Magnetic characteristics of LaMnO$_{3+\delta}$ thin films deposited by RF magnetron sputtering in an O$_2$/Ar mixture gas

Chen Yufeng, Geming Wang, Sun Zhengfeng, Wang Shenggao, Mao Yangwu, Deng Quanrong and Yang Jingjing

Provincial Key Laboratory of Plasma Chemistry and Advanced Materials, Wuhan Institute of Technology, Wuhan 430073, People’s Republic of China

E-mail: wanggemingwit@163.com, yangjingjingwit@sina.com and dqrwit@163.com

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Abstract

In this work, LaMnO$_{3+\delta}$ thin films have been successfully fabricated by RF magnetron sputtering using different O$_2$/Ar flux ratios. The crystal structures, morphologies, stoichiometry, surface chemical states and magnetic properties of films are thoroughly characterized by x-ray powder diffraction (XRD), Raman spectrometer, scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and superconducting quantum interference device (SQUID). The magnetic characteristics of LaMnO$_{3+\delta}$ films are systematically studied with the transformation from Mn$^{3+}$ to Mn$^{4+}$, which is strongly controlled by the deposited O$_2$/Ar flux ratios. We demonstrate that LaMnO$_{3+\delta}$ films undergo an antiferromagnet, the coexistence of ferromagnetism and antiferromagnetism and a robust ferromagnetism ordering by the variation of Mn$^{3+}$/Mn$^{4+}$ ratios. The LMO film deposited in pure argon atmosphere shows negligible FM signal and an inconspicuous T$_C$. With the increase of deposited O$_2$/Ar flux ratios, the Curie temperature of LMO films increases from 100 K to 224 K and then decreases to 140 K and meanwhile the irreversibility temperature fluctuates between 24 K and 100 K. The appearance of cluster glass state and the unexpected exchange bias phenomenon where the film deposited at highest O$_2$/Ar flux ratio has a H$_{EB}$ ~ 115 Oe is observed. All these evolutions of magnetization characteristics are discussed in terms of the strength of ferromagnetic interactions and the degree of competition between ferromagnetic and antiferromagnetic interactions in LaMnO$_{3+\delta}$ films. Our work serves as prerequisites for LaMnO$_3$-based magnetic heterostructures grown by RF magnetron sputtering.

1. Introduction

Recently, LaMnO$_3$ (LMO) compounds has triggered great research for being an building block in perovskite-type oxides heterostructures that demonstrates novel and unexpected magnetic characteristics, such as interface ferromagnetism (FM) between two antiferromagnetism (AFM) LMO and SrMnO$_3$ [1], unexpected exchanges bias in (111)-oriented LaNiO$_3$/LMO multilayers [2] and tunable FM via interfacial octahedral rotation in LMO/SrTiO$_3$ or LMO/LaCoO$_3$ superlattices [3, 4]. The stoichiometric LMO bulk material exhibits AFM behavior with the Neel temperature of ~140 K, where part of Mn electrons occupies 3d electron spins order and the cooperative Jahn-Teller (JT) distortion of MnO$_6$ octahedron conjointly leading to A-type AFM orbital ordering ground state [5, 6]. However, when LMO appears in thin film form, it usually exhibits complex magnetic characteristic, for instance, FM, cluster glass state, exchange bias effect or AFM and its underlying mechanisms remain controversial [7–11]. As we known, LMO perovskite structure is easy to adopt excess oxygen during preparation especially under oxygen-sufficient atmosphere to form non-stoichiometric LMO with global composition LaMnO$_{3+\delta}$ which results in the notorious La/Mn cation vacancies [7]. To compensate for the charge unbalance, the oxidation of Mn$^{3+}$ to Mn$^{4+}$ occurs and it has been proposed as the origin of FM state via Mn$^{3+}$–O–Mn$^{4+}$ double-exchange interactions in LaMnO$_{3+\delta}$ films [8, 9]. On the contrary, the saturation magnetization and the Curie temperature of LMO films increase with decreasing the deposited
The x-ray diffraction (XRD) and Raman analyses

