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Epitaxial Nature and Transport Properties in $(LaBa)Co_2O_{5+\delta}$ Thin Films[†]

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Epitaxial $(LaBa)Co_2O_{5+\delta}$ thin films were grown on (001) $LaAlO_3$ single-crystal substrates using pulsed laser deposition. Microstructure characterizations from X-ray diffraction and electron microscopy indicate that the films are highly *c*-axis oriented with cube-on-cube epitaxy. Transport property measurements indicate that the films have typical semiconductor behavior with a novel phase transition and hysteresis phenomena at 540 K. The chemical dynamic studies reveals that the resistance of the film changes drastically with the change of redox environment, i.e., the magnitude of resistance changes, $\Delta R = 1 \times 10^2 \Leftrightarrow 1 \times 10^6\ \Omega$, is found within a short response time (~700 ms). These phenomena suggest that the as-grown $(LaBa)Co_2O_{5+\delta}$ film have extraordinary sensitivity to reducing-oxidizing environment and the exceedingly fast surface exchange rate.

Introduction

Mixed ionic/electronic conducting materials are of increasing interest owing to their potential applications in various novel devices such as ceramic membranes, ultra sensitive chemical sensor, partial oxidation reactors as well as electrodes in solid oxide fuel cell (SOFC).[1−4] To improve the performance of those devices, the mixed ionic electronic conducting materials should meet the requirements of both high oxygen diffusivity and great enhancement of surface exchange rate,[5,6] These two desirable attributes are typically found in the oxygen deficient doped perovskite cobaltates $(Re,A)Co_2O_{5+\delta}$, where Re is a rare earth element and A is an alkaline earth element. The A-site cation average valence favors a compensating population of oxygen vacancies at low oxygen partial pressures and therefore leads to the observed high ionic conductivity. $(LnBa)Co_2O_{5.5+\delta}$ is one family of compounds that have received significant interest due to many intriguing mixed ionic/electronic conducting phenomena. The nature of the A-site cations, especially their size, and their distribution, ordered or disordered, may drastically influence the mixed conductivity. Taskin and co-workers have observed a remarkable enhancement of the oxygen diffusivity in A-site ordered $GdBaCo_2O_{5.5+\delta}$.[7] Our recent research showed that A-site ordered $PrBaCo_2O_{5.5+\delta}$ has unusually rapid oxygen transport kinetics at low temperatures ranging between 300 and 500 °C.[8,9] Various interesting physical phenomena have been observed in the perovskite cobaltate family. In particular, the layered perovskite $LaBaCo_2O_{5.5+\delta}$ becomes a unique case with some distinctive properties, such as the weakest tendency to A-site ordering and smallest oxygen nonstoichiometry due to the small difference between the radii of A-site cations' La^{3+} and Ba^{2+}.[10] Recently, Eeva-Leena Rautama et al. have fabricated and characterized the fully oxidized nanoscale-ordered $LaBaCo_2O_6$, disordered $La_{0.5}Ba_{0.5}CoO_3$, and the oxygen-deficient ordered $LaBaCo_2O_{5.5}$. They have also observed various interesting new phenomena in this system, such as the unusual magnetization and magnetotransport properties associated with the spin state of cobalt in low temperature.[11,12] It is well-known that the physical properties are strongly dependent

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upon the crystal structures and grain orientations. To minimize the effects from the porosity and grain boundaries in the polycrystalline structure, the single-crystalline $LaBaCo_2O_{5.5+\delta}$ is required. Recently, we have studied the epitaxial nature $(LaBa)Co_2O_{5+\delta}$ thin films on (001) $LaAlO_3$ and characterized the microstructures and transport properties with changing oxygen nonstoichiometry. By optimizing the growth conditions, we obtained the highly epitaxial perovskite $(LaBa)Co_2O_{5+\delta}$ single-crystalline thin film on (001) $LaAlO_3$ (LAO) by using pulsed laser deposition (PLD). Here we report the epitaxial nature and transport properties as well as the kinetic phenomena observed from the as-grown $(LaBa)Co_2O_{5+\delta}$ film. Various unique phenomena have been found in the films, such as extraordinary sensitivity to reducing-oxidizing environment and their exceedingly fast surface exchange rate. Those new findings will potentially make the epitaxial $(LaBa)Co_2O_{5+\delta}$ thin film a promising candidate for ultrasensitive chemical gas sensor and/or cathode component in IT-SOFC.

