The influence of substrate orientation and annealing condition on the properties of LaMnO₃ thin film grown by polymer assisted deposition

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Abstract: The epitaxial films of LaMnO₃ were fabricated via a simple polymer assisted deposition method. The effects of substrate orientation and annealing condition on the structure and properties of LaMnO₃ films have been investigated. It is found by X-ray diffraction and Raman spectroscopy that the oxygen content increasing results in a decrease in unit cell volume along with a reduction in Jahn–Teller distortion. Besides, with the annealing temperature increasing, the resistivity of the film decreases and the insulator-metal transition temperature T_{IM} shifts to higher temperature. The maximum of the resistivity is highly substrate-orientation dependence in ascending order of (100) < (110) < (111). Furthermore, the T_{IM} of LaMnO₃ film increases with the substrate orientation changing from (111) to (100). It is shown that magnetic order correlates well with an insulator to metal behavior. All results reveal that the lattice distortion of MnO₆ octahedron can be tuned by different annealing condition and the substrate orientation, which can be effective methods to adjust the structure, electrical and magnetic property of LaMnO₃ film.

Key Words: LaMnO₃ epitaxial film, Annealing condition, Substrate orientation, Electronic transport property

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1. Introduction

LaMnO_3 (Mn^{3+} , $t_{2g}^3 e_g^1$ 3d configuration) [1], as a Mott insulator, like many insulator-metal transition oxides, the electrical properties are dominated by electron-electron interactions leading to a localization of the e_g conduction electrons. For a perfect stoichiometric LaMnO_3 (LMO), the magnetic ground states are expected to be A-type antiferromagnetic (A-AFM) [1]. However, LMO thin films grown on SrTiO_3 (STO) substrates have been experimentally found to be ferromagnetic (FM) [2]. The discrepancy could be traced back by considering lattice distortions in real manganites, which could severely be effected by extrinsic effects such as slight deviation from the chemical composition [3-4], oxygen content [5], and strain state [6-9] in real thin-film system.

The excess (deficit) oxygen can introduce Mn^{4+} (Mn^{2+}) ions along with Mn^{3+} ions in the system. It is well known that the presence of Mn^{4+} (Mn^{2+}) is associated with the change of distortion of oxygen octahedral leading to structural modification. Moreover, Mn^{4+} (Mn^{2+})- Mn^{3+} double exchange interaction drives the system into ferromagnetic and metallic states. It is reported that the different oxygen content of LMO bulk can be obtained by annealing conditions (annealing process and annealing atmosphere) [10-11]. Besides, the investigation on $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [12], $\text{Sm}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [13], and $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ [14] has demonstrated that the substrate orientation is another factor to induce anisotropic strain in manganites film. However, there are little reports about the effects of annealing condition and the orientation of the substrate on the property of LMO thin film, which are two effective ways to tune the lattice distortion of manganites film. The aim of this work is to figure out the effects of the annealing condition and the substrate orientation on the electronic transport

property of LMO thin film.

2. Experimental

LMO thin films were fabricated by polymer assisted deposition (PAD) technique, which shows favorable features compared to the traditionally used vacuum techniques, including a low investment cost, fast deposition with high yield, and most importantly it is an easily scalable and continuous process [15-17]. In order to obtain the LMO films, the necessary precursor solution was prepared as follows. First high purity (>99.99%) metal salts $\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (0.5 mmol) and $\text{Mn}(\text{NO}_3)_2$ (0.5mmol, AR, 50 wt. % in H_2O) were dissolved in deionized water with 0.2922 g Ethylene Diamine Tetraacetic Acid (EDTA) and 0.2922 g polyethylenimine (PEI, 1:1 mass ratio to EDTA) with molecular weight of 70,000. The mixed solution was stirred by a magnetic stirring apparatus for 10 h at room temperature, and then kept being stirred in a 60 °C oil-bath until the solution remaining ~5 mL. To obtain the LMO polymeric films, the stable precursor solution were coated on pretreatment (100)-, (110)-, and (111)-oriented SrTiO_3 (STO) and (100)-oriented LaAlO_3 (LAO) substrates with 5000 rpm (revolutions per minute) over 40s by the dip-coating method. Such a technique allowed us to obtain epitaxial thin film effectively. The thickness of film can be easily controlled by the concentration of precursor and the coating speed. According to the thermal decomposition analysis of PEI, the coated polymeric films were heated up in a muffle furnace in different atmospheres. A low ramp rate of 0.5 °C min⁻¹ was used from room temperature to 700 °C in order to make sure that the water evaporated and PEI burned up to avoid the formation of bubbles on the film surface. The samples were then ramped (at the rate of 5 °C min⁻¹) to annealing temperature. After 2 h heat treatment, the films were slowly cooled down to room

temperature with a rate of $1^{\circ}\text{C min}^{-1}$.

