PO₂ dependant resistance switch effect in highly epitaxial (LaBa)Co₂O_{5+δ} thin films

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Giant resistance switching behavior in mixed conductive (LaBa)Co₂O_{5+δ} epitaxial thin film were discovered in high temperature and reducing environments during the reduction and reoxidation process. A reproducible resistance response of over 99% was achieved in the films during a change of 4% H₂/96% N₂ to oxygen at temperature range of 400–780 °C. The results indicate that at, low oxygen partial pressure, the extension of oxygen deficiency is an essential factor to the high temperature physical properties of (LaBa)Co₂O_{5+δ} and demonstrates its potential application as a chemical sensor device for reducing environments at high temperature. © 2010 American Institute of Physics. [doi:10.1063/1.3484964]

Cobalt based perovskite oxides have received increasing attention in the past decade due to their high mixed ionic-electronic conductivity in chemical sensor and green energy device development.^{1,2} Recent studies indicate that oxygen deficient doped double perovskite cobaltates (LnBa)Co₂O_{5+δ} (Ln=La,Pr,Gd) have excellent mixed ionic-electronic conductivity with a fast surface exchange coefficient.^{3–5} In this family of compounds, the A-site cationic ordered arrangement is favored due to the large difference in Ba²⁺ and rare earth ionic radii, except (LaBa)Co₂O_{5+δ} (LBCO). In LBCO, the doped bivalent Ba²⁺ is not only inducing plenty of oxygen deficiency but also structurally providing the capability to achieve the smallest oxygen deficiency in this family of compounds due to the very similar ionic radii between Ba²⁺ and La³⁺. Therefore, LBCO provides a unique platform with the geometrical stabilized perovskite phase and a wide range of oxygen deficiency, which enables one to study the electrical conductivity, defect structures and stability at high temperature over a wide range of oxygen partial pressure.

Up to now, studies on LBCO are only limited to the bulk polycrystalline samples for low temperature transport and magnetic properties.^{6–8} The high temperature physical properties of LBCO are rarely studied due to the structure failure of the bulk material in a reducing environment. Recently, we have fabricated epitaxial single crystalline LBCO thin films on (001) LaAlO₃ (LAO), enabling one to systematically study the electrical transport properties of LBCO under various environments. A reproducibly dramatic resistance change is observed as the LBCO film is exposed to oxidizing and reducing environment over a wide range of temperature. Especially, it is interesting to note that the re-oxidation of the LBCO film has a very short response time, suggesting that an exceedingly fast oxygen exchange rate occurs at the film surface.

A KrF excimer pulsed laser deposition system with a wavelength of 248 nm was employed to deposit the (LaBa)Co₂O_{5+δ} thin films on (001) LaAlO₃ substrates. An energy density of 2.0 J/cm² and a laser repetition rate of 5 Hz were adopted during film deposition. A high density, single phase, stoichiometric (LaBa)Co₂O_{5+δ} target was purchased from Praxair Inc. The deposition is carried out at 850 °C with an oxygen pressure in 10–250 mTorr. The as-grown films were annealed in 200 Torr oxygen for 15 min at 850 °C and cooled down to room temperature at a rate of 5 °C/min.

Microstructural characterization reveals that the as-grown LBCO films have excellent single crystallinity and a high quality epitaxial nature. Briefly, Fig. 1(a) is a cross-sectional transmission electron microscopy (TEM) image of an LBCO film on (001) LaAlO₃ substrate showing that the as-grown LBCO thin film, with a thickness of ~150 nm, has a flat surface and an atomically sharp interface. Figure 1(b) is a selected-area electron diffraction (SAED) pattern taken from an area covering the film and the substrate with the electron-beam parallel to the [010]_{LAO}. The interface relationship between the LBCO film and LaAlO₃

FIG. 1. (a) Cross-section TEM of LBCO/LAO; (b) SAED pattern from LBCO/LAO interface; (c) cross-section HRTEM of LBCO/LAO.

