Effect of film thickness and strain state on the structure, magnetic and transport properties of La$_{0.9}$Sr$_{0.1}$CoO$_3$ films*

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A R T I C L E   I N F O

Keywords:
Thin films
Strain
Microstructure
Physical properties

A B S T R A C T

In this paper, we investigate the effects of film thickness and strain state on the structure, magnetism and electrical transport properties of La$_{0.9}$Sr$_{0.1}$CoO$_3$ (LSCO) thin films. The x-ray diffraction analysis shows that the out-of-plane lattice parameters of LSCO films grown on different substrates gradually approach those of the bulk LSCO with increasing film thickness, indicating that the strain induced by the substrates is partially relaxed in thick films, i.e. 100 nm. The film magnetism is gradually enhanced with increasing film thickness. For the 20-nm-thick film, it is almost non-magnetic. However, the film becomes ferromagnetic when its thickness increases up to 100 nm. The magnetism is stronger for the film under compressive strain than that under tensile strain. The change in the magnetic properties of films is attributed to the lattice strain, which can affect the spin state of Co ions. Regarding the conductivity, all the samples show a semiconducting-like behavior, and the resistivity is inversely proportional to the film thickness. The electrical transport mechanism of the films with different thickness transforms from a three-dimensional variable range hopping (VRH) to a small-polaron hopping conduction (SPC) with increasing temperature. Fascinatingly, the temperature for transport mechanism transformation decreases gradually with increasing film thickness. This work could shed light on the electrical transport mechanism of LSCO films with different thickness.

1. Introduction

Among the mixed-valence metal oxides with perovskite structures, Sr-doped lanthanum cobaltites of general formula La$_{1-x}$Sr$_x$CoO$_3$ have attracted considerable interest due to their fascinating physical properties [1–4]. In particular, La$_{1-x}$Sr$_x$CoO$_3$ thin films drew extensive attention in the past decades because some unexpected physical phenomena including the non-magnetic window around $x = 0.2$ [5], the ferromagnetic insulator [5,6], and strain-induced high coercivity [7], etc., which are absent in bulk counterparts, can be induced by lattice strain in thin films.

Although some excellent work [8–10] was carried out to explore the electrical transport mechanism and ferromagnetic-paramagnetic transition mechanism of La$_{1-x}$Sr$_x$CoO$_3$ films, we noticed that most previous work [11–13] about strained La$_{1-x}$Sr$_x$CoO$_3$ films focused on two cases, i.e. $x = 0$ and 0.3, for which two different mechanisms prevail, namely, super-exchange (SE) and double-exchange (DE). For the intermediate doping range, the SE and the DE strongly compete with each other, and a unique strain effect could be produced when their equilibrium is broken. Recent studies have shown that the lattice strain can dramatically modify the properties of La$_{1-x}$Sr$_x$CoO$_3$ thin films, leading to a high coercivity, which indicates that the physical properties of La$_{1-x}$Sr$_x$CoO$_3$ films can be adjusted by changing the external factors such as film thickness and the substrate [14–16]. Particularly, when the Sr-doping content ranges from 0 to 0.2, the effects of substrate and film thickness will become more evident because the dominance of DE and SE is nearly equal, which could result in some fascinating physical properties such as a ferromagnetic insulator around $x = 0$ and a non-magnetic around $x = 0.2$ [5]. Therefore, it is urgent to investigate the effects of the substrate and film thickness on the physical properties of the strained La$_{1-x}$Sr$_x$CoO$_3$ ($0 < x < 0.2$) films.

In this work, La$_{0.9}$Sr$_{0.1}$CoO$_3$ (LSCO) films with different thickness were chosen to clarify the effects of substrate and film thickness on the physical properties. The film magnetism is gradually enhanced with increasing film thickness, which is attributed to lattice strain. The magnetism is stronger for the film under compressive strain than that under tensile strain. For the electrical transport mechanism, there is a crossover from a three-dimensional variable range hopping (VRH) to a small-polaron hopping conduction (SPC) with increasing temperature for all the LSCO films with different thickness.

