Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2579–2581

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Short communication

Room temperature ultrahigh magnetoresistance nanostructure $(La_{2/3}Sr_{1/3})MnO_3$ films growth on $SrTiO_3$ substrate

Dan Liu [a,*], Wei Liu [b]

[a] Materials Research and Education Center, Auburn University, Auburn, AL 36849, USA
[b] Department of Physics, Wuhan University, Wuhan 430072, People's Republic of China

Received 13 September 2011; received in revised form 5 October 2011; accepted 5 October 2011
Available online 12 October 2011

Abstract

Nanostructure $(La_{2/3}Sr_{1/3})MnO_3$ thin films were epitaxial grown on $SrTiO_3$ (0 0 1) single crystal substrate by pulsed laser deposition. Both high Curie temperature (T_c = 360 K) and high magnetoresistance (MR = −38% at 500 Oe magnetic fields and 320 K) were simultaneously achieved. The high Curie temperature was attributed to the high quality epitaxial LSMO films. The high low field magnetoresistance (LFMR) was attributed to the regular square nanostructure of the deposited LSMO films, where the boundaries serve as the barrier for spin-polarized tunneling and/or spin-dependent scattering. The high T_c and large MR made the LSMO film very useful in room temperature magnetic devices.
Published by Elsevier Ltd and Techna Group S.r.l.

Keywords: Low field magnetoresistance (LFMR); LSMO; Epitaxial growth

1. Introduction

The colossal magnetoresistance (CMR) property has been observed in many perovskite structure manganite materials. CMR effect was generally interpreted by Zener's Mn^{3+}–O–Mn^{4+} double-exchange theory [1]. By replacing partial of the La with Sr, the Curie temperature (T_c) of $(La_{2/3}Sr_{1/3})MnO_3$ (LSMO) could be elevated to ~370 K, which makes it very useful for room temperature magnetic devices [2–4].

For practical applications, it is critical to obtain high magnetoresistance ($MR = (R_h - R_0)/R_0 \times 100\%$, where R_h/R_0 are the resistivity measured with/without magnetic field respectively) at high temperature and low magnetic field. Many efforts to enhance the MR have been focus on improving the transport properties by superlattice, tunneling junctions or nanostructure/nanocomposite material. Venimadhav [5] reported 98% MR at 6–7 T magnetic fields in the LCMO/PCMO superlattice. Yan [6] and Liu [7] observed enhanced MR on LSMO based nanocomposite. Zhang [8] reported the high MR LSMO films with ordered nanometer structure with nano-size cracks as the tunneling barriers.

Here we report the deposition of high quality nanostructure LSMO films on $SrTiO_3$ (STO) substrate by pulsed laser deposition (PLD). Both high Curie temperature (T_c = 360 K) and high magnetoresistance (MR = 38% at 500 Oe magnetic fields and 320 K) were simultaneously achieved on the deposited LSMO films. PLD has been proved to the successful tool in complex composition oxide thin films growth, such as and superconducting $YBa_2Cu_3O_{7-\delta}$ [9], different electroceramics films [10–16], as well as semiconductors [17–19]. In this paper, we showed high quality epitaxial nanostructure LSMO films deposited by PLD. The mechanisms of the ultra high low field magnetoresistance (LFMR) of LSMO films were discussed.

2. Experiment

LSMO films were deposited by PLD on single crystal STO substrate at 650 °C and 400 mTorr oxygen pressures. The target–substrate distance was ~5 cm. The laser density was ~4 J/cm^2 with 2 Hz rep-rate. After growth, the LSMO films were cooled down in chamber at rate ~10 °C/min. No further treatment was applied. X-ray scan diffraction was used to characterize the films quality. Secondary electrons microscopy was used to observe the films surface morphology. The physical properties, including Curie temperature, magnetoresistance and

* Corresponding author. Tel.: +1 334 728 2389.
E-mail address: colin_liud@hotmail.com (D. Liu).

0272-8842/$36.00. Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2011.10.017

coercive force were measured by Physical Properties Measurement System (PPMS).