3. Results and discussion

3.1. XRD and Raman analyses

The x-ray diffraction (XRD) patterns of LMO films grown on quartz glass substrates are displayed in figure 1. Obviously, the LMO films without post annealing exhibit amorphous and non-crystalline characteristics, which can be ascribed to low substrate temperature during deposition process [19]. Except for as-grown LMO film, the...
sharp and intense peaks indicate that the post-annealed LMO films are highly crystallized and no impurity phases are founded. Those post-annealed LMO films have peaks of (100), (110), (111), (200) and (210), which can be well indexed by a single-phase perovskite-type rhombohedral structure with R3 C space group [14]. Notably, comparing with (111) and (210) peaks, the relative intensities of (100) and (200) peaks in the samples S4 are much strong than other samples, which demonstrates that the LMO film has a preferential (100) orientation and a large exposed (100) surface when the O2/Ar flux ratios reach 3 sccm/20 sccm. These observations reveal that the O2/Ar flux ratios can also affect the anisotropic growth of the crystal. In general, the crystal structure of LMO depends on stoichiometry, varying from orthorhombic (Pbnm) to rhombohedral (R3C) as the oxygen content increases [11, 21]. Therefore, their rhombohedral structures imply that the as-prepared LMO films are non-stoichiometric of LaMnO3+δ with excessive oxygen in lattices. Furthermore, the crystallite size of S1, S2, S3, S4 and S5 are estimated to be 22, 30, 32, 32 and 31 nm respectively by using FWHM of the highest (110) diffraction peak.

The Raman spectroscopy is a powerful technique to further study structure distortion in perovskite manganite oxides. Figure 2 shows Raman spectra for all films in the frequency range of 100 cm\(^{-1}\) to 1200 cm\(^{-1}\). Three distinct vibrational bands at around 220 cm\(^{-1}\), 528 cm\(^{-1}\) and 620 cm\(^{-1}\) are observed, which is consistent with those previously reported rhombohedral LMO thin films [14]. The peak centered at ~528 cm\(^{-1}\) is attributed to an antisymmetric stretching (S) model of MnO\(_6\) octahedron, at ~620 cm\(^{-1}\) are related to the bending (B) model of MnO\(_6\) octahedron and both are associated with JT distortion of MnO\(_6\) octahedron in LMO structure [22]. From the sample S1 to S5, the phonon frequency of peak at ~620 cm\(^{-1}\) seems unchanged,
while the peak located at 528 cm$^{-1}$ move to the low frequency side (~511 cm$^{-1}$ in the sample S5), which suggests a strong spin-phonon coupling and a reduction of polaron-activated JT distortion [23]. The reduction of JT interaction has been proven to influence the magnetic behavior in LMO film. Moreover, the movement of frequency to lower wave numbers generally implies the increasing of oxygen content in LaMnO$_3$ structure induced by increasing O$_2$/Ar flux ratios during deposition [11]. Our XRD and Raman results demonstrate that high-quality LMO films have been synthesized by RF magnetron sputtering and give evidences that the oxygen content in films increases with increasing O$_2$/Ar flux ratios.

3.2. FESEM analyses
The surface morphologies images of representative LMO films (S1 and S5) are displayed in figure 3. The surface of the sample S1 (figure 3(a)) is relatively smooth with regular grains when deposited in pure argon atmosphere and cracks can be observed distributing randomly on its surface. After O$_2$/Ar flux ratios increase to 4 sccm/20 sccm (figure 3(b)), cracks and gaps between grains are also easily found on the surface. On the one hand, those cracks induced by the coarsening process of crystallization are almost inevitable in perovskite-type manganite thin films after post-annealing [24]. On the other hand, residual stress exists in the internal of LMO films during RF magnetron sputtering process will cause defects on surfaces of LMO films [25]. Moreover, while deposited at a higher oxygen partial pressure, the film will exhibit more cracks and gaps due to the fragmentation of oxide particulates, as evidenced by surface morphology of the sample S5 [19]. Furthermore, the atomic chemical compositions of oxygen in LMO films are detected by EDX. The oxygen composition in the S1 and S5 are 58.99% and 64.26% respectively. The increase of oxygen content in LMO films with increasing O$_2$/Ar flux ratios will promote the conversion of Mn$^{3+}$ from Mn$^{4+}$. In addition, the thickness for LMO films deposited at different O$_2$/Ar flux ratios of 0 sccm/20 sccm to 4 sccm/20 sccm are determined to be about 684 nm, 632 nm, 574 nm, 458 nm and 431 nm, respectively. As is seen, the corresponding deposition rate increases with decreasing O$_2$/Ar flux ratios, which is in coincident with the deposition rate trend of other oxide films grown by RF magnetron sputtering [20]. These results indicate that the O$_2$/Ar flux ratios have a significant effect on the surface morphologies and the oxygen content in LMO films.

