Nanodomain induced anomalous magnetic and electronic transport properties of $\text{LaBaCo}_2\text{O}_{5.5+\delta}$ highly epitaxial thin films

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A giant magnetoresistance effect ($\sim 46\%$ at 20 K under 7 T) and anomalous magnetic properties were found in a highly epitaxial double perovskite $\text{LaBaCo}_2\text{O}_{5.5+\delta}$ (LBCO) thin film on (001) MgO. Aberration-corrected Electron Microscopy and related analytical techniques were employed to understand the nature of these unusual physical properties. The as-grown film is epitaxial with the c -axis of the LBCO structure lying in the film plane and with an interface relationship given by $(100)_{\text{LBCO}} \parallel (001)_{\text{MgO}}$ and $[001]_{\text{LBCO}} \parallel [100]_{\text{MgO}}$ or $[010]_{\text{MgO}}$. Orderly oxygen vacancies were observed by line profile electron energy loss spectroscopy and by atomic resolution imaging. Especially, oxygen vacancy and nanodomain structures were found to have a crucial effect on the electronic transport and magnetic properties. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4861406>]

I. INTRODUCTION

Oxygen vacancies play an important role in functionality of transition metal oxide materials and devices, such as in photoluminescence,^{1,2} gas sensors,^{3,4} solid oxide fuel cells,^{5,6} polarization orientation of ferroelectric thin films,⁷ magnetic properties, and resistive switching.⁷⁻⁹ Among them, oxygen deficient perovskite cobaltates $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Y}$ and *Lanthanide*) have attracted much attention due to their important and interesting physical properties, such as high chemical stability, good oxygen permeability and mixed electronic and ionic conductivity at high temperature (500°C – 700°C)¹⁰⁻¹² since they were discovered in 1950's.^{13,14} Because of these complicated and important physical properties, perovskite cobaltates are suitable materials for energy conversion, catalysts, sensing materials, and solid oxides fuel cells.¹⁵⁻¹⁸ Furthermore, many fascinating physical phenomena were discovered in perovskite cobaltates since magnetic ordering was first reported in the 1960's.¹⁹ These include crystal structure transformations, successive paramagnetic-ferromagnetic-antiferromagnetic (PM-FM-AFM) transitions upon cooling, metal insulator transitions, and orbital and spin-state ordering. The discovery of large values of magnetoresistance in $\text{LnBaCo}_2\text{O}_{5.4}$ ($\text{Ln} = \text{Eu}, \text{Gd}$)²⁰ has led to great interest due to strong spin and orbital interactions and the strong correlation between induced cobalt valence states, phase separation, and competition between ferromagnetism and antiferromagnetism. Further understanding of the physical nature of perovskite cobaltates can provide important information relevant to advanced material research and novel device development based on these strong correlated electronic and

magnetic properties.²¹⁻²³ Among the $\text{LnBaCo}_2\text{O}_{5+\delta}$ family, $\text{LaBaCo}_2\text{O}_{5+\delta}$ (LBCO) ($0 \leq \delta \leq 1$) exhibit some unique physical properties,^{24,25} because the similar ionic sizes of *La* and *Ba* lead to the formation of both A-site disordered and A-site ordered structures. In disordered structure, *La/Ba* randomly occupy A site of perovskite structure surrounded by eight corner sharing CoO_6 octahedra. In the ordered structure, two kinds of AO layers are present (*LaO* and *BaO*) leading to the repeat pattern of $(\text{CoO}_2)(\text{LaO})(\text{CoO}_2)(\text{BaO})$ layers in the ordered structure. Different cobalt-oxygen ion coordination environments, such as pyramidal, octahedral or both are present in the structures of the $\text{LaBaCo}_2\text{O}_{5+\delta}$ phases depending on the oxygen content ($0 \leq \delta \leq 1$).^{22,23,26} The crystal structure of $\text{LaBaCo}_2\text{O}_5$ is tetragonal with $P4/mmm$ space group, corresponding to a double of the original perovskite unit cell along the c direction due to alternating *BaO* and *La* layers; and contains double layers of CoO_5 square pyramids. The crystal structure of oxygen nonstoichiometric $\text{LaBaCo}_2\text{O}_{5+\delta}$ ($0 < \delta < 1$) is more complicated because both CoO_6 octahedra and CoO_5 pyramids are present, the ratio depending on δ . As an example $\text{LaBaCo}_2\text{O}_{5.5}$ has an orthorhombic structure with space group $Pmmm$. *BaO* and $\text{LaO}_{0.5}$ layers are alternating along the c direction, and CoO_6 octahedra and CoO_5 pyramids alternating along the b direction. In other words, the oxygen vacancies are ordered along b direction. $\text{LaBaCo}_2\text{O}_6$ ($\delta = 1$), has a tetragonal structure with $P4/mmm$ symmetry, containing *BaO* layers alternating with *LnO* layers along the c direction; no oxygen vacancies are present in the *LnO* layers.