3. Results and discussion

The X-ray diffraction (XRD) patterns of LMO films grown on (100) STO annealed at 750 °C, 800°C, 900 °C and 1000 °C in air, respectively, are shown in Fig. 1(a), in which only the $(00l)$ peaks for both the film and substrate can be found, indicating the preferential c-axis orientation of the thin film along with the $(00l)$ substrate crystallographic direction. No secondary phase is detectable. The in-plane ϕ scan (asymmetric Bragg reflection) for (101) reflection of the LMO thin film annealed at 900 °C as well as that of the STO substrate are shown in Fig. 1(b). The ϕ scans of LMO films grown on STO reveal that the films are of good epitaxial quality. Moreover, the epitaxial relationship between the LMO films and the (100) STO substrate is confirmed to be $(001) \text{ LMO} // (001) \text{ STO}$ and $(100) \text{ LMO} // (100) \text{ STO}$, which indicates that the LMO films grown on substrate as a “cube-on-cube” mode [18]. Besides, the surface morphology characteristic of LMO grown on STO with different annealing temperature were detected by SEM as shown in Fig. 2, which reveals that the LMO film becomes denser, less grain boundary by increasing the annealing temperature. In order to further confirm the thickness for LMO film with high accuracy, the X-ray reflectivity for LMO/STO was taken as shown in Fig. 3, from which the thickness of LMO/STO annealed at 900 °C is obtained to be about 40 nm. The results of XRD and SEM indicate that the PAD is a simple and effective method to obtain epitaxial perovskite film.

The temperature-dependent resistivity of the LMO film grown on (100) STO annealed at different temperature is shown in Fig. 4. It can be found that the electronic transport properties of LMO/STO show large variations in the resistivity and insulator-metal transition

temperature (T_{IM}) with the annealing temperature increasing. The T_{IM} shifts to a higher temperature and the resistivity decreases with the annealing temperature increasing, which may be ascribed to the following points: (a) the better crystallinity and surface morphology. With the annealing temperature increasing, the denser and less grain boundary for films is responsible for the resistivity decreasing (see in Fig. 2); (b) the different oxygen content. Töpfer et al have reported that the annealing temperature has an effect on the oxygen content of the LMO bulk [11]. From the XRD patterns of LMO films in this work, it is easy to find that c -axis lattice parameters c of films decrease with the annealing temperature increasing. It is worth to note that similar results were found by Ni et al in LMO film [19] and Khanduri et al in LMO bulk [20], which is attributed to the increasing in oxygen content. Because the excess O^{2-} can't be accommodated interstitially in the closed packed perovskite structure, the vacancies in La and Mn sites will be induced [21], when the oxygen content increases. In other words, the vacancies of cations result in the decrease of c axis. Meanwhile, the vacancies in La and Mn sites also introduce Mn^{4+} ions in the system to ensure the conservation of positive and negative charges. The T_{IM} change maybe due to the different ratio of Mn^{4+}/Mn^{3+} , which is consistent with previous reports [22-24]. By reducing the grain boundary, roughness and oxygen deficiencies of the film, the transport property of LMO film is improved with the annealing temperature increasing.

