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Influence of Lattice Strain on Phase Separation and Percolative Behaviors in $La_{0.325}Pr_{0.3}Ca_{0.375}MnO_3$ Thin Films

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The compressive and tensile strains induced by different substrates on $La_{0.325}Pr_{0.3}Ca_{0.375}MnO_3$ (LPCMO) thin films have been investigated. It is found that the in-plane compressive strain favors the ferromagnetic metallic phase by increasing the hopping amplitude between neighboring elections and decreasing the tilt of the MnO_6 octahedron, leading to the weakening of the phase separation. On the other hand, the in-plane tensile strain in films prefers to increase the stability of long-range COO phase. Under 5 T magnetic field, the 30 nm LPCMO films on NGO and LSAT substrates show an obvious metal-insulator transition, indicating that the COO phase can be melted by the magnetic field at low temperature in the film with small in-plane tensile strain. Whereas, the LPCMO film on STO substrate keeps insulating in the entire measuring temperature range even under 5 T magnetic field, suggesting that the COO phase in the film with a large tensile strain is more robust.

***Index Terms*— competition, electronic phase separation, giant magnetoresistance, perovskite manganite**

I. Introduction

THE $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ systems has been extensively studied in recent years as a typical electronic phase separation(PS) system[1]-[4], which is very sensitive to the external parameters, such as magnetic field, electric field/current, pressure, and light illumination [5]-[9]. As well known, the average radius of A sites in the ABO_3 structure plays a key role in determining the band (W) and electronic characteristics of the perovskite manganites. *Uehara et al* have found that the chemical replacement of Pr for La (Pr is smaller than La) could reduce the W [1], as a result, the ferromagnetic (FM) metallic phase transforms into the charge/orbital ordering (COO) partially. Therefore, the coexistence and competition of the FM metallic phase with the COO insulating phase emerge upon Pr doping. On the other hand, the strain exerted by the lattice mismatch between the substrate and bulk also plays an important role in controlling the magnetic and transport properties of films, which can influence the balance of free energy between the coexistent COO insulating and FM metallic phases by adjusting the strength of the double exchange interaction and the Jahn-Teller (JT) electron-lattice coupling [4], [10]-[12]. Here, we report the strain effects on the phase separation and the competition between COO and FM metallic phases in $La_{0.325}Pr_{0.3}Ca_{0.375}MnO_3$ (LPCMO) thin films.

II. Experimental

Four kinds of substrates with (100) orientation, $LaAlO_3$ (LAO, 3.788 Å), $NdGaO_3$ (NGO, 3.853 Å), $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ (LSAT, 3.868 Å) and $SrTiO_3$ (STO, 3.905 Å) were used to deposit LPCMO films by pulsed laser deposition technique (PLD), a KrF excimer laser (248 nm) with a pulsed energy of 200 mJ and a repetition of 1 Hz was used. During the deposition, the oxygen pressure was kept at 100 Pa and the temperature of substrate was 650 ℃. After the deposition, the samples were cooled down to room temperature in 1 atm pure oxygen atmosphere for compensating the oxygen deficiency [13]. The thicknesses of films were controlled to be 30, 100 and 200 nm. The transport property was measured by a superconducting quantum interference device-vibrating sample magnetometers (SQUID–VSM), equipped with a home-made electric-measurement module for performing four-point electrical resistance measurements.

III. Results and Discussion

The crystalline structure of the LPCMO bulk and films are determined by X-ray diffraction (XRD) using Cu-Kα radiation. It is found that the bulk crystallizes in orthometric structure with space group of Pnma and the pseudo-cubic lattice parameters are determined to be 3.823 Å (a=5.430 Å, b=7.658 Å and c=5.433 Å). Fig. 1 shows the typical XRD patterns for 30 nm LPCMO films on different substrates. It is found that all films were epitaxially grown along [100] direction and no other impurity phases were found. From the XRD patterns, the out-of-plane lattice parameter c was determined to be 3.914, 3.912 and 3.861 Å for 30, 100 and 200 nm films on LAO substrate, and the out-of-plane strains are correspondingly 2.22%, 2.16% and 0.83% by using $\varepsilon_{zz}=(c_{film}-c_{bulk})/c_{bulk}$, indicating that the films on LAO undergo the tensile strain along the out-of-plane. Meanwhile, the corresponding in-plane

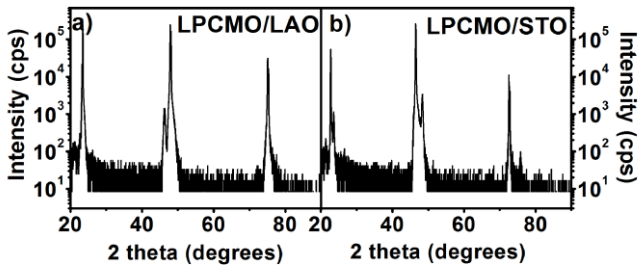

Fig. 1. Typical X-ray diffraction patterns for 30 nm LPCMO films on a) LAO and b) STO.