Due to the wide range of oxygen non-stoichiometry present in LBCO, high quality single crystals for systematic study of their intrinsic physical properties are difficult to obtain. Therefore, fabrication of epitaxial LBCO thin films with good single crystal quality becomes a practical approach to study material science issues in the LBCO system. In the past few years, we have investigated the epitaxial

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growth of LBCO thin films with controllable microstructures on various single crystal substrates and observed various anomalous physical properties in this system.^{3,4,27} Here, we report new results on the nature of the intrinsic anomalous physical phenomena.

II. EXPERIMENTAL

LBCO thin films on (001) MgO substrate were fabricated by using a KrF excimer pulsed laser deposition with a wavelength of 248 nm. The optimal growth conditions were with a deposition temperature of 850 °C, an oxygen pressure of 250 mTorr and laser energy of 2.0 J/cm². The LBCO films were annealed at 850 °C for 15 min in a pure oxygen atmosphere at 200 Torr after the fabrication and then slowly cooled down to room temperature at a rate of 5 °C/min. The microstructure, crystallinity, and epitaxial behavior of the LBCO films were systematically examined by transmission electron microscopy (TEM) and aberration corrected scanning transmission electron microscopy (STEM) imaging at 200 kV in a JEOL ARM 200F microscope. Electron energy loss spectroscopy (EELS) measurements were taken with a Gatan Tridium spectrometer fitted in the microscope. Samples were prepared in plan-view and cross-section by mechanical polishing followed by Ar⁺ ion milling. The transport behavior and magnetic properties of the thin films were determined using a Quantum Design Physics Property measurement system.

III. RESULTS AND DISCUSSIONS

The temperature dependence of the electrical resistance of LBCO thin film on MgO measured under the applied magnetic fields from 0 T to 7 T is shown in Figure 1, similar to our previous work.^{28,29} The magnetoresistance, MR (%), is defined as $MR(\%) = [R(H) - R(0)]/R(0) \times 100\%$, where $R(H)$ is electrical resistance under the magnetic field and $R(0)$ is at zero magnetic field, respectively. The films show typical semiconductor behavior in the measurement temperature range. A giant MR

FIG. 1. Resistance of LBCO thin film on MgO substrate versus temperature under different magnetic field. The top of the inset is the Magnetoresistance (MR) as a function of applied magnetic field at 40 K and 20 K. The bottom of the inset is magnetic hysteresis loop measured at 200 K, 117 K, and 30 K.

effect value of 46% was achieved at 20 K under an applied magnetic field of 7 T. Under the application of a magnetic field to the film, the resistance decreases with increase of the applied magnetic field, resulting from the fact that Co ion spin is aligned along the external magnetic field direction to reduce the scattering rate of charge carriers and to increase the conductivity for inducing the negative magnetoresistance. This giant negative magnetoresistance value is near three times of that from its bulk materials. The inset (top) of Figure 1 is the magnetic field dependent isotherm MR behaviors at 20 K and 40 K with the external magnetic fields changed from 0 T to 7 T. The magnetic hysteresis loop measurements were conducted by cooling the film under zero magnetic field from room temperature to the registered temperature, 200 K, 117 K, and 30 K, respectively, at which the changes of magnetic moment with the applied magnetic field were measured. The hysteresis loop achieved at 30 K shows a very large coercive field of ~5000 Oe, as seen in the inset (bottom) of Figure 1. It is interesting to note that the giant negative magnetoresistance value and very large coercive field behaviors are quite different from those from its bulk material.

