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The modulation of oxygen vacancies by the combined current effect and temperature cycling in $La_{0.7}Sr_{0.3}CoO_3$ film

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Modulating the oxygen defect concentration has been accepted as an effective method to obtain high catalytic activity in perovskite cobaltites. However, controllably modifying the oxygen vacancy is still a challenge in this type of materials, which strongly obstructs their application. Here, we report a successful oxygen vacancies modulation in the $La_{0.7}Sr_{0.3}CoO_3$ (LSCO) film by using combined current effect and temperature cycling. The temperature dependent transport properties of the LSCO/LAO film were investigated. The results revealed that the resistance of the film keeps increasing under the repeated measurements. It was found that the accumulation of the oxygen vacancy by current effect transforms the Co⁴⁺ ion into Co³⁺ ion, which results in the enhancement of the resistance and thus the transport switching behavior. Moreover, the resistance in the cooling process was found to be much higher than that in previous cooling and heating processes, which indicates that the oxygen escapes more quickly in the high temperature region. On the other hand, our analysis indicates that the CoO₆ distortion may contribute to the switching of transport behaviors in the low temperature region. Our work provides an effective and controllable way to modulate oxygen defect in the perovskite-type oxides. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5007013

It has attracted a lot of interests to induce novel electronic, magnetic and structural properties in transition-metal oxides and their interfaces by introducing and modulating oxygen defects.^{1,2} Owing to the high ionic and electronic conductivity, the oxygen-deficient perovskite oxides can be exploited in many applications such as gas sensors, oxygen separation membranes, oxidation catalysts and electrode materials for solid oxide fuel cells.^{3–6} Further experiments indicated that the oxygen vacancies can affect the electronic structure of perovskite oxides by changing the metal cation valence.^{7,8} As a result, oxygen vacancies engineering is considered to be an efficient method to obtain high catalytic activity in perovskite oxides. Usually, the formation of oxygen off-stoichiometry is achieved by annealing at high temperature in vacuum or reducing atmosphere.^{7–9} However, the rigorous reaction conditions under elevated temperatures or the reducing atmosphere make the oxygen vacancies engineering difficult.

As a member of perovskite oxides, $La_{1-x}Sr_xCoO_3$ ($0 \le x \le 1$) shows a strong redox activity.⁸ Doped with Sr²⁺, the material behaves in ferromagnetic cluster glass and metallicity for x >0.18.¹⁰ As x increases, Co³⁺ ions transform into Co⁴⁺ ions, leading to the mixed valence



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Co ions in La_{1-x}Sr_xCoO₃.¹¹ The introduction of Co⁴⁺ triggers itinerant ferromagnetic double exchange (DE) interactions with the adjacent IS Co³⁺ ($5t_{2g}1e_g$) ions.^{10–12} Meanwhile, the high energy of Co⁴⁺ valence state can drive the conversion of Co⁴⁺ into relatively stable Co³⁺ or/and Co²⁺ valence states, generating oxygen vacancies.⁹ Accordingly, oxygen vacancies could decrease the Co⁴⁺/Co³⁺ ratio, which strongly restrains the DE between Co⁴⁺ and Co³⁺ and weakens the ferromagnetism.^{13,14} In this paper, we report a new avenue to modulate the oxygen vacancies in La_{0.7}Sr_{0.3}CoO₃ (LSCO) film by means of temperature cycling assisted with pulsed electric current.

The LSCO thin films with thickness of 31 nm were grown on (001)-cut LaAlO₃ (LAO) substrate by pulsed laser deposition (PLD) technique. The oxygen pressure and deposition temperature were 10 Pa and 740°C, respectively. The film was slowly cooled down in the same oxygen background pressure after deposition. The LAO (space group: R-3c) substrate has a pseudo cubic structure with a lattice parameter of 3.792 Å and an a⁻a⁻ tilt of the oxygen octahedron. Lattice parameters and strain of the LSCO/LAO film were checked by X-ray diffraction (XRD) and reciprocal space maps (RSM) with the Cu K α radiation ($\lambda = 1.5406$ Å) on a Bruker AXS D8-Discover. The magnetization and electrical transport measurements were performed by using a superconducting quantum interference device-vibrating sample magnetometer (SQUID–VSM), which equips with a Keithley 2182 nanovoltmeter and a 2601current sourcemeter. The applied electric current is 1 μ A. The duration of the applied current at each measuring point is set to 1 s.

Figure 1a) and b) show the detailed X-ray diffraction θ -2 θ scan patterns and the RSM of the LSCO/LAO film, respectively. The XRD patterns of the LSCO/LAO film shown in Figure 1a) indicate a single phase oriented in [001] direction. The out-of-plane lattice parameter of LSCO is calculated as 3.90 Å from the patterns. The RSM around (103) Bragg reflection of the LSCO/LAO film confirms the coherently strained growth of LSCO (31nm) on the LAO substrate. Meanwhile, it was found that the lattice parameter in [100] direction equals to the LAO's. The strain could be analyzed by the equation of $\varepsilon = (c_{film} - c_{bulk})/c_{bulk}$. Taking into account the bulk lattice parameter of 3.82 Å, one can obtain the ε_{100} and ε_{001} , respectively (-0.73% and 2.09%). Obviously, the LSCO film undergoes in-plane compressive strain and out-of-plane tensile strain on the LAO substrate.