In order to further study the effect of oxygen content on LMO film, the structure and property of LMO films grown on (100) $LaAlO_3$ are investigated due to the insensitivity of $LaAlO_3$ to oxygen pressure compared to $SrTiO_3$. The films grown on (100) LAO are annealed under Ar, Air, and O_2 , respectively, at 900 °C for 120 min, to obtain the LMO films with

different oxygen contents, which are denoted as S1, S2, and S3, respectively. According to the XRD patterns (see in Fig. 5), it is obtained that the c-axis lattice parameter decreases with the annealing atmosphere varying from Ar to O₂. Similar to the previous analysis, the film obtained at higher oxygen pressure can induces more Mn⁴⁺ ions combining with the Mn³⁺ ion concentration lowering, which results in the c-axis lattice parameter decreasing due to the different ionic radii (Mn⁴⁺ 0.53 Å < Mn³⁺ 0.645 Å). Similar results have been reported on the bulk compounds [10-11, 25] that with oxygen pressure increasing, the unit cell volume decreases. For the highly contracted films on LAO, to ensure epitaxial matching between the films and the substrate, the reciprocal space mapping was taken. The mapping around (103) peak in reciprocal space of LMO film grown on LAO (100) substrate annealed in air is shown in Fig. 5. Since the lattice parameter *a* of pseudocubic bulk LMO is about 3.87 Å [11], the lattice mismatch between film and LAO substrate (3.79 Å) is about 2.1%. As can be seen in Fig. 5, the peak position of the LMO (103) reflection has slightly shifted from that of the LAO substrate along the Q₁₀₀ axis, which confirms that the LMO film is grown epitaxially on the LAO substrate with a lattice mismatch. Furthermore, the 2.1% lattice mismatch between the film and substrate will cause the relaxation in the LMO structure.

The Raman spectra for S1, S2 and S3 are shown in Fig. 6. By lattice dynamical calculations [26] it is known that the Raman modes centered at 420 cm⁻¹ and 622 cm⁻¹ are originated from Jahn-Teller (JT) distortion. It is obviously that large changes appear in the intensity of JT activated Raman modes as the annealing atmosphere varying in Fig. 6. The intensity of 622 cm⁻¹ peak decreases significantly with the annealing oxygen pressure increasing, indicating reduction in JT distortion. This result is consistent with the previous

reports [11, 22, 25], which revealed that LaMnO_3 film transforms from an orthorhombic phase (sustain the cooperative JT deformation) to a rhombohedral phase (suppresses any static, cooperative JT deformation) [21].

The temperature-dependent resistivity of the S1, S2, and S3 are shown in Fig. 7. For S1 the resistivity increases as the temperature decreasing, and an insulator to metal transition (IMT) is observed at $T_{\text{IM}} \sim 185\text{K}$. After crossing the temperature T_{IM} , the film starts to behave like an insulator, and the resistivity keeps on increasing up to the lowest measurement temperature. The S2 film shows a perfect metallic behavior below T_{IM} ($\sim 215\text{K}$). According to the previous study [19], film S1 possesses a majority insulating phase along with a small fraction of metallic phase below T_{IM} and film S2 possesses only a metallic phase below T_{IM} . An increase of T_{IM} and a decrease of resistivity can be observed as oxygen pressure increasing. Nevertheless, the film annealed in O_2 shows a semiconducting-type behavior. The similar results were reported by Töpfer et al [11,27], which were suggested that at higher oxygen pressure, an oxygen-excess $\text{LaMnO}_{3+\delta}$ accommodates the excess oxygen by creating cation vacancies to give $\text{La}_{1-x}\text{Mn}_{1-y}\text{O}_3$. With increasing δ , the oxygen vacancies are first eliminated to give $\text{La}_{1-x}\text{MnO}_3$ before vacancies are created on the second cation array. At high δ , the oxygen positions are filled up and cation vacancies are found at both La and Mn positions in analogy to the system $\text{LaMnO}_{3+\delta}$ pointed by Töpfer [27]. The peculiar behavior of our LMO film annealed in O_2 may associated with the presence of Mn vacancies, which induces the electron potential of $\text{Mn}_{1-x}\text{O}_3$ array that is more effect on the film than that annealed in the related lower oxygen pressure [27].