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compressive strain is calculated as -1.74%, -1.69% and -0.65% for 30, 100 and 200 nm films on LAO by Poisson relation $\varepsilon_{xx}=-((1-\upsilon)/2\upsilon)\varepsilon_{zz}$ (υ is the Poisson ratio). The value of υ is usually located between 0.3 and 0.5 for most materials, and υ=0.39 was chosen here, similar to the one of $La_{2/3}Ca_{1/3}MnO_3$ [14]. For clarity, the full information of the lattice parameter and lattice strain are listed in Table I for all films. It can be found that the films on NGO, LSAT and STO suffer out-of-plane compressive strains and in-plane tensile strains due to the positive lattice mismatch between the substrate and the LPCMO bulk. As expected, for the film with identical thickness on different substrate, the in-plane tensile strain shows a monotonic increase with the increase of the lattice mismatch. Specially, for 30 nm films, in-plane tensile strain increases from 0.47% on NGO to 1.39% on STO.

Table I Summary of lattice mismatch, thickness, c-axis lattice constants, out-of-plane strain and in-plane strains of LPCMO film on various substrates.

	lattice constant (Å)	lattice mismatch (Å)	thickness (nm)	c-axis lattice constant of the film (Å)	out-of-plane strain	in-plane strain
$LaAlO_3$	3.788	-1.38%	30	3.914	2.22%	-1.74%
			100	3.912	2.16%	-1.69%
			200	3.861	0.83%	-0.65%
NGO	3.853	0.32%	30	3.806	-0.61%	0.47%
			100	3.811	-0.47%	0.37%
			200	3.819	-0.27%	0.21%
LSAT	3.868	0.71%	30	3.790	-1.01%	0.79%
			100	3.793	-0.93%	0.83%
			200	3.796	-0.87%	0.68%
$SrTiO_3$	3.905	1.67%	30	3.761	-1.78%	1.39%
			100	3.763	-1.72%	1.35%
			200	3.764	-1.70%	1.33%
Bulk LPCMO	Lattice parameter: a=b=3.841 Å c=3.823 Å					

Meanwhile, the thinner film undergoes a lager strain from the lattice mismatch between the substrate and bulk. Such strain will relax as the film grows thicker. For example, the in-plane tensile strain in LPCMO/NGO films decreases from 0.47% to 0.21% with the thickness increases from 30 nm to 200 nm.

Fig. 2 shows the temperature dependence of the resistance (R-T) for LPCMO bulk through a full cooling-warming cycle. The bulk shows an insulator-metal transition (IMT) in a percolative manner with an obvious thermal hysteresis (~19 K) around 193 K (defined as the peak temperature in R-T curves on cooling). The results indicate the competition between COO and FM metallic phases at low temperature, which is consistent with previously reported result in LPCMO [1]. At room temperature, the sample is dominated by the COO insulating state. With decreasing temperature, FM metallic droplets appear in a COO insulating matrix around the IMT temperature. Further decreasing temperature causes the FM metallic domains develop and coalesce, and when a percolation threshold is reached, a sudden drop of resistance appears. Finally, the sample is completely occupied by FM metallic state at low temperature [15].

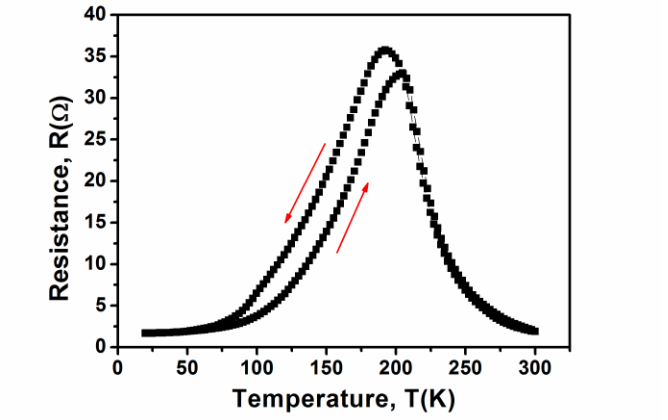

Fig. 2. Temperature dependence of the resistance for LPCMO bulk.