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* Electronic supplementary information (ESI) available: Fitting curves of resistivity using $\ln \rho$ vs $T^{-1/3}$, $\ln \rho$ vs $T^{-1}$, and $\ln \rho$ vs $T^{-1/3.5}$. E-mail address: yqwang@qdu.edu.cn (Y. Wang).

https://doi.org/10.1016/j.ssi.2018.01.034

Received 5 September 2017; Received in revised form 5 January 2018; Accepted 23 January 2018

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2. Experimental

The LSCO thin films were epitaxially grown on the SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) substrates using pulsed laser deposition (PLD) technique. The target was prepared by solid state reaction from the ceramic powders of La$_2$O$_3$, SrCO$_3$, and Co$_2$O$_3$. The wavelength of the excimer laser was 248 nm, the laser energy density was 1.5 J/cm$^2$, and the repetition rate was set to 1 Hz. During the deposition process, the substrate was maintained at 800 °C and the oxygen pressure was kept at 50 Pa. The thickness of the obtained films was 20 nm, 50 nm and 100 nm, determined by deposition time. After the deposition, the films were naturally cooled down to room temperature at 50 Pa.

Specimens for transmission electron microscopy (TEM) examinations were prepared in cross-sectional orientations using conventional techniques of mechanical polishing and ion milling. The ion milling was performed using a Gatan model 691 precision ion polishing system (PIPS). The bright-field (BF) imaging, and high-resolution TEM (HRTEM) examinations were carried out on a JEOL JEM 2100F electron microscope operated at 200 kV. The structure of the films was analyzed by x-ray diffraction (XRD) using RIGAKU x-ray diffractometer containing CuK$_α$ radiations. Reciprocal space mappings (RSM) were measured using a D8 Bruker x-ray diffractometer with monochromatic CuK$_α$ radiation. The magnetic properties of the films were measured using a superconducting quantum interference device-vibrating sample magnetometers. The electrical transport properties of the LSCO films were characterized by a physical property measurement system (PPMS) using direct current (DC) four-point probe technique with a current of 10 μA. The applied magnetic field up to 13 T and was parallel to the sample surface as well as the current direction.

3. Results and discussion

3.1. Structural properties

Fig. 1(a) is a typical BF TEM image of a cross-sectional LSCO/STO sample with a thickness of ~20 nm. The white arrows indicate the interface between the film and substrate. It can be clearly seen that the interface is fairly clean and sharp, and the surface is flat without any wave. Fig. 1(b) shows the HRTEM image of the LSCO/STO film where the dashed lines illustrate the interface between film and substrate. It indicates that the LSCO film grows coherently on the substrate without obvious dislocations and the interface is sharp demonstrating a good epitaxial growth of the LSCO film. Fig. 1(c) shows a typical BF TEM image of a cross-sectional LSCO/STO sample with a thickness of ~50 nm. The interface between the film and substrate is fairly clean and sharp, as confirmed by HRTEM in Fig. 1(d), which emphasizes the perfect lattice coherence on the LSCO/STO interface. The TEM results demonstrate a good epitaxial growth of all LSCO films and the increasing film thickness produces few dislocations, indicating that the linear defect is not a main reason for the change in physical properties. Fig. 2 shows the XRD patterns of the LSCO films with different thickness on STO and LAO substrates. It is observed from Fig. 2 that increasing film thickness affects the peak positions of (002) reflections of LSCO films. For the films grown on LAO substrates, the (002) reflections shift to large angles with increasing film thickness, meaning that the lattice of the film is compressed along the c-axis. While for the films grown on STO, the (002) reflections shift to the small angles with increasing film thickness, indicating that the lattice of the film is elongated along the c-axis. The different behaviors are associated with the substrates which induce different types of strain.