To further understand the relationship between the as-observed anomalous physical properties and the microstructure of the as-grown LBCO films, TEM and STEM imaging were performed in cross-section and plan-view. An aberration-corrected STEM image of the sample prepared in cross-section, in which the 100 nm-thick LBCO layer and the substrate MgO were studied, is shown in Fig. 2(b). Figures 2(a) and 2(c) correspond to selected area electron diffraction (SAED) patterns taken along the [010] zone axis from the marked areas shown in Fig. 2(b): interface and film, respectively. The high quality of the epitaxial film is

FIG. 2. LBCO/MgO interface: (a) and (c) show selected area electron diffraction patterns along [010] zone axis of the interface and LBCO film, respectively. (b) High resolution HAADF-STEM image of the LBCO and MgO. (d) A HAADF-STEM image and schematic crystal structure views in 2D and 3D, showing the atomic positions of the cations in the [010] oriented LBCO film.

apparent from the SAED patterns. The lattice mismatch 7.7% is computed from the electron diffraction spots in Figure 2(a) using $(a_{\text{LBCO}} - a_{\text{MgO}})/a_{\text{MgO}}$, where a is the lattice parameter. This is in good agreement with the X-ray diffraction result from our previous report.^{28,29} Weak diffraction spots at the midpoints between two strong spots can be seen in Figures 2(a) and 2(c) (identified with arrows in the SAED patterns) indicating the formation of nanoscale regions of ordered tetragonal structure²⁸ or of the ordered oxygen vacancy structure in the LBCO film.

In HAADF-STEM images the contrast depends on the atomic number of the present elements (so called Z-contrast). This operation mode works remarkably well in materials with different Z number and homogenous thickness because the intensity dependence on atomic number is close to $Z^{3/2}$ with minimum dependence on microscope defocus.³⁰ In the LBCO double-perovskite structure, barium and lanthanum occupy the perovskite A site positions while cobalt ions are located on the B sites. Ba^{2+} and La^{3+} have larger atomic numbers ($Z=56$ and $Z=57$, respectively) compared with Co ($Z=27$). In Fig. 2(d), a HAADF-STEM image shows the cation positions in the film together with 2D and 3D views of the structure of LBCO. Light elements such as oxygen are not detectable by HAADF imaging. In the JEOL ARM200F microscope bright field (BF) images can be collected at the same time as the HAADF images are recorded. The BF detector in the microscope has been configured so that it can register light atoms (extremely weak scattering) using the circular beam stopper in the center of the optical axis.³¹ Under these conditions, annular bright field (ABF) and HAADF images can be recorded at the same time as well. ABF imaging has proven to be an effective mean of visualization for lighter atoms, such as oxygen.³¹

The images of the LBCO thin-film shown in Figure 3 have been recorded with three different STEM imaging modes: HAADF in Fig. 3(a), BF in Fig. 3(b), and ABF in Fig. 3(c). The lighter atomic columns contain cobalt and oxygen and contribute less to the intensity of the features in the HAADF image, these columns are overlaid in red in Fig. 3(a). From one domain to another the Co/O columns show a weaker intensity. This slightly change in contrast is perceived in the anti-phase boundary (APBs) domain from the left, which is around 2 nm wide as illustrated in Fig. 3(a). A weaker intensity compared with the stoichiometric region shows where the vacancies reside,⁵ meaning that the Co/O atomic columns with lower intensity are oxygen-deficient. Several others APBs have been observed in the film that range in size up to 12 nm. The vacancy ordered phases tend to form domains accommodated by the APBs. In the HAADF image from Fig. 3(a) the La, Ba, and Co/O columns are displayed as bright spots and in the BF image from Fig. 3(b) as dark spots, but the O columns are not visible in neither. On the other hand, in the ABF image from Fig. 3(c), there is a mid-tone contrast that identifies the oxygen positions in the structure not seen in the HAADF and BF images. The image in Fig. 3(c) shows enhanced contrast in lighter atoms since ABF phase-contrast imaging requires the object only to modify the phase of a wave.³² The oxygen atomic columns are marked with black circles alongside the other colored atomic positions.

FIG. 3. STEM (a) HAADF, (b) BF and (c) ABF images along the [010] LBCO zone axis showing the atomic structure. The representation of the atomic columns positions corresponding to Co/O are overlaid in red, the cations are overlaid in blue and green, and the oxygen positions are marked with dark circles. Anti-phase boundaries (APBs) are signaled by arrows in the top of the image.