3.3. XPS studies
To investigate the surface elemental compositions and the valence state of manganese for as-obtained samples, XPS measurements are employed. In the XPS survey spectra for the representative LMO film (the sample S1, figure 4(a)), characteristic La, Mn, O and C elements are found, of which the presence of C elements is due to the hydrocarbon contaminants. As described in figures 4(b) to (f), the classic signals of core level Mn 2p of all films are given via the high-resolution XPS spectrum. The Mn 2p spectrum for LMO films display two distinct peaks at around 641.6 eV and 642.6 eV, corresponding to Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ [26]. The peak values of Mn 2p$_{3/2}$ can be deconvoluted into two peaks at 641.6 eV and 642.6 eV, which are assigned to Mn$_2$O$_3$ (Mn$^{3+}$) and MnO$_2$ (Mn$^{4+}$) respectively [24]. That is, the coexistence of Mn$^{3+}$ and Mn$^{4+}$ valence state appears in all samples, even in the LMO film deposited in pure argon atmosphere. As shown in figures 4(b) to (f), the percentage of Mn$^{4+}$ in the films increases with increasing O$_2$/Ar flux ratios, which is calculated to be about 17% (figure 4(b)), 21% (figure 4(c)), 30% (figure 4(d)), 33% (figure 4(e)) and 42% (figure 4(f)) for the sample S1, S2, S3, S4 and S5 respectively by peak fitting analysis. Correspondingly, the percentage of Mn$^{3+}$ in the films gradually decreases from about 83% (figure 4(b)), 79% (figure 4(c)), 70% (figure 4(d)), 67% (figure 4(e)) to 58% (figure 4(f)) with increasing O$_2$/Ar flux ratios. In general, the Mn$^{3+}$/Mn$^{4+}$ ratio is sensitive to oxygen content in manganite films, which is strongly affected by deposition condition [10]. The increase of oxygen content in non-stoichiometric LaMnO$_{3+\delta}$ lattice (seen from EDX data) will favor the presence of higher valence of Mn$^{4+}$ and accelerate the
transition from Mn$^{3+}$ to Mn$^{4+}$ [9, 24]. As we know, the double exchanges of Mn$^{3+}$–O–Mn$^{4+}$ are ferromagnetic interactions and the superexchanges of Mn$^{3+}$–O–Mn$^{3+}$ are antiferromagnetic interactions [27]. Consequently, the ferromagnetic interactions and antiferromagnetic interactions will coexist in LMO films, which conjointly determine their overall magnetic. Moreover, the double exchange interactions are strongest when the Mn$^{3+}$/Mn$^{4+}$ ratio is about 2:1 [13]. It is clear that the sample S4 has the strongest ferromagnetic interaction with the optimum Mn$^{3+}$/Mn$^{4+}$ ratio, thereby has the highest Curie temperature and negligible competition between ferromagnetic and antiferromagnetic interactions. The variation of Mn$^{3+}$/Mn$^{4+}$ ratios tuned by O$_2$/Ar flux ratios in LMO films are responsible for their magnetic characteristics, which will be discussed below.

3.4. Magnetic properties

In order to clarify effects of O$_2$/Ar flux ratios on magnetic properties of LMO films, the temperature-dependent magnetization (M–T, 5–300 K) curves under a magnetic field of 0.1 T for all films are recorded in both ZFC and FC modes, as shown in figure 5. The corresponding magnetic field-dependent magnetization (M–H) loops in a range of ±1 T at 10 K are also measured, and the data are displayed in figure 6. Moreover, we also test M–H loops at 300 K of all samples (Those figures not presented), which exhibit paramagnetic characteristics. However, LMO films show ferromagnetic behavior (as seen in figure 6) below the transition temperature.