To obtain more information about the growth and structure of the films, we calculated the out-of-plane lattice parameters, as shown in Fig. 3. For the 20-nm-thick LSCO film grown on STO, the out-of-plane lattice parameter is 3.753 Å, less than that of bulk LSCO (~3.820 Å), indicating that an out-of-plane compressive strain exists in the film. When the film thickness increases from 20 to 100 nm, the out-of-plane lattice parameter becomes closer to that of the bulk materials, and a strain relaxation is evidenced by an increase (from 3.753 to 3.785 Å) of the out-of-plane lattice parameters of LSCO films on STO. In addition, the lattice strain is detected in the LSCO films grown on LAO substrate, which is relaxed with increasing film thickness. Besides, the difference is that the lattice parameters of LSCO/LAO exhibit a monotonic decrease (from 3.875 to 3.832 Å), while the lattice parameters of LSCO film on STO substrate increase continuously with increasing film thickness.

Fig. 1. Cross-sectional BF TEM image (a) and HRTEM image (b) of 20-nm-thick LSCO film on STO. Cross-sectional BF TEM image (c) and HRTEM image (d) of 50-nm-thick LSCO film on STO. The inset in Fig. 1(d) is Fourier-filtered lattice image.
thickness. This further proves that the films grown on LAO and STO substrates suffer from different types of out-of-plane strain.

To further investigate the nature of strain, the lattice mismatch is also calculated for LSCO/LAO and LSCO/STO, which is 2.23% and −0.73%, respectively. This implies that LAO substrate \((a_{\text{LAO}} = 3.792 \text{ Å})\) imposes an in-plane compressive strain while STO substrate \((a_{\text{STO}} = 3.905 \text{ Å})\) exerts an in-plane tensile strain. To clarify the effect of strain on the in-plane lattice parameters, we carried out the reciprocal space mapping (RSM) of the \((103)\) reflections of LSCO/STO films, as shown in Fig. 4. For the 20-nm-thick film, the diffraction peak of the film locates above that of the substrate, which indicates that the in-plane lattice parameter of the film is the same as that of the substrate. In addition, the diffraction spot of the 20-nm-thick film is symmetric (Fig. 4a), indicating that the films are fully strained. In contrast, an irregular diffraction spot is observed when the film is 100 nm thick (Fig. 4b), demonstrating that considerable lattice relaxation occurs with increasing film thickness. Based on RSM, it is found that the lattice parameter \(a\) decreases from 3.905 to 3.884 Å, whereas \(c\) increases from 3.753 to 3.785 Å when the film thickness increases from 20 nm to 100 nm. Notably, lattice strain still exists even in well-relaxed 100-nm-thick film, which is consistent with the XRD results in Fig. 3. Based on the XRD analysis, we conclude that the strain can be tuned by changing the substrate materials and/or the film thickness, which will further affect the microstructure of films.

### 3.2. Magnetic properties

To reveal the relationship between the strain and magnetism of the films, the temperature dependent magnetism of LSCO films \((M\text{-}T)\) was measured in both zero-field cooling (ZFC) and FC mode under an applied field of 500 Oe. Fig. 5 and Fig. 6 show the ZFC and FC curves of LSCO films grown on LAO and STO, respectively. One can see that the magnetism change of the films under compressive strain (Fig. 5) is similar to that of the films under tensile strain (Fig. 6). For the ZFC curves of the LSCO films, the magnetization reaches a maximum value at a temperature around 110–120 K, which usually represents a glass-like behavior [19]. In addition, the ZFC curves are separated from the FC curves at low temperature, while they begin to coincide with each other above a certain temperature. The FC curves of the LSCO films show a ferromagnetic (FM) - paramagnetic (PM) transition, and the transition temperature \((T_c)\) is defined by the inflection point in the FC curves. The LSCO films exhibit FM characteristics below \(T_c\), while they show a PM state above \(T_c\). Notably, no evident change in \(T_c\) was found for the LSCO films with different thickness grown on different substrates. However, the FC character of the films under tensile strain is greatly weakened in comparison with that of the films under compressive strain, indicating
that the total magnetic moments of the films are greatly influenced by the strain state of the films.