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substrate was determined to be $(001)_{\text{LBCO}} // (001)_{\text{LAO}}$ and $\langle 100 \rangle_{\text{LBCO}} // \langle 100 \rangle_{\text{LAO}}$. The SAED pattern in Fig. 1(b) shows a set of weak diffraction spots located in the middle of two neighboring adjacent strong spots along the $[001]_{\text{LBCO}}$ direction or perpendicular to the interface. This pattern suggests a possible formation of ordered oxygen vacancies along the $[001]_{\text{LBCO}}$. Figure 1(c) is a cross-sectional high resolution TEM image of an LBCO/LAO film taken with the incident electron beam parallel to the $[010]_{\text{LAO}}$ showing the interface microstructure and epitaxial nature of the film and substrate.

To understand the transport property of the as-grown LBCO films, standard two-probe method with a Lakeshore 370 AC Bridge was employed to monitor the in-plane resistance under various chemical environments. The sample, with Pt electrode leads and silver paste contact, was mounted on an alumina rod with thermocouple and placed in a sealed alumina tube furnace. The temperature dependence of the resistance in a mildly reducing environment was characterized on the as-grown LBCO thin film in pure nitrogen, ($P_{\text{O}_2} \leq 1 \times 10^{-5}$ atm) [Fig. 2(a)]. It is interesting to note that as the sample undergoes its first temperature increasing process (~ 1 °C/min), an abnormal increase in resistance was found to start at 150 °C and reach a maximum at 442 °C followed by a sudden drop.

The first order derivative analysis of the resistance reveals that the first change process occurs in the temperature interval of 150–300 °C which can be attributed to the loss of adsorbed oxygen molecular: $\text{O}_{\text{ad}}^{2-} \rightarrow 1/2\text{O}_{2(\text{g})} + 2e^-$. The released electrons interact with the charge carrier hole in *p*-type semiconducting LBCO resulting in the loss of conductivity. The second resistance change, between 300–440 °C, with the resistance being almost tripled, is associated with the reduction in the cobalt ion. In LBCO, partial substitution of La^{3+} with Ba^{2+} introduces unstable Co^{4+} and oxygen vacancies $\text{V}_{\text{O}}^{\bullet\bullet}$. Oxygen deficiencies can be generated when Co^{4+} transfers into Co^{3+} and Co^{3+} to Co^{2+} , the reaction can be expressed as

Therefore, the electrons associated with the generated oxygen vacancy compensate the holes and reduce the conductivity. But interestingly, with the temperature further increased from 440 to 494 °C, the resistance undergoes a drastic drop. Although the mechanism of the sudden resistance drop during this heating process remains unclear, this phenomenon may somewhat relate to the reduction in the stoichiometric $\text{LaBaCo}_2\text{O}_6$ in to $\text{LaBaCo}_2\text{O}_{5.5}$, reported in the previous studies.⁹ This evidence indicates that the complete reduction in Co^{4+} to Co^{3+} can result in an oxygen stoichiometry very close to 5.5. Thus, due to the comparable crystal field energy and the intra-atomic exchange energy, the low spin, intermediate spin and high spin states of Co^{3+} may coexist in perovskite structure.^{8,10,11} The oxygen deficient concentration and distribution also influences the chemical environment of the cobalt ion.¹² Therefore, this irregular resistance behavior can be attributed to the coupling between the reduction in Co^{4+} to Co^{3+} and the spin state transition of Co^{3+} in the epitaxial LBCO thin films.