The temperature-dependent resistivity and magnetizations of the films on

different-orientation STO substrates are shown in Fig. 8, which reveals that the maximum resistivity $\rho_{\max}$ is highly orientation dependence in ascending order of $(100) < (110) < (111)$. Moreover, the value of T_{IM} also shows an orientation dependence of substrate. The T_{IM} (T_c) of LMO/STO is 324K (320K), 305K (295K), and 256K (273K), respectively. The T_{IM} closely coincides with the T_c determined by magnetic data. It is interesting to note that the $\rho_{\max}$ appears to be inversely correlated with the observed magnitude of magnetization. From the magnetizing data, it is easy to find that both the FM transition temperature and the magnetization M decrease with the substrate orientation changing from (100) to (111), indicating the magnetic interaction weakening. According to the previous report [28], it is known that there mainly exists tetragonal distortion of MnO_6 octahedron in LMO film on (100) STO but rotation of MnO_6 octahedron in LMO film on (111) STO. Furthermore, the change of MnO_6 octahedron induced by the biaxial tensile strain in LMO film on (110) STO is intervenient between them, i.e. containing both the tetragonal distortion and the rotation of MnO_6 octahedron. Based on these points, it can be inferred that the strain direction of MnO_6 octahedron in the LMO film grown on (110) or (111) STO causes not only the tetragonal distortion of MnO_6 octahedron but also the rotation of MnO_6 octahedron and the deviation of the bond angle $\theta_{\text{Mn-O-Mn}}$ from 180° . Because of the different structural distortion of MnO_6 octahedron, the magnetic and electronic properties show dependence of oriented substrate.

4. Conclusions

In summary, we have fabricated LMO thin films on STO and LAO substrates by a simple PAD method. All results reveal that the annealing condition and orientation of substrate have remarkable effect on the structure and properties of LMO film. With the

annealing temperature increasing, the resistivity of the film decreases and T_{IM} shifts to a higher temperature. The maximum resistivity is highly orientation dependence with the resistivity in ascending order of $(100) < (110) < (111)$. Furthermore, the T_{IM} of LaMnO_3 film increases with the substrate orientation changing from (111) to (100). The lattice distortion can be tuned by different annealing condition and the orientation of the substrate, which can be effective ways to adjust the electrical and magnetic property of manganites.

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Reference

- [1] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. 344 (2001) 1.
- [2] A. Gupta, T. R. McGuire, P. R. Duncombe, M. Rupp, J. Z. Sun, W. J. Gallagher, and G. Xiao, Appl. Phys. Lett. 67 (1995) 3494.
- [3] P. Murugavel, J. H. Lee, J.-G. Yoon, T. W. Noh, J.-S. Chung, M. Heu, and S. Yoon, Appl. Phys. Lett. 82 (2003) 1908.
- [4] C. Aruta, M. Angeloni, G. Balestrino, N. G. Boggio, P. G. Medaglia, A. Tebano, B. Davidson, M. Baldini, D. Di Castro, P. Postorino, and P. Dore, J. Appl. Phys. 100 (2006) 023910.
- [5] M. Sirena, N. Haberkorn, M. Granada, L. B. Steren, and J. Guimpel, J. Appl. Phys. 105

(2009) 033902.

[6] A. Chaturvedi, and V. Sathe, thin solid films, 548 (2013) 75.

[7] R. K. Zheng, H.-U. Habermeier, H. L. W. Chan, C. L. Choy, and H. S. Luo, Phys. Rev. B 81 (2010) 104427.

[8] S. El Helali, K. Daoudi, A. Fouzri, M. Oumezzine, M. Oueslati, and T. Tsuchiya, Appl Phys A 108 (2012) 379.

[9] Z. Huang, L. F. Wang, P. F. Chen, G. Y. Gao, X. L. Tan, B. W. Zhi, X. F. Xuan, and W. B. Wu, Phys. Rev. B 86 (2012) 014410.

[10] C. Ritter, M. R. Ibarra, J. M. De Teresa, P. A. Algarabel, C. Marquina, J. Blasco, J. Garcia, S. Oseroff, and S. W. Cheong, Phys. Rev. B 56 (1997) 8902.

[11] J. Töpfer, and J. B. Goodenough, J solid state chem. 130 (1997) 117.

[12] Z. Huang, L. F. Wang, P. F. Chen, G. Y. Gao, X. L. Tan, B. W. Zhi, X. F. Xuan, and W. B. Wu, Phys. Rev. B 86 (2012) 014410.

[13] C. Y. Li , Y. Q. Wang , R. S. Cai, Y. Z. Chen, J. R. Sun, Mater. Lett. 95 (2013) 70.

[14] Y. Z. Chen, J. R. Sun, S. Liang, W. M. Lv, BG Shen, W. B. Wu. J Appl. Phys. 103 (2008) 096105.