Fig. 7 shows the magnetic hysteresis loops (M–H) of the films measured at 10 K. It can be seen that M_s strongly depends on the thickness and the strain state of the films. The saturation magnetization (M_s) increases continuously with increasing film thickness. In addition, the M_s of LSCO on LAO is ~0.75 μ_B/Co, which is almost five times larger than that of LSCO on STO (M_s~0.14 μ_B/Co), indicating that the magnetism of LSCO film on LAO is stronger than that on STO substrate. From the above, we can conclude that the magnetic properties of LSCO films can be modulated by the strain, which is associated with substrate materials and film thickness.

For LSCO, Sr doping leads to the formation of Co^{4+} ions in the lattice, and the LSCO film magnetization originates from the alternative arrangement of Co^{3+} and Co^{4+} ions [12,17,18]. The ferromagnetic character of the LSCO films can be depressed by a transition from high to low spin state of Co ions induced by strain, together with the Jahn-Teller distortions [5]. For the LSCO films under the tensile strain, the in-plane Co–O bonds are stretched within ab plane and the out-of-plane Co–O bonds are compressed along c-axis. However, for the films under compressive strain, the in-plane Co–O bonds are compressed within ab plane and the out-of-plane Co–O bonds are stretched along c-axis. In both cases, the Jahn-Teller distortions are reinforced, and the ferromagnetic coupling is further restrained [5]. However, the Jahn-Teller distortion in LSCO film grown on LAO is weaker than that in LSCO film grown on STO because of smaller lattice mismatch, thus the magnetization of LSCO/LAO is higher than that of LSCO/STO. With the release of lattice strain, the effect of lattice strain on the magnetism becomes weak. Therefore, the film magnetism is gradually enhanced with increasing film thickness.

### 3.3. Electrical transport properties

The effect of the strain on LSCO films is further evidenced by studying the electrical transport properties. Fig. 8 shows the temperature-dependent resistivity (R vs T) of LSCO films with different thickness. The electrical resistivity decreases with increasing temperature, viz. dρ/dT < 0, showing a semiconducting-like behavior. For the LSCO films, the SE between Co^{3+}–O^{2−}–Co^{3+} and (Co^{4+}–O^{2−}–Co^{4+}) competes with the DE between Co^{3+}–O^{2−}–Co^{4+} for dominance because of small fraction of Co^{4+}. Therefore, few mobile charge carriers contribute to the electrical conductivity [21], resulting in the semiconductor behavior. Noticeably, the ln vs T^{1/3} curves shown in Fig. 9 fit well with the equation of $\rho(T) = \rho_0 \exp(T_0/T)^{1/3}$ [22], which means that the electrical transport mechanism of LSCO films is a three-dimensional VRH, consistent with the previous report [23]. To verify the rationality of the three-dimensional VRH model, different fitting curves, ln vs T^{1/3} (Fig. S1 in ESI), ln vs T^{1/2} (Fig. S2 in ESI), and ln vs T^{1/3} (Fig. S3 in ESI) are included in the ESI. After careful examination, it is found that the three-dimensional VRH model is more appropriate.

In the three-dimensional VRH model, $T_0$ calculated from the fitting curves is elevated with decreasing film thickness, as shown in Table 1. Combining Fig. 8 and Fig. 9, we conclude that the increase of $T_0$ means the increase of resistivity. From a theoretical point of view, however, the localized length $\ell$ varies inversely as $T_0$ from the equation of $T_0 = 18/(k_B N_0 \ell^3)$ [24], namely, $\ell$ decreases continuously with increasing $T_0$. It is proved that decreasing $\ell$ can enhance the disorder of this system, which enhances the resistivity [25]. In a word, increasing $T_0$ results in an enhanced resistivity.