Fig. 3 displays the selected temperature-dependent normalized resistance R(T)/R(300K) for 30, 100 and 200 nm films on a) LAO and b) STO substrates, and black square, red circle and blue triangle curves stand for the corresponding films, respectively. From Fig. 3, one can find that the hysteresis gap of the film of 200 nm on LAO reduces to 14 K with the IMT temperature decreasing by 35 K in comparison with the bulk, which indicates that the in-plane compressive strain suppresses the COO phase and enhance the FM metallic phase. As known, the balance and competition between the COO and FM metallic phase can be adjusted by the strength of the double exchange interaction and the JT distortion. The in-plane compressive strain tends to decrease the Mn-O-Mn bond length and increase the Mn-O-Mn bond angle [16]. Thereby, decreasing the tilt of the MnO_6 octahedron leads to weakening of the collective JT distortion and enhancements of the hopping amplitude between the neighboring elections. As a result, the FM metallic phase are greatly enhanced, resulting in the shrinking of the hysteresis. On the other hand, the films under in-plane tensile strain show different behaviors. The IMT temperature and the hysteresis gap are 120 K and 21 K for 200 nm LPCMO/STO, respectively, implying that the in-plane tensile strains can enhance the stabilities of the long range COO phase and the competition between the COO and FM metallic phases. Actually, the in-plane tensile strain leads to the in-plane expansion and out-of-plane contraction of the MnO_6 octahedrons [4], [17], resulting in an enhancement of the JT distortion and a reduction of the effective one-electron bandwidth of the e_g electron. Thus, the electronic localization is strengthened, which is unfavorable for the formation of FM metallic phase but assist the robustness of COO phase. Meanwhile, by comparing the results of films with different thickness on the same substrate (shown in Fig. 3(a) and 3(b)), one can find that the IMT temperature is highly sensitive to the film thickness. As the thickness decreasing, the IMT temperature moves to lower temperature rapidly owing to the larger strains in thinner films. For the LPCMO/LAO films, the IMT temperature is determined as 158 K, 107 K and 65 K for 200 nm, 100 nm and 30 nm, respectively. It is noteworthy that the thinner film has a higher residual resistance at low temperature. This is probably because that the FM metallic

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phase does not fully occupy the sample and some short-range COO phase may retain at the temperature below the metal-insulator transition in thinner films. Note that the 30 nm film on STO shows an insulating behavior in the entire temperature range, indicating that its percolation threshold is not reached under present measurement conditions [4].

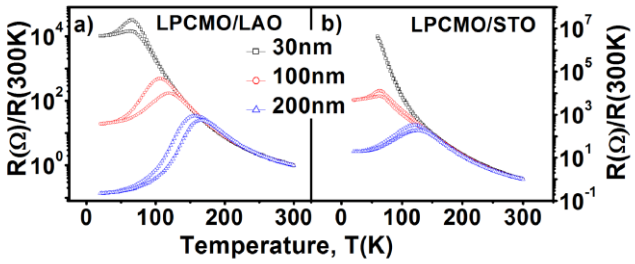

Fig. 3. The temperature-dependent normalized resistance R(T)/R(300K) for 30,100 and 200 nm LPCMO films on a) LAO and b) STO substrates.

Moreover, we also investigate the influence of magnetic field on the competition between COO and FM phase. Fig. 4 shows the dependence of normalized resistivity on temperature under 0 and 5 T magnetic field for 30 nm LPCMO films on LAO, NGO, LSAT and STO substrates, respectively. Under zero magnetic field, films on LAO substrate with in-plane compressive strain and on NGO with small tensile strain show a metal-insulator transition at low temperature 65 K and 62 K, respectively, while the films with bigger tensile strain (on LSAT and STO substrates) show insulating behavior in the entire temperature range of 60~300 K. Upon 5 T magnetic field, the resistance of LPCMO/LAO film, which experiences in-plane compressive strain, reduces remarkably and the hysteresis gap becomes insignificant, indicating that the magnetic field can melt the COO state and make the phase separation become trivial for the LPCMO/LAO film. Whereas, the LPCMO/NGO film with a