A STEM-EELS analysis is used to probe the oxygen signal in the LBCO structure. The line scan is shown in Figure 4. An intensity profile extracted from the EELS spectrum at the O K edge is correlated with the HAADF image

FIG. 4. HAADF image and line scan intensity profile of [010] oriented LBCO film and the corresponding intensity line profile extracted from the O K edge EELS signal. The green arrow indicates the direction of the line scan. The red arrows indicate a darker contrast observed in the HAADF image and an expansion between the horizontal planes. This is also perceived in the intensity of the HAADF signal profile. The variation of the O K edge intensity is related to the different oxygen concentration along these planes.

FIG. 5. HAADF-STEM images of the (a) Cross section view showing individual columnar nanodomains and (b) Plan-view showing isolated domains of the LBCO film. Figures (c) and (d) are the enlarged regions indicated in the rectangular regions of (a) and (b), respectively. Nanodomains with the same width are appreciated in cross-section and in plan-view.

intensity profile of the same scanned region. During the acquisition, the spectrum of the O K edge intensity is recorded simultaneously with the HAADF signal. The significant reduction in the O K edge intensity profile observed in some columns can be interpreted as a variation in O concentration. Not directly translated into local stoichiometry due to possible artifacts,⁵ the result, however, indicates that these columns are oxygen deficient. The HAADF image shows a darker contrast every other horizontal plane, suggesting a relaxation of the lattice due to oxygen deficient layers. Lattice expansion in the perovskite structure has been observed to be related to oxygen-depleted layers that reveal a variation in oxygen content.^{5,33} The strain due to the lattice mismatch plays an important role in the generation of defects and a high density of oxygen vacancies may arise because of the increase in the lattice parameters induced by the strained film. A compression and expansion of the lattice cell is expected. The data acquired from the EELS line scan revealed a reduction in oxygen composition along scanned columns in which the spacing between subsequent layers is shifted.

In Figure 5, HAADF-STEM cross section (Fig. 5(a)) and plan-view (Fig. 5(b)) images show boundaries within the material of the LBCO film. In the plan-view image, the crystal structure is observed to outlast as nano-patterns preferentially between the APBs, where amorphous material has been formed possibly during the sample preparation process. This phenomenon might be related to the one observed in LBCO films grown on SrTiO_3 where it has been suggested that the regions inside the APBs are more stable than the crystal defect-free.³⁴ Such stability may have influence on the physical properties of the films. The dimensions of these nano-domains observed in plan-view correlate very well with the size of the observed APBs domains in cross-section, which are of the order of 2 to 12 nm (see the enlarged regions in Figs. 5(c) and 5(d)).

The observation of APBs domains from 2 to 12 nm and the confirmation of oxygen vacancies in the structure provide

insight into the physical properties of the film. A tendency of Co-3d and O-2p orbitals to hybridize in $\text{LaBaCo}_2\text{O}_6$, as mixed $d^6/d^7\bar{L}$ for Co^{3+} and $d^5/d^6\bar{L}$ for Co^{4+} , allows the hole on the apical oxygen of the CoO_6 octahedra to couple with e_g electrons, leading to ferromagnetism and metallic conductivity.^{35,36} The fact that the film exhibits semiconductor behavior with the coexistence of ferromagnetic and antiferromagnetic behaviors may result from the oxygen vacancies created on the apical oxygen sites of LBCO. Such a structure will dramatically reduce the coupling between e_g electrons and holes and increase the number of $\text{Co}^{3+}\text{--O--Co}^{3+}$ antiferromagnetic super exchange interactions, inducing the appearance of electronic phase separation, where AFM and FM states are competing. At the same time, the presence of oxygen vacancies which play the role of pinning centers may result in the larger coercive field of ~ 5000 Oe and anisotropic effect of MR observed for the film. The APBs domains from 2 nm to 12 nm in size may also contribute to the observed phenomena. The APBs will influence the magnetization alignment along the magnetic field.

IV. CONCLUSIONS

In summary, giant magnetoresistance ($\sim 46\%$ at 20 K under 7 T) and anomalous magnetic properties were found in the highly epitaxial double perovskite $\text{LaBaCo}_2\text{O}_{5.5+\delta}$ (LBCO) thin film on (001) MgO. Microstructural studies reveal that these anomalous physical phenomena originate from the oxygen vacancy structures and the APBs in the LBCO film. The APB domains with oxygen vacancy structures may strongly affect the electronic transport and magnetic properties and could interpret the nature of giant magnetoresistance and anomalous physical properties.

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