3. Results and discussion

The LSMO films growth rate was ~100 nm/h. Fig. 1 shows a typical log scale XRD scan of a 200 nm thickness LSMO films. The LSMO phase was indexed as a pseudo-cubic phase: only (0 0 *l*) diffraction peaks of the perovskite phase were present, which clearly showed epitaxial growth relationship LSMO (0 0 1)||STO (1 0 0). The embedded was the (0 0 2) rocking curve scan, with Full Width Half Maximum ~0.08°, which further confirmed the high quality LSMO films.

Fig. 2 shows the SEM image of LSMO films top surface. Square nanostructure with ~40 nm dimension was observed, which is consistent to the reported isolated magnetic domains [20]. Fig. 3 shows the magnetic momentum measurement of LSMO films from 150 K to 400 K. A magnetic field of 500 Oe perpendicular to the film was applied during the measurement. The measured T_c was ~360 K, which is close to the bulk LSMO material. The hysteresis loop of the LSMO films with coercivity force of 130 Oe at 300 K were also embedded in Fig. 3.

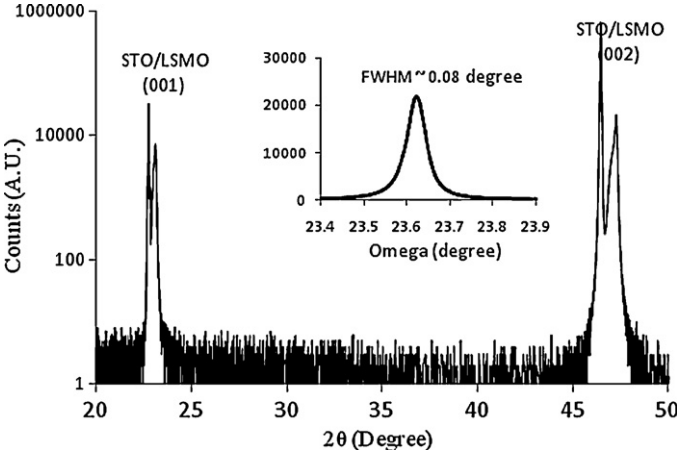

Fig. 1. XRD θ–2θ and rocking curve scan of LSMO (200 nm) showing high quality epitaxial growth on STO substrate.

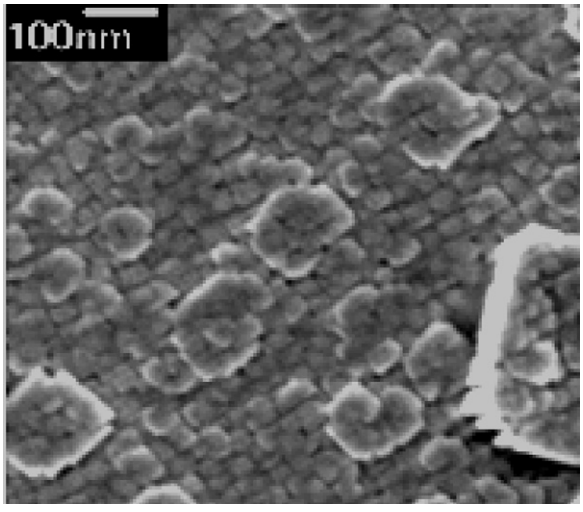

Fig. 2. SEM observation of typical LSMO films with regular spare pattern of ~40 nm size grain nano-structure on $SrTiO_3$ substrate.

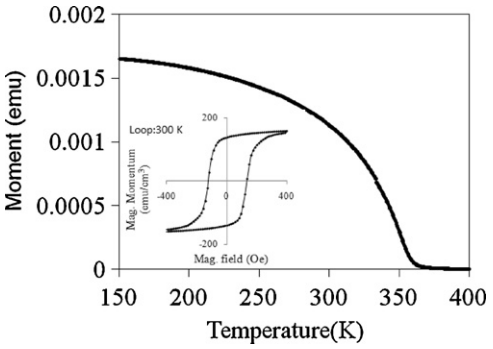

Fig. 3. *M–T* scan curve of deposited LSMO films grown on STO substrate. Note the Curie temperature as high as 360 K and coercivity force of 130 Oe at 300 K.

