the presence of the temperature field could play a beneficial role for a deeper insights into the resistance switching effect.

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