It is observed that all M–T curves (except for S1) for LMO films increase steeply with decreasing temperature below their Curie temperature ($T_C$), exhibiting clear paramagnetic–ferromagnetic transition, which is typical characteristics for FM behavior. By observing the inflection points in M–T curves, the $T_C$ values of the sample S2, S3, S4 and S5 are identified to be about 110, 135, 224 and 140 K respectively. The $T_C$ values of LMO films first increase and then decrease as O$_2$/Ar flux ratios increase. And the highest $T_C$ value (∼224 K) can be obtained in the sample S4, which suggest that the film has the strongest strength of ferromagnetic interaction among all samples. On the contrary, the M–T curve of the S1 sample varies litter or even fluctuates as the temperature decrease and exhibits almost negligible FM signals, leading to an inconspicuous $T_C$ [28]. Please note that the prominent discrepancies between ZFC and FC curves at irreversibility temperature ($T_{irr}$) can be observed in S2, S3 and S5, which confirm that a cluster glass state (CGS) occur in those films [13, 29]. The $T_{irr}$ values of films are determined to be about 24, 65 and 100 K for S2, S3 and S5 respectively. A similar behavior of bifurcation has been also observed in LaMnO$_3$+$\delta$ films deposited on LaAlO$_3$ substrate, indicating the ferromagnetic nanoclusters are embedded in the antiferromagnetic matrix [22, 30]. Moreover, the corresponding ZFC curves show obvious freezing temperatures ($T_f$), where magnetizations reach the maximum, implying that ferromagnetic property originate from ferromagnetic nanoclusters [7, 9]. The separation of $T_{irr}$ and $T_f$ is also another critical indicator of CGS phenomena [29]. While for the sample S4, both ZFC and FC magnetization