Temperature-dependent magnetization (*M*-*T* curve) of LSCO/LAO film along the [100] direction is plotted in Figure 2a). The magnetization of the film was measured during warming process under 500 Oe field after zero field cooling (ZFC) and field cooling (FC, H = 500 Oe), respectively. The Curie temperature (T_c) of LSCO/LAO film was determined as ~210 K from the *M*-*T* curve, which is a little bit lower than that of bulk. This result agrees with previous reports.^{11,15} Figure 2b) shows



FIG. 1. a) Detailed X-ray diffraction θ -2 θ scans of the LSCO/LAO film. Numbers in parentheses denote the corresponding crystallographic planes. b) The RSM of LSCO/LAO film in the (103) crystalline plane. nm⁻¹ represents the reciprocal space units, Q₁₀₀ and Q₀₀₁ represent projected directions in the reciprocal space.

056435-3 Li et al.



FIG. 2. a) Temperature-dependent in-plane magnetization of LSCO/LAO film measured in both FC and ZFC modes at a magnetic field of 500 Oe along the [100] direction. b) Magnetic hysteresis loop of the film at 10 K.

the magnetic hysteresis loop of LSCO/LAO film at 10 K. The much higher coercive force of 3810 Oe in comparison with that of bulk may be attributed to the biaxial strain from LAO substrate, despite that the detailed mechanism is still unclear at present. The macroscopic magnetic measurements indicate that LSCO/LAO shows a ferromagnetic state under T_c , with a saturated magnetization of 1.4 μ_B per cobalt ion.

The evolution of the temperature-dependent transport behaviors (*R*-*T* curves) for the LSCO/LAO film was shown in Figure 3a), where the numbers represent the cycle index of the transport measurements with temperature cycling. The applied current is 1 μ A. And the current density was estimated to be 1.08×10^5 A/m². The results reveal that the resistance of the LSCO/LAO film increases continuously under repeated transport measurements below room temperature. Such a supernormal variation indicates that the Co⁴⁺/Co³⁺ ratio decreases, leading to the transformation of conductive mechanism in the LSCO/LAO film. These results are similar to our previous study in LSCO/PMN-PT film.¹⁶



FIG. 3. a) Repeated temperature-dependent resistance measurements of the LSCO/LAO film with a current of 1 μ A. b) Temperature-dependent resistance difference between warming and cooling curves at each cycle. c) The magnetic hysteresis after repeated measurements (red) compared with the original one (black) at 10 K. d) Temperature-dependent in-plane magnetization measured in the FC mode after repeated measurements (red) compared with the original one (black). The index numbers in the image represent the cycle index of measurements.

056435-4 Li et al.

The applied current in LSCO/LAO plays an important role in the continuous enhancement of the resistance during the temperature cycling. The applied current may generate the oxygen defects near the electrical channels in LSCO/LAO film, and thus transforms the Co^{4+} ions into the Co^{3+} ions. The decreasing of the Co^{4+}/Co^{3+} ratio and the accumulation of the oxygen vacancies could make the DE interaction fade out, resulting in the enhancement of the overall resistance. Furthermore, it is found that the *R*-*T* curves of the cooling and heating processes are not consistent in the same cycle. With the increase of temperature, the resistance in the heating process gradually increases and deviates from that in the cooling process in each cycle, especially in the high temperature section (>250K). Moreover, the resistance in the succeeding cooling process is much higher than that in both heating and cooling ones of the previous cycle. This surprising result indicates that the electric transport property of the LSCO film changes more quickly in the high temperature region. Usually, the temperature drift could result in the curve misalignment in certain circumstances. However, if there exists a temperature drift during the measurement process, the resistance of the LSCO/LAO film will decrease in the high temperature region. In our experiment results, the resistance of the LSCO/LAO film increases during the warming process in the high temperature region at the first three cycles. So we exclude the possibility of temperature drift. In fact, the escape rate of the oxygen in the LSCO/LAO film is higher at high temperature.¹⁰ The enhanced O²⁻ ion mobility and larger lattice parameter due to thermal expansion make the oxygen vacancies formed more easily in the high temperature range, resulting in a sudden increase in the resistivity around the temperature approaching room temperature (as shown in Figure 3a)). Thus, more oxygen vacancies are accumulated in the LSCO/LAO film at high temperature in the warming process, leading to much higher resistance in the succeeding cooling process. On the contrary, the accumulation of the oxygen vacancies at low temperature is less than that at high temperature. As a result, the magnitude of the resistance enhancement in the succeeding warming process is smaller than that in the previous cooling process.