Experimental Section

A KrF excimer pulsed laser deposition (PLD) system with a wavelength of 248 nm was employed to deposit the $(LaBa)Co_2O_{5+\delta}$ thin films on (001) LAO substrates. An energy density of 2.0 J/cm^2 and a laser repetition rate of 5 Hz were adopted during film deposition. A high density, single phase, stoichiometric $(LaBa)Co_2O_{5+\delta}$ target was purchased from MTI Crystal Inc. Single-crystal (001) LAO (c_{LAO} = 3.788 Å) was selected as the substrate for epitaxial growth of $(LaBa)Co_2O_{5+\delta}$ thin film because of the desirable lattice matching. The optimal growth conditions were found to be 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 to room temperature at a rate of 5 °C/min. The films were then annealed at 445 °C in a tube furnace individually under pure oxygen or 4% hydrogen in nitrogen (1 atm) for 3 h. Microstructure, crystallinity, and epitaxial behavior of the $(LaBa)Co_2O_{5+\delta}$ films were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The transport properties of the after-annealed samples were measured by resistance measurements in the temperature range from 78 to 295 K and 295 to 700 K with The Lake Shore model 370 AC resistance bridge. Platinum lead wire was connected on the sample with silver paste which had been air-dried at room temperature and annealed before measurement.

Results and Discussions

Microstructure Characterizations Using XRD and TEM. Figure 1 shows the XRD $\theta-2\theta$ scans of the as-grown $(LaBa)Co_2O_{5+\delta}$ thin film deposited on LAO (001). (all orientations in this article will be given in terms of the prototype cubic perovskite structures) The as-grown film is pure $(LaBa)Co_2O_{5+\delta}$ phase with highly oriented along the c axis with only (00l) peaks observed. The in-plane Φ scan along the ⟨101⟩ directions of the $(LaBa)Co_2O_{5+\delta}$ and LAO reveals that only the {101} reflections separated by 90° were presented in the scan with sharp peaks, confirming that the $(LaBa)Co_2O_{5+\delta}$ films have excellent single crystallinity, as seen the inset of Figure 1. The in-plane relationship between the $(LaBa)Co_2O_{5+\delta}$ film and the LAO substrate was therefore determined to be $[001]_{LBCO}//[001]_{LAO}$ and $(100)_{LBCO}//(100)_{LAO}$. This interface relationship suggests that the as-grown $(LaBa)Co_2O_{5+\delta}$ films be cube-on-cube epitaxy.

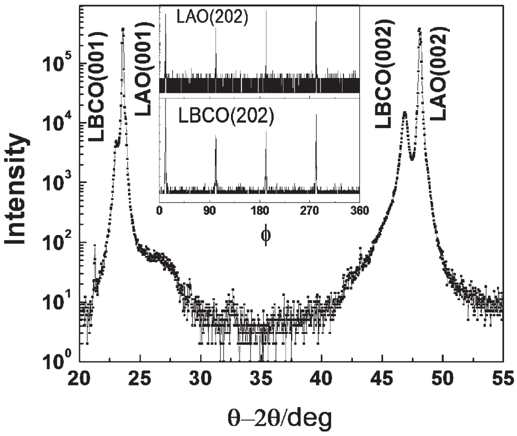

Figure 1. XRD pattern of as grown $(LaBa)Co_2O_{5+\delta}$ film. Inset: Φ scan of LAO substrate and $(LaBa)Co_2O_{5+\delta}$ films.

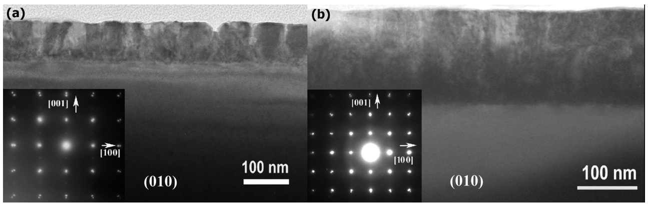

Figure 2. TEM cross-section images and the corresponding SAED patterns taken along the [010] direction of $LaAlO_3$ for (a) oxygen and (b) hydrogen annealed films.