Figure 4. XPS spectra of LaMnO$_3$+$\delta$ films (a) survey, (b) Mn 2p.
changes almost simultaneously with the temperature, which is the typical characteristic of the FM state. That is to say, the magnetic characteristics of the S1 and S4 sample are mainly robust AFM and FM state respectively; while for the S2, S3 and S5 samples, the coexistence and competition between ferromagnetic and antiferromagnetic interactions conjointly dominate their magnetic behavior. In detail, the variations of $T_C$ and $T_{irr}$ can be evaluated by different strength of ferromagnetic interaction and the degree of competition between ferromagnetic and antiferromagnetic interactions in LMO films originated from the transition from Mn$^{3+}$ to Mn$^{4+}$, which are confirmed by Raman and XPS observations. When LMO films deposited in a pure argon atmosphere (S1), most of Mn ions are trivalent (83%), which results in the negligible FM state. In the S2 and S3 films, the percentage of Mn$^{3+}$ ions decreases, while the percentage of Mn$^{4+}$ ions increases. Thus, the double exchange ferromagnetic interactions between Mn$^{3+}$ and Mn$^{4+}$ and the competition between ferromagnetic and antiferromagnetic interactions are gradually enhanced, as evidenced by the increase of $T_C$ and $T_{irr}$ from S2 to S3. As discussed above, the S4 film has the strongest ferromagnetic interaction due to the optimum Mn$^{3+}$/Mn$^{4+}$, while the competition between competition between ferromagnetic and antiferromagnetic interactions become weakest correspondingly, as is featured by the highest $T_C$ and the illegible $T_{irr}$. In our oxygen-sufficient film (S5), a lower Mn$^{3+}$/Mn$^{4+}$ ratio leads to a weaker ferromagnetic interactions between Mn$^{3+}$ and Mn$^{4+}$ due to the deviation of Mn$^{3+}$/Mn$^{4+}$ ratio from 2:1 [13]. As a consequence, the competition between ferromagnetic and antiferromagnetic interactions increases intensively in the S5 film, as evidenced by the reduction of $T_C$ and the enhancement of $T_{irr}$. Similar FM/AFM competition and CGS behavior have also been observed in LMO$_{3+\delta}$ films [30], LaMnO$_3$/SrMnO$_3$ superlattices [28] and lightly doped manganite nanostructures [31].
More magnetic information can be acquired from hysteresis loops, as shown in figure 6. With O₂/Ar flux ratio increases from 0 sccm/20 sccm to 4 sccm/20 sccm, the saturated magnetization (Mₛ) is enhanced by almost seven times in magnitude, which is mainly due to the enhancement of Mn⁵⁺–O–Mn⁴⁺ double exchange interaction. In addition, the reduction JT interaction means the suppression of AFM, as is evidenced by Raman results. It is evident from figure 5 that the sample S4 reaches a high saturated magnetization (Mₛ) of ~130 emu cm⁻³ and miniscule coercivity (Hᵥ) of ~185 Oe, further suggesting a typical ferromagnetic behavior. In comparison with the S4 sample, the sample S5 exhibits a remarkable increase of Hᵥ (~700 Oe). The enhanced Hᵥ mainly originates from the CSG, which pins or disturbs the ferromagnetic part below Tᵥ [13]. Furthermore, the exchange bias (EB) effect (HₐEB = 115 Oe) is only found in the S5 film by a shift of loop along the magnetic field axis, as clearly shown in the inset of figure 6. Zhou et al observes a similar EB phenomenon in LMO films and contributes the EB to the pinning of FM part by the AFM region [5]. The strongest degree of competition between ferromagnetic and antiferromagnetic interactions in the S4 sample among all films will lead to the obvious CGS, thereby forming EB. Moreover, surface morphology affected by growth atmosphere also plays an influence on the magnetic properties of films [32]. The grain boundary and cracks can also restrain the carrier scattering and contribute to the increase of carrier mobility, which may promote the double exchange interaction and enhance magnetization [20]. Accordingly, the sample S5 has a relatively high magnetization. However, the residual strain in LMO films which bring about racks and gaps on its surfaces can decrease the Mn–O–Mn bond length and bond angle, which may weaken the double exchange interaction [33]. Therefore, the saturation magnetization of all as-prepared LMO films is still much lower than that of bulk LMO materials [19]. All these magnetic characteristics in LMO films can be well explained by the conversion from Mn³⁺ to Mn⁴⁺, which is strongly dependent on O₂/Ar flux ratios during deposition.

4. Conclusions

A seizes of LaMnO₃⁺δ thin films have been successfully fabricated on quartz glass substrate via a RF magnetron sputtering deposition method. The as-prepared films are amorphous and crystallized into rhomboedral structure with R3C space group after post-annealing process. The LaMnO₃⁺δ films have a higher oxygen content and smoother surface under a higher O₂/Ar flux ratio. The valence state of the manganese ions in LaMnO₃⁺δ films gradually transfer from Mn³⁺ to Mn⁴⁺ as the O₂/Ar flux ratio increases. The magnetic characteristics of LaMnO₃⁺δ films show strong dependence on the Mn³⁺/Mn⁴⁺ ratio. The LaMnO₃⁺δ film grown under pure argon atmosphere demonstrates negligible ferromagnetism. As O₂/Ar flux ratio increases, the Curie temperature and the irreversibility temperature first increase to and then decreases as well as the appearance of the CGS-like behaviors are ascribed to the variation strength of ferromagnetic interaction and the variation degree of competition between ferromagnetic and antiferromagnetic interactions. The high Tᵥ (~224 K), the large saturated magnetization Mₛ (~130 emu cm⁻³) and the miniscule coercivity Hᵥ (~185 Oe) are found in the sample S4, suggesting its strong strength of ferromagnetic interaction. In addition, the exchange bias (HₐEB = 115 Oe), the large coercivity (~700 Oe) and the high irreversibility temperature (T_irr = 100 K) are achieved in the LMO film with high O₂/Ar flux ratio of 4 sccm/20 sccm, which can be due to the strong competition between ferromagnetic and antiferromagnetic interactions. Our study reveal that the magnetic characteristics of LaMnO₃⁺δ thin films deposited by RF magnetron sputtering are sensitive to O₂/Ar mixture gas background, which is beneficial for the future design of LaMnO₃-based magnetic spintronic devices.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Conflict of Interest Statement