Regardless of the substrate materials, from the R vs T curves, the film conductivity is improved with increasing film thickness. We believe that the change observed in electrical transport properties is essentially originated from the lattice strain induced by the substrates. The conductivity of LSCO films has a great correlation with DE between Co^{3+} and Co^{4+} cations. It is proved that the strain can make the Co ions localized, [13,20,27] which could trap the electron carriers. This implies that the DE is destroyed by strain, which results in high resistivity at low temperature. For all the LSCO films, however, the Co ions become delocalized with increasing temperature, which leads to an increase of mobile carrier concentration and ameliorates the film conductivity (for LSCO/STO, 1 Ω cm at 45 K and 0.01 Ω cm at 300 K). Besides, the number of mobile carrier increases with increasing film thickness because of the strain relaxation, which results in a high conductivity for the thick films.
The lnρ vs T^{−1/4} curves slightly deviate from a linear relationship in the high temperature range, indicating that the VRH model is not applicable. We note that every fitting curve has a deflection when the temperature approaches a special point. Fascinatingly, we find a close relationship between the turning point of the temperature and the film thickness in Fig. 9. As can be seen, the turning point shifts to the low temperature with increasing film thickness. We infer that the special turning point indicates a change of the electrical transport mechanism.

To study the electrical transport mechanism at high temperature, the resistivity of the 100-nm-thick film is fitted. The ln(ρ/T) vs 1/T curve in Fig. 10 fits well with the equation ρ/T = Aexp(Ea/k_B T) in the high temperature range [26], which means that the electrical transport mechanism is dominated by SPC, where E_a is the activation energy.

In the high temperature range, the hopping of carriers can easily be thermally activated, indicating that the transport behavior is dominated by the SPC rather than the VRH. Noticeably, for all the films, increasing thickness brings low turning-point temperature. The lattice strain is gradually relaxed with increasing film thickness, resulting in a weak trapping to carriers. Accordingly, the thermally-activated hopping of the carriers becomes easy for thick films, leading to a low mechanism-transformation temperature (T_{trans}).

Based on the above analysis, it is found that both magnetic moment and film conductivity increases with the film thickness. In fact, an increase in film thickness weakens the Jahn-Teller distortion, thus favors the ferromagnetic coupling. This explains why the thick films possess enhanced magnetic ordering. In addition, the carrier localization is weakened due to the depression of Jahn-Teller distortions, resulting in improved conductivity. In a word, the film conductivity is ameliorated with the increase of film magnetism. However, it is found that T_c and T_{trans} present different changing tendency with increasing film thickness. T_c does not strongly change with different thicknesses, while T_{trans} decreases obviously with increasing film thickness. This fact suggests that the exact relation between magnetic and electrical properties may not be perfectly explained by only one model, in which T_c can be completely correlated to T_{trans}. The other factors, like the carrier scattering, etc., need to be considered.

4. Conclusions

In summary, we present a systematic study to decipher the role of
film thickness and substrates on the structure, magnetism and electrical transport properties of LSCO films. The 20-nm-thick films are fully strained while the thicker films are partially relaxed. In addition, the LSCO films present an evolution of in-plane and out-of-plane lattice parameters towards those of bulk materials with increasing film thickness. The film magnetism strongly depends on the thickness and the strain state of the LSCO films. For the conductivity of the films with different thickness, the electrical transport mechanism of all LSCO films transforms from VRH to SPC. Our results could help to better understand the effects of the film thickness and substrate on structure, magnetism and electrical transport properties of strained LSCO, and pave the way for adjusting the physical properties of LSCO thin films.

Acknowledgements

The authors would like to thank the financial support from the National Key Basic Research Development Program of China (Grant No. 2012CB722705), the National Natural Science Foundation of China (Grant No. 10974105), and the Program for Foreign Cultural and Educational Experts (Grant No. GDW20173500154 and GDW20163500110). Y. Q. Wang would also like to thank the Educational Experts (Grant Nos. GDW20173500154 and GDW20163500110). Y. Q. Wang would also like to thank the Provincial Natural Science Foundation of Shandong Province, China, and Qingdao International Center for Semiconductor Photoelectric Nanomaterials, and Shandong Provincial University Key Laboratory of Optoelectrical Material Physics and Devices.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ssi.2018.01.034.

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