To further investigate the epitaxial nature and the interface microstructure of the $(LaBa)Co_2O_{5+\delta}$ films on (001) LAO, we performed the TEM studies on both $(LaBa)Co_2O_{5+\delta}$ films that were postannealed in oxygen and hydrogen at 445 °C. As seen in Figure 2, both $(LaBa)Co_2O_{5+\delta}$ films have a smooth surface, uniform thickness, and clearly defined interface with the (001) LAO substrate. The inset of Figure 2a is the selected area electron diffraction (SAED) pattern taken from the $(LaBa)Co_2O_{5+\delta}$ /$LaAlO_3$ interface annealed in oxygen. The diffraction pattern contains one set of strong reflections corresponding to a cubic cell but close inspection shows the presence of an additional set of weak half-integer reflections indicating a doubling of perovskite unit cell parameter along the $\langle 001\rangle_C$ directions. The $(LaBa)Co_2O_{5+\delta}$ film is therefore tetragonal with lattice parameters of $c \approx 2a_p$ (a_p = lattice parameter of the corresponding perovskite structure), which is oriented perpendicular to the substrate surface. The superstructure clearly identified along the c axis can be resulted either from the 1:1 ordered stacking of LaO and BaO layers or from the orderly oxygen vacancies in the $(LaBa)Co_2O_{5+\delta}$ film. Electron diffraction further confirms that the interface orientation relationship between the film and substrate is $[001]_{LBCO}//[001]_{LAO}$ and $(100)_{LBCO}//(100)_{LAO}$, which was obtained from the X-ray diffraction. Furthermore, the sharp diffraction sports and clean diffraction pattern (no diffusion or extra diffraction spots) indicate that the $(LaBa)Co_2O_{5+\delta}$ films have good single crystallinity and excellent epitaxial quality. The TEM image of the $(LaBa)Co_2O_{5+\delta}$ film annealed in 4% hydrogen is shown in Figure 2b. Although the epitaxial nature and interface relationship of the film with hydrogen treatment are similar to the film treated in oxygen, no superlattice reflections can be observed.

The SAED pattern of both oxygen and hydrogen annealed samples indicates a slightly distorted tetragonal structure with the out-of-plane lattice parameter (*c* axis) is increased by 1.5 and 2.9%, respectively. Such a distorted lattice is probably due to the compressive stress from the lattice mismatch or the loss of oxygen during the annealing, which is similar to the behavior observed in the $(La,Sr)CoO_3$ thin films.[13] Further investigations are needed and will be reported later.

Resistance Response. To understand the transport behavior of the $(LaBa)Co_2O_{5+\delta}$ films, the changes in the film resistance when switching from pure oxygen to 4% hydrogen in nitrogen environment were monitored by using a highly precise AC resistance bridge at 412 °C. In order for the resistance of $(LaBa)Co_2O_{5+\delta}$ film to reach a stable value, the as-grown film was annealed in pure oxygen for three hours. As the gas flow was switched from oxygen to 4% hydrogen in nitrogen, the resistance increases 4 orders of magnitude, which is from $1 \times 10^2\ \Omega$ to $1 \times 10^6\ \Omega$ ($\Delta R = 1 \times 10^4\ \Omega$). Measurements were made at intervals of 100 ms. The resistance change can be reversed by changing the gas back to oxygen. The kinetics of the reduction process occurring in the film is shown in more detail in Figure 3b. The resistance change in reducing conditions at such a short time interval suggests that $(LaBa)Co_2O_{5+\delta}$ is extremely sensitive to hydrogen. The substantial changes occur in the conductivity indicate the rapid adsorption of reducing gases (H_2) on the film surface, dissociation and reaction with lattice oxygen to produce water. Since the $(LaBa)Co_2O_{5+\delta}$ film is very thin (100 nm), the dominate contribution to the rate of the change in conductivity arises from the surface exchange rate, which can be represented by