The authors declare that they have no conflict of interest.
References

[1] Marius K et al 2020 High-TC interfacial ferromagnetism in SrMnO$_3$/LaMnO$_3$ superlattices Adv. Funct. Mater. 30 1808270

[2] Marta G, Parlo Z, Raoul S, Jorge I and Jean-Marc T 2012 Exchange bias in LaNiO$_3$–LaMnO$_3$ superlattices Nat. Mater. 11 195–8

[3] Zhai X et al 2014 Correlating interfacial octahedral rotations with magnetism in (LaMnO$_3$)$_n$/(SrTiO$_3$)$_n$ superlattices Nat. Commun. 5 1–8

[4] Guan X et al 2019 Tuning magnetism and crystal orientations by octahedral coupling in LaCoO$_3$/LaMnO$_3$ thin films Phys. Rev. B 100 014427

[5] Zhou G, Ji H, Bai Y, Quan Z and Xu X 2019 Intrinsic exchange bias effect in strain-engineered single antiferromagnetic LaMnO$_3$ films Sci. China. Mater. 62 1042–52

[6] Marton Z, Seo A, Egami S and Lee T 2010 Growth control of stoichiometry in LaMnO$_3$ epitaxial thin films by pulsed laser deposition J. Cryst. Growth 312 2923–7

[7] Roqueta J, Pomar A, Ballells I, Fronteras C, Valencia S, Abrudan R, Rozzo B, Konstantinovic Z, Santos J and Martinez B 2015 Strain-Engineered Ferromagnetism in LaMnO$_3$. Thin Films Cryst. Growth Des. 15 5332–7

[8] Choi W et al Effects of oxygen-reducing atmosphere annealing on LaMnO$_3$ epitaxial thin films. J. Phys. D: Appl. Phys. 42 165401 2009

[9] Kim H and Christen H 2010 Controlling the magnetic properties of LaMnO$_3$ thin films on SrTiO$_3$(100) by deposition in a O$_2$/Ar gas mixture J. Phys. Condens. Matter 22 146007

[10] Zhao R, Jin K, Xu Z, Guo H, Wang L, Ge C, Lu H and Yang G 2013 The oxygen vacancy effect on the magnetic property of the LaMnO$_3$$_{1.5}$ thin films Appl. Phys. Lett. 102 122402

[11] Zhang A, Zhang W, Wu X and Lin J 2017 Abnormal enhancement of ferromagnetism for LaMnO$_{3+e}$ thin films with decreasing oxygen pressure Appl. Adv. 7 035837

[12] Xie C, Shi L, Zhao J, Li Y, Zhou S and Yao D 2015 The influence of substrate orientation and annealing condition on the properties of LaMnO$_3$ thin film grown by polymer assisted deposition Appl. Surf. Sci. 351 186–92

[13] Liang Y, Wang Z, Bai Y, Wu Y, Ning X, Zhao X, Liu W and Zhang Z 2019 Strain-induced cluster glass state in LaMnO$_3$ films J. Phys. Chem. C 123 14842–8

[14] Khanduri M, Dimri M, Vasala S, Leinberg S, Lohmus R, Ashworth T, Mere A, Krustok J, Karppinen M and Stern R 2013 Magnetic and structural studies of LaMnO$_3$ thin films prepared by atomic layer deposition J. Phys. D: Appl. Phys. 46 175003

[15] Liu Y, Hong H, Lam M, Mak C and Leung C 2019 Tuning ferromagnetic properties of LaMnO$_3$ films by oxygen vacancies and strain J. Magn. Magn. Mater. 481 85–92

[16] Vila-Fangueiro R, Rivas-Muñias B, Rodríguez-González B, Txoperformance O, Ciudad D, Hueso E, Lazzari L, Rivadulla M and Room F 2015 temperature ferromagnetism in thin films of LaMnO$_3$ deposited by a chemical method over large areas. ACS Appl. Mater. Interfaces 7 5140–414