The resistivity–temperature relationship of the LSMO films was plot in Fig. 4. The sample was cooled down from 400 K to 5 K at zero magnetic field, and then warm up to 400 K with 500 Oe magnetic fields. Fig. 5 is the MR curve of deposited LSMO films, a maximum MR of 38% was achieved at 320 K at low magnetic fields (500 Oe). This MR is comparable or even higher than those LSMO based complicated tunneling device or nanocomposite materials [6–8,21–24]. Two mechanisms could possible explain the ultrahigh LFMR properties of the nanostructure LSMO films: spin-dependent scattering (SDS) or spin-polarized tunneling (SPT). As shown in Fig. 2, the deposited LSMO films have very regular square pattern nanostructure. The boundaries of the nanostructure films could serve as spin scattering center in SDS mechanism. On the other hand, the boundaries could also be the tunneling barrier in the SPT mechanisms; or both mechanisms played the role at the same time. The SDS mechanism is similar to the partial-crystallized LSMO films where the nanosize ferromagnetic LSMO crystals embedded in the nonferromagnetic amorphous matrix [7]. However, in that study, the Curie temperature is very low because of the low quality amorphous matrix. Ordered nanostructure LSMO films [8,25–27] were reported with high MR ratio, and the nano-size cracks between the LSMO grains [8] serves as the effective tunneling barrier in SPT mechanism. In our study, the nanostructure LSMO films is fully packed as shown in Fig. 2, the SDS mechanism is more likely. Further detailed study, including high resolution SEM/TEM structural

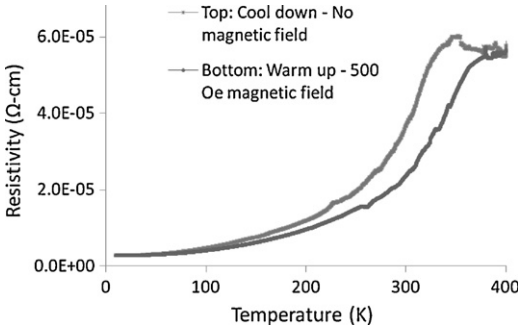

Fig. 4. *R–T* scan curve of deposited LSMO films with and without magnetic field.

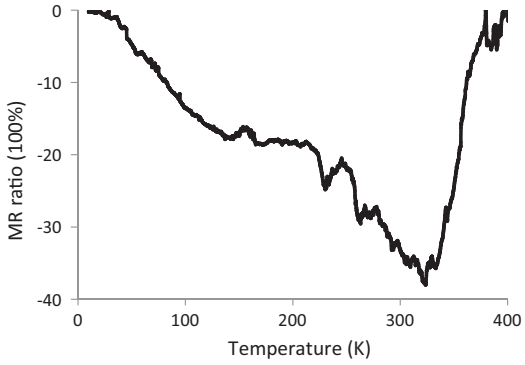

Fig. 5. MR curve of deposited LSMO films.

and *I–V* electrical transport characterization will be used to explore the fundamental mechanism of the ultrahigh LFMR of this regular pattern nanostructure LSMO films.

4. Conclusion

Epitaxial nanocrystalline $(La_{2/3}Sr_{1/3})MnO_3$ (0 0 1) films was grown on single crystal $SrTiO_3$ (0 0 1) substrate by pulsed laser deposition. The Curie temperature of LSMO films as high as 360 K was achieved, because of high quality epitaxial growth. The deposited LSMO films had very regular square pattern nanostructure with size of 50 nm. MR ratio of 38% was observed at 320 K temperature with 500 Oe magnetic fields on the nanostructure LSMO films. The ultrahigh LFMR should be attributed to the regular nanostructure pattern of the LSMO films. The nanostructure boundary could serve as the electron scattering center or tunneling barrier between each LSMO grains. As a result, the MR effect was significantly enhanced. This high quality LSMO films could be very useful for sensitive room temperature magnetic devices.

References

[1] C. Zener, Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with perovskite structure, Phys. Rev. 82 (1951) 403–405.