The conductivity behavior of LBCO thin film was further studied in water saturated 4% H_2/N_2 [Fig. 2(b)]. Two major resistance changing processes occur at 470–550 °C and 570–645 °C, which correspond to the reduction in Co^{3+}

FIG. 2. (Color online) Temperature dependence of $(\text{LaBa})\text{Co}_2\text{O}_{5.5}$ thin film resistance (a) 100% N_2 ; (b) 4% $\text{H}_2/3\%$ $\text{H}_2\text{O}/\text{N}_2$; and (c) resistance response at different temperature; (Inset: resistance change in alternating pure oxygen and 4% hydrogen at 780 °C.)

to Co^{2+} and Co^{3+} to Co^{2+} , where the resistance is first increased from 10^3 to 10^5 Ω and finally reaches 10^6 Ω. Since the reduced metal Co should be in a highly dispersed state on a matrix composed of the oxide,¹³ the high resistance of the reduced sample is the result of an absence of conductive Co–O layers in the crystal structure. Each resistance changing rate peak is split into two parts, indicating two slightly different reducing temperatures. The distribution of oxygen vacancies and coexistent A-site ordered and disordered phases of LBCO film¹⁴ leads a significant diversity of oxygen exchange and chemical properties of the cobalt ion, and is reflected in this reduction process.

The conductivity of the reduced LBCO thin film can be fully recovered by reoxidizing in pure oxygen. The resistance change was measured during the reduction-reoxidation cycles in the temperature range of 400–780 °C with a time interval of 100 ms [inset of Fig. 2(c)]. The resistance response is expressed as $\Delta R/R_{\text{H}}(\%)$ where R_{H} is the reference resistance in 4% $\text{H}_2/96\%$ N_2 , and its relationship with tem-

TABLE I. Features of high temperature O_2 sensors based on oxide semiconductors.

Semiconductor	Response time (t_{90})	Temperature ($^{\circ}C$)	Reference
LBCO thin film	0.5–8 s	780–400	This work
Ga ₂ O ₃ thin film	10–20 s	1000	16
Mg-doped SrTiO ₃	1–2 s	800–600	17
Pd–TiO ₂ anatase phase	70 s	400	18
V ₂ O ₅ –TiO ₂ thin-film	~5 min	200–350 $^{\circ}C$	19

perature is shown in of Fig. 2(c). The film exhibits over 99% response to the pure oxygen with the response time, defined as the time necessary to reach 90% of the final resistance, varying from 8 s (400 $^{\circ}C$) to 0.5 s (780 $^{\circ}C$). For comparison, Table I shows the response time of various resistive oxygen sensors at intermediate temperature and high temperature so far reported. The response time of LBCO epitaxial thin film is about one order lower than previous sensors at ~400 $^{\circ}C$ and comparable with the Mg-doped SrTiO₃ sensor at high temperature.

According to the Goldschmidt tolerance factor obtained for LnCoO₃ system, if only considering the geometric factors, lanthanum forms the most stable perovskite structure, so that the re-oxidation of reduced cobalt to form the perovskite structure is more favorable for LaCoO₃.¹⁵ Because Ba²⁺ and La³⁺ have very close ionic size, the same conclusion should apply to (LaBa)Co₂O_{5+ δ} . Also, the reduced LBCO thin film contains a high density of oxygen vacancies with quick diffusion speed. Considering the thin film thickness (150 nm), the reaction of oxygen and oxygen vacancy could reach equilibrium instantly in the presence of the oxygen molecules in the gas phase. With the catalytic activation of oxygen molecular by cobalt, the reoxidation reaction of LBCO thin film is sped up thermodynamically and kinetically, so that this drastic resistance change can be achieved within such a short time and indicates its potential application to high temperature resistive gas sensors.

In summary, the resistance evolution with temperature of the mixed conductive (LaBa)Co₂O_{5+ δ} single crystalline epitaxial thin film under reducing environment was investigated. The film shows a drastic resistance change during the

reduction and re-oxidation in the temperature range of 400–780 $^{\circ}C$. The superior performance of LBCO thin film in a reducing environment at high temperature has opened a great avenue for the development of various resistive chemical sensors and electrochemical devices in the harsh industrial conditions.

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