[17] Rodríguez-Lamas R et al 2019 Integration of LaMnO$_{3+e}$ films on platinized silicon substrates for resistive switching applications by PI-MOCVD Beilstein J. Nanotechnol. 10 289–398

[18] Zhang F, Xiong J, Yang K, Xia Y, Xue Y, Zhao X and Tao B 2014 Epitaxial growth and characterization of RF-sputtered LaMnO$_3$ cap layers on homo-epi MgO/IBAD-MgO templates J. Supercond. Nov. Magn. 27 543–6

[19] Fang S, Pang Z, Wang F, Lin L and Han S 2011 Annealing effect on transport and magnetic properties of La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films grown on glass substrates by RF magnetron sputtering. J. Mater. Sci. Technol. 27 223–6

[20] Li Y, Chen L, Deng Q, Shen Y, Wang G and Wang S 2018 Effect of lack of oxygen on optical and electrical properties of RF magnetron sputtering deposited CuFeO$_2$x thin films Mod. Phys. Lett. B 32 1850379

[21] Dubey A and Sathe V 2007 The effect of magnetic order and thickness in the Raman spectra of oriented thin films of LaMnO$_3$. J. Phys. Condens. Matter 19 346232

[22] Sun Q, Luo X, Xia Q, Guo Y, Su J, Li Q and Mao G 2020 Enhanced ferromagnetism and conductivity in epitaxial LaMnO$_3$ thin films by oxygen-atmosphere annealing J. Magn. Magn. Mater. 499 166317

[23] Bhat I, Hussain S and War T 2016 Magnetic and Raman spectroscopic study of laser ablated 100 (nm) thin film of La$_{0.85}$Te$_{0.15}$MnO$_3$ deposited on LaAlO$_3$, J. Alloy. Compd. 667 225–8

[24] Yin L, Wang C, Li L, Shen Q and Zhang L 2018 Large room temperature magnetoresistance in La$_{0.2}$Sr$_{0.8}$MnO$_3$ thin films. J. Alloy. Compd. 730 327–32

[25] Xi B, Zhang G and Luo Y 2015 Effect of heat temperature on phase structure, composition and resistivity of LaMnO$_3$ film. Nonferrous Metals (Extractive Metallurgy) 11 51–4

[26] Wu Y, Ning X, Wang Z, Wang Q and Zhang Z 2016 Separation of Curie temperature and insulator-metal transition temperature in the La$_{0.6}$Sr$_{0.4}$MnO$_3$ polycrystalline films and its effect on low field magnetoresistance. J. Alloy. Compd. 667 317–22

[27] Niu W et al 2018 Direct demonstration of the emergent magnetism resulting from the multivalence Mn in a LaMnO$_3$ epitaxial thin film system Adv. Electron. Mater. 1800055

[28] Wang G, Du R, Wu D and Li A 2012 Magnetic and transport characteristics of long-period ([LaMnO$_2$]$_n$/(SrMnO)$_n$)[Mn]$_n$ (n ≠ 3) superlattices J. Appl. Phys. 112 103917

[29] Huang X, Ding J, Jiang Z, Yin Y, Yu Q and Li X 2009 Dynamic properties of cluster glass in La$_{0.25}$Ca$_{0.75}$MnO$_3$ nanoparticles. J. Appl. Phys. 106 083904

[30] Zhang A, Cheng S, Lin J and Wu X 2015 Strain controlled orbital state and magnetization in insulating LaMnO$_{3+e}$ films Appl. Phys. Lett. 117 178325

[31] Sultan K, Ikram M, Gautam S, Lee H, Chae K and Asokan K 2015 Electrical and magnetic properties of the pulsed laser deposited Ca doped LaMnO$_3$ thin films on Si (100) and their electronic structures RSC Adv. 5 69073

[32] Ma C, Hau S, Wong K, Chan P and Choy C 1996 The role of ambient gas scattering effect and lead oxide formation in pulsed laser deposition of lead-zirconate-titanate thin films Appl. Phys. Lett. 69 2030–2

[33] Ju H and Krishnan K M 1998 Evolution of strain-dependent transport properties in ultrathin La$_{0.6}$Sr$_{0.4}$MnO$_3$ films. J. Appl. Phys. 33 7073–5