[2] C. Moreno, C. Munuera, S. Valencia, F. Kronast, X. Obradors, C. Ocal, Reversible resistive switching and multilevel recording in $La_{0.7}Sr_{0.3}MnO_3$ thin films for low cost nonvolatile memories, Nano Lett. 10 (2010) 3828–3835.

[3] A. Ozbay, E.R. Nowak, Z.G. Yu, W. Chu, Y. Shi, S. Krishnamurthy, Z. Tang, N. Newman, Large magnetoresistance of thick polymer devices having $La_{0.67}Sr_{0.33}MnO_3$ electrodes, Appl. Phys. Lett. 95 (2009) 232507–232509.

[4] O.J. González, E. Castaño, J.C. Castellano, F.J. Gracia, Magnetic position sensor based on nanocrystalline colossal magnetoresistances, Sens. Actuators A 92 (2001) 137–143.

[5] A. Venimadhav, M.S. Hegde, R. Rawat, I. Das, M. El Marssi, Enhancement of magnetoresistance in $La_{0.67}Ca_{0.33}MnO_3/Pr_{0.7}Ca_{0.3}MnO_3$ epitaxial multilayers, J. Alloys Compd. 326 (2001) 270–274.

[6] C. Yan, F. Luo, Y. Huang, X. Li, Z. Wang, C. Liao, H. Zhao, B. Shen, Enhanced room temperature magnetoresistance in $La_{0.7}Sr_{0.3}MnO_3/Sm_{0.7}Sr_{0.3}MnO_3$ nanocomposites, J. Appl. Phys. 91 (2002) 7406–7408.

[7] J.-M. Liu, J. Li, Q. Huang, L.P. You, S.J. Wang, C.K. Ong, Z.C. Wu, Z.G. Liu, Y.W. Du, Partially crystallized $La_{0.5}Sr_{0.5}MnO_3$ thin films by laser ablation and their enhanced low-field magnetoresistance, Appl. Phys. Lett. 76 (2000) 2286–2288.

[8] F.C. Zhang, W.Z. Gong, C. Cai, B. Xu, X.G. Qiu, R. Vanfleet, L. Chow, B.R. Zhao, Room temperature ultrahigh magnetoresistance in $La_{0.67}Sr_{0.33}MnO_3$ thin films with ordered nanometer structure, Solid State Commun. 131 (2004) 271–274.

[9] D.K. Fork, F.A. Ponce, J.C. Tramontana, T.H. Geballe, Epitaxial MgO on Si(0 0 1) for Y–Ba–Cu–O thin-film growth by pulsed laser deposition, Appl. Phys. Lett. 58 (1991) 2294–2296.

[10] Z.Z. Tang, S.J. Liu, R.K. Singh, S. Bandyopadhyay, I. Sus, T. Kotani, M. van Schilfgaarde, N. Newman, Growth and characterization of epitaxial $Ba(Zn_{1/3}Ta_{2/3})O_3$ (1 0 0) thin films, Acta Mater. 57 (2009) 432–439.

[11] D. Liu, B. Zhou, S.H. Yoon, Y. Wang, M. Park, B.C. Prorok, D.-J. Kim, Effects of the structural layer in MEMS substrates on mechanical and electrical properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ films, Ceram. Int. 37 (2011) 2821–2828.

[12] S. Bandyopadhyay, S.J. Liu, Z.Z. Tang, R.K. Singh, N. Newman, Leakage-current characteristics of vanadium- and scandium-doped barium strontium titanate ceramics over a wide range of DC electric fields, Acta Mater. 57 (2009) 4935–4945.

[13] S.H. Yoon, D. Liu, D. Shen, M. Park, D.-J. Kim, Effect of chelating agents on the preferred orientation of ZnO films by sol–gel process, J. Mater. Sci. 43 (2008) 6177–6181.

[14] F. Pailloux, R. Lyonnet, J. Maurice, J. Contour, Twinning and lattice distortions in the epitaxy of $La_{0.67}Sr_{0.33}MnO_3$ thin films on (0 0 1) $SrTiO_3$, Appl. Surf. Sci. 177 (2001) 263–267.