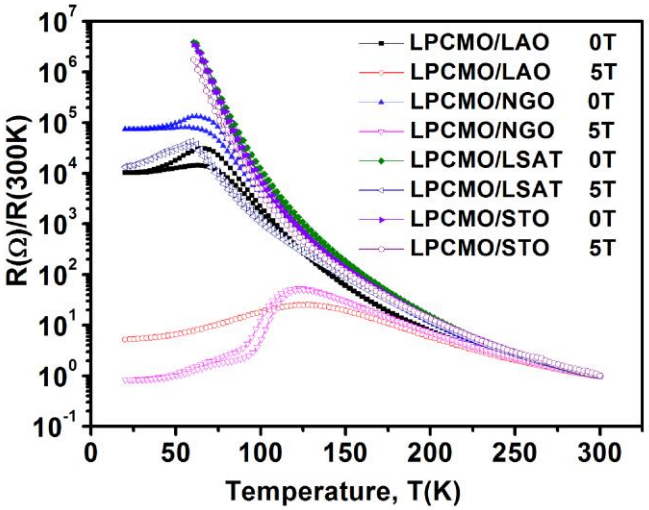

Fig. 4. The dependence of normalized resistivity on temperature under 0 and 5 T magnetic field for 30 nm LPCMO films on LAO, NGO, LSAT and STO substrates, respectively.

small in-plane tensile strain shows a large magnetoresistance (MR) under applied magnetic field of 5 T (the MR=(R(0)-R(5 T))/R(5 T) reaches 9.2×10^{-4} at 57 K) and the IMT increases from 62 K to 122 K. Moreover, for the LPCMO/LSAT film, a metal-insulator transition appears at temperature 60 K as a 5 T magnetic field was applied, indicating partially melting of COO phase at low temperature. In contrast, for the LPCMO/STO film, the insulating behavior retains even under 5 T field, which suggests that the COO phase in LPCMO/STO films is much more robust than that in LPCMO/LSAT and LPCMO/NGO films due to the larger in-plane tensile strain (1.39%)[17]. These results further confirm that the in-plane tensile strain can enhance the stability of COO phase through increasing the JT distortion and thus the carriers localization.

IV. Conclusion

In summary, the strain effect on the phase separation and the competition between COO insulating and FM metallic phases in LPCMO thin films on different substrates have been studied. It was observed that the compressive and tensile strain impose obvious different effects on the phase separation. The in-plane compressive strain suppresses the COO by enhancing the tilt of the MnO_6 octahedron, leading to weakening of the collective JT distortion. An application of magnetic field can melt the COO state and make the phase separation become trivial for the film with in-plane compressive strain. On the other hand, the tensile strain can increase the stability of long-range COO phase by enhancing the JT distortion and thus the carriers localization. Upon applying a 5 T magnetic field, an obvious metal-insulator transition appears in the 30 nm LPCMO films on NGO and LSAT substrates, indicating that the COO phase can be melt partially by the magnetic field in the film with small in-plane tensile strain. Moreover, the LPCMO film on STO substrate that experiences a larger tensile strain keeps insulating in the entire temperature range under 5 T magnetic field, suggesting that the COO phase in LPCMO/STO films is much more robust than that in those films with relative small tensile strain and even a 5 T magnetic field cannot melt it.

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References

[1] M. Uehara, S. Mori, C. H. Chen, and S. W. Cheong, "Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites," *Nature*, vol. 399, no. 6736, pp. 560-563, Jun 10, 1999.

[2] T. Z. Ward, J. D. Budai, Z. Gai, J. Z. Tischler, L. F. Yin, and J. Shen, "Elastically driven anisotropic percolation in electronic phase-separated manganites," *Nature Physics*, vol. 5, no. 12, pp. 885-888, Dec, 2009.

[3] M. C. Dekker, A. D. Rata, K. Boldyreva, S. Oswald, L. Schultz, and K. Dorr, "Colossal elastoresistance and strain-dependent magnetization of phase-separated $(Pr_{1-y}La_y)_{0.7}Ca_{0.3}MnO_3$ thin films," *Physical Review B*, vol. 80, no. 14, Oct, 2009.

[4] D. Gillaspie, J. X. Ma, H. Y. Zhai, T. Z. Ward, H. M. Christen, E. W. Plummer, and J. Shen, "Influence of different substrates on phase

separation in $La_{1-x-y}Pr_yCa_xMnO_3$ thin films," *Journal of Applied Physics*, vol. 99, no. 8, Apr 15, 2006.