[15] Q. X. Jia, T. M. Mccleskey, A. K. Burrell, Y. Lin, G. E. Collis, H. Wang, A. D. Q. Li, and S. R. Foltyn, Nat. Mater. 3 (2004) 529.

[16] R. Cobas, S. Munoz-Perez, J. M. Cadogan, T. Puig, and X. Obradors, Appl. Phys. Lett. 99 (2011) 083113.

[17] H. F. Liu, L. Shi, S. M. Zhou, J. Y. Zhao, Y. Q. Guo, C. L. Wang, and L. F. He, Surf. Coat.Technol. 226 (2013) 108.

- [18] D. Fuchs, E. Arac, C. Pinta, S. Schuppler, R. Schneider, and H.v. Löhneysen, Phys. Rev. B 77 (2008) 014434.
- [19] H. Ni, D. Yu, K. Zhao, Y.-C. Kong, H. K. Wong, S. Q. Zhao, and W. S. Zhang, J Appl. Phys. S 110 (2011) 033112
- [20] H. Khanduri, M. Chandra Dimri, S. Vasala, S. Leinberg, R. Löhmus, T. V. Ashworth, A. Mere, J. Krustok, M. Karppinen and R. Stern, J. Phys. D: Appl. Phys. 46 (2013) 175003.
- [21] J. M. Vila-Funqueiriño, B. Rivas-Murias, B. Rodríguez-González, O. Txoperena, D. Ciudad, L. E. Hueso, M. Lazzari, and F. Rivadulla, ACS Appl. Mater. Inter. 7 (2015), 5410.
- [22] A. Dubey, V. G. Sathe, and R. Rawat, J Appl. Phys. 104 (2008) 113530.
- [23] A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, Y. Tokura, Phys. Rev. B 51 (1995) 14103.
- [24] A. Gupta, T. R. McGuire, P. R. Duncombe, M. Rupp, J. Z. Sun, W. J. Gallagher, and G. Xiao, Appl. Phys. Lett. 67 (1995) 3494.
- [25] E. Granado, A. García, J. A. Sanjurjo, C. Rettori, I. Torriani, F. Prado, R. D. Sánchez, A. Caneiro, and S. B. Oseroff, Phys. Rev. B 60 (1999) 11879.
- [26] M. N. Iliev, M. V. Abrashev, J. Laverdière, S. Jandl, M. M. Gospodinov, Y.-Q. Wang, and Y.-Y. Sun, Phys. Rev. B 73 (2006) 064302.
- [27] J. Töpfer, J. B. Goodenough, chem. Mater. 9 (1997) 1467.
- [28] H. F. Liu, S. Lei, Y. Q. Guo, S. M. Zhou, J. Y. Zhao, C. L. Cai, L. F. He, Y. Yang, J Alloy compd. 594 (2014) 158.

Figure captions

FIG.1. (a) XRD $\theta/2\theta$ symmetric scan for LMO epitaxial thin films grown on (100) STO at different annealing temperature; (b) ϕ scan of the (101) reflections of the LMO thin film annealed at 900 °C (top) and the STO substrate (bottom).

FIG.2. The SEM micrographs of the LMO/STO epitaxial thin films annealed at different temperature: the surface morphologies of LMO films annealed at (a)750 °C, (b)800 °C , and (c)900 °C, respectively ; (d) the typical cross-sectional area of LMO film annealed at 900 °C.

FIG.3. X-ray reflectivity for LMO/STO annealed at 900 °C in air.

FIG.4. Temperature-dependent resistivity of the LMO grown on the (100) STO annealed at different temperature and the evolution of the T_{IM} and ρ_{max} of the LMO films with the annealing temperature.

FIG.5.The XRD $\theta/2\theta$ spectra for LMO/LAO films annealing in different atmosphere (left) and the mapping around (103) peak in reciprocal space of LMO/LAO annealed in air (right).

FIG.6. Raman spectra for LMO/LAO films annealed in different annealing atmosphere.

FIG.7. Resistivity vs temperature behavior for LMO annealed in different atmosphere grown on (100) LAO.

FIG.8. Temperature-dependent resistivity and magnetization for LMO films grown on (100), (110), and (111) STO substrates.

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