[15] A. Husmann, D.A. Wesner, J. Schmidt, T. Klotzbücher, M. Mergens, E.W. Kreutz, Pulsed laser deposition of crystalline PZT thin films, Surf. Coat. Technol. 97 (1997) 420–425.

[16] D. Liu, S.H. Yoon, B. Zhou, S.-B. Kim, H. Ahn, B.C. Prorok, S.-H. Kim, D.J. Kim, Determination of the true Young's modulus of $Pb(Zr_{0.52}Ti_{0.48})O_3$ films by nanoindentation: effects of film orientation and substrate, J. Am. Ceram. Soc. (2011), doi:10.1111/j.1551-2916.2011.04867.x.

[17] K. Moriya, K. Tanaka, H. Uchiki, Fabrication of Cu_2ZnSnS_4 thin-film solar cell prepared by pulsed laser deposition, Jpn. J. Appl. Phys. 46 (2007) 5780–5781.

[18] Z.Z. Tang, L. Zhang, R.K. Singh, D. Wright, T. Peshek, T. Gessert, T. Coutts, M. van Schilfgaarde, N. Newman, Characterization of ZnGeAs2 thin films produced by pulsed laser deposition, in: 34th IEEE PVCS, 2009, 00437–00439.

[19] T. Peshek, Z.Z. Tang, L. Zhang, R.K. Singh, B. To, T. Gessert, T.J. Coutts, N. Newman, M. van Schilfgaarde, ZnGeAs2 thin films properties: a potentially useful semiconductor for photovoltaic applications, in: 34th IEEE PVCS, 2009, 001367–001369.

[20] M.-J. Casanove, C. Roucau, P. Baulès, J. Majimel, J.-C. Ousset, D. Magnoux, J.F. Bobo, Growth and relaxation mechanisms in $La_{0.66}Sr_{0.33}MnO_3$ manganites deposited on $SrTiO_3$(0 0 1) and MgO (0 0 1), Appl. Surf. Sci. 188 (2002) 19–23.

[21] J. Liu, G. Yuan, H. Sang, Z. Wu, X. Chen, Z. Liu, Y. Du, Q. Huang, C. Ong, Low-field magnetoresistance in nanosized $La_{0.7}Sr_{0.3}MnO_3/Pr_{0.5}Sr_{0.5}MnO_3$ composites, Appl. Phys. Lett. 78 (2001) 1110–1112.

[22] D. Liu, W. Liu, Growth and characterization of epitaxial $(La_{2/3}Sr_{1/3})MnO_3$ films by pulsed laser deposition, Ceram. Int. 37 (2011) 3531–3534.

[23] Z.Z. Tang, J.H. Hsieh, S.Y. Zhang, C. Li, Y.Q. Fu, Phase transition and microstructure change in Ta–Zr alloy films by co-sputtering, Surf. Coat. Technol. 198 (2005) 110–113.

[24] S. Gupta, R. Ranjit, C. Mitra, P. Raychaudhuri, R. Pinto, Enhanced room-temperature magnetoresistance in $La_{0.7}Sr_{0.3}MnO_3$-glass composites, Appl. Phys. Lett. 78 (2001) 362–364.

[25] X.W. Li, A. Gupta, G. Xiao, Low-field magnetoresistive properties of polycrystalline and epitaxial perovskite manganite films, Appl. Phys. Lett. 71 (1997) 124–126.

[26] Z. Zhang, R. Ranjith, B.T. Xie, L. You, L.M. Wong, S.J. Wang, J.L. Wang, W. Prellier, Y.G. Zhao, T. Wu, Enhanced low field magnetoresistance in nanocrystalline $La_{0.7}Sr_{0.3}MnO_3$ synthesized on MgO nanowires, Appl. Phys. Lett. 96 (2010) 222501–222503.

[27] B. Ghosh, S. Kar, L.K. Brar, A.K. Raychaudhuri, Electronic transport in nanostructured films of $La_{0.67}Sr_{0.33}MnO_3$, J. Appl. Phys. 98 (2005) 094302–094307.