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-$$

Because electrons are released upon reduction, this process results in a decrease in the p type $(LaBa)Co_2O_{5+\delta}$ film conductivity due to the reduction of the concentration of electron holes. The analysis of the shape of the resistance curve shows two different reaction rate peaks in the derivative curve (see Figure 3b). This may originate from the various oxidation states of cobalt ions in $(LaBa)Co_2O_{5+\delta}$. For $\delta \leq 0.5$, Co^{2+}:Co^{3+} = $0.5-\delta$:$0.5+\delta$, and for $\delta \geq 0.5$, Co^{4+}:Co^{3+} = $\delta - 0.5$:$1.5 - \delta$. Thus, the $(LaBa)Co_2O_{5+\delta}$ film annealed in oxygen has the lowest oxygen nonstoichiometry with $\delta \geq 0.5$ and with coexistence of Co^{4+} and Co^{3+}. The first step in the reduction corresponds to the reduction of Co^{4+} to Co^{3+} (as indicated by "*" in Figure 3b) followed by reduction of Co^{3+} (indicated by "**"), which is most likely a mixture of Co^{2+} and Co^{3+} oxidation states represented by the composition $(LaBa)Co_2O_{5+\delta}$ with $\delta \leq 0.5$. The hydrogen annealed $(LaBa)Co_2O_{5+\delta}$ film becomes insulator-like with a room temperature resistivity of $2 \times 10^5\ \Omega$ cm as a consequence of the lower the concentration of p type charge carriers on reduction. The reoxidation of the reduced sample is exceedingly fast. The maximum rate of change of the resistance is about $3 \times 10^6\ \Omega$/s, indicating a rapid surface exchange rate.

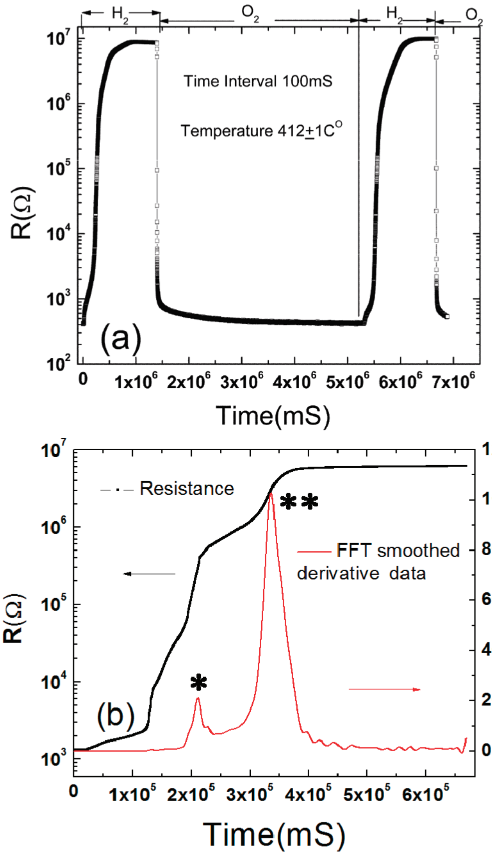

Figure 3. Oxygen–hydrogen responses with reversible conducting–insolating transition monitored by resistance measurements at 412 °C.

Temperature Dependence of the Electrical Resistance. The temperature dependences of the electrical resistance for the ordered layered 112-type $(LaBa)Co_2O_{5+\delta}$ films were systematically studied in the temperature range of 78–295 K and 295–700 K. The resistances of $(LaBa)Co_2O_{5+\delta}$ films decrease exponentially with the increase in temperature in the range of 78–295 K, indicating that the $(LaBa)Co_2O_{5+\delta}$ films have typical semiconductor behavior at low temperatures (see Figure 4). However, the slope from a plot of $\ln(\rho)$ versus $1/T$ plot (inset of Figure 4a) shows slight dependence on the temperature and deviates from a linear relationship. This suggests that *R* does not have a simple activation behavior, possibly because of a transition from low spin state to a thermally excited intermediate spin state of cobalt ions.