To further understand the physical process during the repeated R-T measurements, we processed the original transport data. Considering that the resistance of the warming process is higher than the cooling one in all temperature range at each cycle, we calculate the difference between the warming process and the cooling process, ΔR , at each cycle (see Figure 3b)). We surprisingly find that the ΔR changes regularly during the repeated measurements with temperature cycling. It is more interesting that the six ΔR curves meet in one point at 210K, which is related to the T_c. When $T < T_c$, ΔR gradually increases at low temperatures and then decreases at high temperatures as the repeated measurements go on. When $T > T_c$, the higher temperature would make LSCO/LAO film accumulate more oxygen vacancies, resulting in a sudden increase in the resistivity around the temperatures approaching room temperature. Moreover, the largest ΔR occurs at the first cycle, due to the highest oxygen content at the beginning. The oxygen content gradually decreases with the cycle number of the repeated measurement increasing, leading to the decline of the oxygen releasing rate and thus the decrease of the ΔR . As $T < T_c$, the accumulating rate of oxygen vacancies is lower than that in the high temperature range $(T > T_c)$. The concentration of the oxygen vacancies slightly changes in this temperature range. The LSCO grown on the LAO substrate exists an a a a CoO₆ octahedron rotation. The oxygen vacancies in LSCO/LAO film could aggravate the CoO₆ octahedron distortion. And this distortion would develop with the repeated measurements going on. It was found that the *R*-*T* curves show thermal hysteresis, which may be an accumulated effect, depending on the scale of the CoO₆ octahedron rotation. It has been reported that the reduction of lattice symmetry could result in a pronounced thermal hysteresis in oxides.^{17,18} In our case, more concentration of the oxygen vacancies may lead to larger CoO6 octahedron rotation and thus larger thermal hysteresis. At the beginning of the repeat measurements, there are less oxygen vacancies in the LSCO/LAO film, so the thermal hysteresis is not obvious. As the cycle number increases, more and more oxygen vacancies are accumulated in the film, leading to the promotion of the CoO_6 octahedron rotation. As a result, obvious thermal hysteresis appears in the R-T curves. When $T=T_c$, ΔR curves at the six cycles meet at the same value, which implies that the thermal hysteresis is relative to not only the concentration of the oxygen vacancy, but also the ferromagnetism in the LSCO/LAO film. Figure 3c) and d) show the identical magnetic hysteresis loops and M-T curves of LSCO/LAO film before (black) and after repeated transport measurements (red), demonstrating that the magnetic

property of the LSCO film keeps nearly unchanged after repeated transport measurements. This result suggests that the spin state of the Co cation doesn't change during the transformation of Co^{4+} ions to Co^{3+} ions resulting from the escape of O^{2-} ion. Previous spectral investigation has indicated that Co^{4+} ions induced by Sr-substitution in the strained $La_{0.7}Sr_{0.3}CoO_3$ film prefers to be a HS ($3t_{2g}2e_g$) state due to the Jahn–Teller (JT) splitting of t_{2g} ,^{19,20} which could be kept during the transformation.

Recent studies have shown that Joule heating by an applied current could momently raise the temperature of the manganite oxide film and modify the oxygen vacancies doping, resulting in an electro-thermal redistribution of oxygen vacancies (in submicrometer level).^{21,22} Lide Yao et al.²¹ have performed an electro-thermal simulation that an electric current of 50 µA could temporarily raise the temperature of the LSMO film to >600K in an area with radius of 100-200nm around the contact. In LSCO/LAO film, Co⁴⁺ ions has high energy, which prefers to convert into more stable Co³⁺ or/and Co²⁺ ions.⁹ The instability of Co⁴⁺ and the high ionic diffusivity in LSCO/LAO film make it possible to induce the same current effect under the 1 µA current, promoting the formation of the oxygen vacancies. In our previous work,¹⁶ we have performed the repeated transport measurements on the bulk sample of $La_{0.7}Sr_{0.3}CoO_3$, which was cut from the target. No obvious change of transport property was observed after repeated measurements, proving that no conductivity transformation caused by current effect assisted with temperature cycling occurs in the bulk sample. Obviously, the lattice strain in the LSCO/LAO plays a key role in the formation of the oxygen vacancies, probably reducing the formation energy of the oxygen vacancies. In addition, further experiments show that the defect can't be effectively modulated with sole current or temperature cycling. In other words, both current and temperature cycling are indispensable to the modulation of oxygen defect in the LSCO/LAO film, despite that the underlying mechanism is still unclear at this moment and worth further study.

To conclude, the oxygen vacancies could be engineered by the repeated transport measurements with temperature cycling in the LSCO/LAO film. Both current effect and temperature cycling play important roles in the formation of oxygen vacancies. Due to the release of oxygen, the high energy Co^{4+} ions transform into more stable Co^{3+} or/and Co^{2+} , leading to the continuous enhancement of the LSCO/LAO film resistance. Furthermore, the enhanced O^{2-} ion mobility and larger lattice parameter make the oxygen vacancies form more easily in the high temperature range, resulting in a sudden increase in the resistivity at the temperature approaching room temperature and a much higher resistance in the succeeding cooling process than that in the previous cycle. Our work demonstrates a novel and highly-efficient method to modulate oxygen vacancies in the perovskite-type oxides, which may bring new opportunities in designing high-efficiency oxidation catalysts.

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056435-6 Li et al.

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