Figure 4b shows the electrical conductivities of $(LaBa)Co_2O_{5+\delta}$ films, which were measured in oxygen

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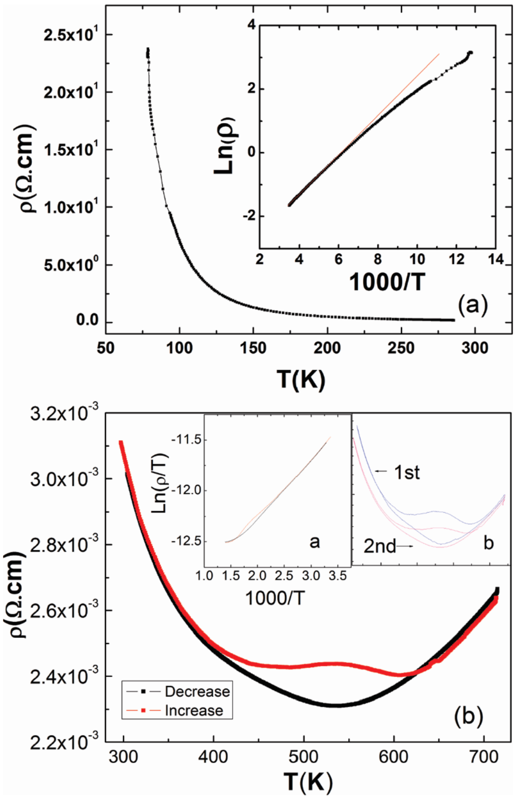

Figure 4. Temperature dependence of electrical resistivity (a) 78−295 K; (b) 295−700 K.

(1 atm) to determine the high-temperature (295−700 K) transport properties with the temperature changing rate of 3 °C/min (Figure 4b). The resistance initially decreases with the increase in temperature and then increases with the increase in temperature with an upturn transition point near 540 K. This phenomena probably results from the thermal activation in the low temperature range and the lost of oxygen associated with the decrease of the hole concentration at higher temperature. The plot of the $\ln(\rho/T)$ versus $1/T$ can be perfectly fitted linearly from room temperature to the transition point, as seen in the inset a of Figure 4b. An unusual result is observed in the high-temperature transport data. A hysteresis gap in the resistance data is observed near the transition point with increasing and decreasing temperature. The resistance change with increasing temperature shows two minimum transition points. Because in the thin film samples the bulk diffusion process can be ignored, this anomaly may be related to the spin state transitions of the Co^{3+} and Co^{4+} ions associated with the oxygen exchange on the surface which can be represented by $O_o'' \leftrightarrow \ddot{V}_o + 1/2O_2 + 2e'$.

The resistance gap decreases with every cycle of measurements carried out under identical conditions (Figure 4b, inset b), which indicates that the oxygen exchange process is not fully reversible and that the concentration of Co (IV) may play an important role in these phenomena.

Conclusions

Highly epitaxial 112-type layered $(LaBa)Co_2O_{5+\delta}$ single crystalline thin films were successfully grown on (001) $LaAlO_3$ substrates by using pulsed laser ablation. The microstructure characterizations from X-ray diffraction and electron microscopy indicate that the films are either A cation ordered or oxygen vacancy ordered and they are highly *c*-axis oriented with cube-on-cube epitaxy. The interface relationship was determined to be $[001]_{LBCO}//[001]_{LAO}$ and $(100)_{LBCO}//(100)_{LAO}$. Transport property measurements indicate that the films have typical semiconductor behavior with a novel phase transition and hysteresis phenomena at 540K. In addition, the chemical dynamic studies reveal that the resistance of the film changes drastically with the change of redox environment. A large magnitude of resistance changes ($\Delta R = 1 \times 10^2 \Leftrightarrow 1 \times 10^6\ \Omega$) is found within an extremely short response time. These phenomena show that the as-grown $(LaBa)Co_2O_{5+\delta}$ films have extraordinary sensitivity to reducing−oxidizing environment and the exceedingly fast surface exchange rate. These results suggest the epitaxial $(LaBa)Co_2O_{5+\delta}$ thin films can be a promising candidate as ultrasensitive chemical gas sensor and cathode component for IT-SOFC.

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