[5] T. Wu, S. B. Ogale, S. R. Shinde, A. Biswas, T. Polletto, R. L. Greene, T. Venkatesan, and A. J. Millis, "Substrate induced strain effects in epitaxial $La_{0.67-x}Pr_xCa_{0.33}MnO_3$ thin films," *Journal of Applied Physics*, vol. 93, no. 9, pp. 5507, 2003.

[6] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, "Magnetic-field-induced metal-insulator phenomena in $Pr_{1-x}Ca_xMnO_3$ with controlled charge-ordering instability," *Physical Review B*, vol. 53, no. 4, pp. R1689-R1692, Jan 15, 1996.

[7] K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, "Photoinduced insulator-to-metal transition in a perovskite manganite," *Physical Review Letters*, vol. 78, no. 22, pp. 4257-4260, Jun 2, 1997.

[8] M. Fiebig, K. Miyano, Y. Tomioka, and Y. Tokura, "Visualization of the local insulator-metal transition in $Pr_{0.7}Ca_{0.3}MnO_3$," *Science*, vol. 280, no. 5371, pp. 1925-1928, Jun 19, 1998.

[9] V. Kiryukhin, B. Kim, V. Podzorov, S. W. Cheong, T. Koo, J. Hill, I. Moon, and Y. Jeong, "Multiphase segregation and metal-insulator transition in single crystal $La_{5/8-y}Pr_yCa_{3/8}MnO_3$," *Physical Review B*, vol. 63, no. 2, 2000.

[10] J. Wang, F. X. Hu, R. W. Li, J. R. Sun, and B. G. Shen, "Strong tensile strain induced charge/orbital ordering in (001)-$La_{7/8}Sr_{1/8}MnO_3$ thin film on 0.7Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.3$PbTiO_3$," *Applied Physics Letters*, vol. 96, no. 5, Feb 1, 2010.

[11] Y. Y. Zhao, J. Wang, H. Kuang, F. X. Hu, H. R. Zhang, Y. Liu, Y. Zhang, S. H. Wang, R. R. Wu, M. Zhang, L. F. Bao, J. R. Sun, and B. G. Shen, "Abnormal percolative transport and colossal electroresistance induced by anisotropic strain in (011)-$Pr_{0.7}(Ca_{0.6}Sr_{0.4})_{(0.3)}MnO_3$/PMN-PT heterostructure," *Scientific Reports*, vol. 4, Nov 17, 2014.

[12] J. Wang, F. X. Hu, Y. Y. Zhao, Y. Liu, R. R. Wu, J. R. Sun, and B. G. Shen, "Effect of epitaxial strain on small-polaron hopping conduction in $Pr_{0.7}(Ca_{0.6}Sr_{0.4})_{0.3}MnO_3$ thin films," *Applied Physics Letters*, vol. 106,no. 10, 2015.

[13] J. F. Wang, Y. C. Jiang, Z. P. Wu, and J. Gao, "Modulation of persistent photoconductivity by electric-field-controlled strain in thin films of $La_{0.39}Pr_{0.24}Ca_{0.37}MnO_3$," *Applied Physics Letters*, vol. 102, no. 7, pp. 071913, 2013.

[14] A. Llobet, L. Ranno, and J. Pierre, "Tuning magnetotransport and magnetic properties of $La_{2/3}Ca_{1/3}MnO_3$ thin films using epitaxial strain," *European Magnetic Materials and Applications*, vol. 373-3, pp. 517-520, 2001.

[15] K. H. Kim, M. Uehara, C. Hess, P. A. Sharma, and S. W. Cheong, "Thermal and electronic transport properties and two-phase mixtures in $La_{5/8-x}Pr_xCa_{3/8}MnO_3$," *Physical Review Letters*, vol. 84, no. 13, pp. 2961-2964, Mar 27, 2000.

[16] S. Hu, H. Huang, Y. Yang, Z. Luo, M. Yang, H. Wang, Y. Dong, B. Hong, H. He, J. Bao, and C. Gao, "Substrate-dependent post-annealing effects on the strain state and electrical transport of epitaxial $La_{5/8-y}Pr_yCa_{3/8}MnO_3$ films," *AIP Advances*, vol. 4, no. 6, pp. 067109, 2014.

[17] Y. Y. Zhao, F. X. Hu, J. Wang, L. Chen, W. W. Gao, J. Shen, J. R. Sun, and B. G. Shen, "Strain effect caused by substrates on phase separation and transport properties in $Pr_{0.7}(Ca_{0.8}Sr_{0.2})_{0.3}MnO_3$ thin films," *Journal of Applied Physics*, vol. 111, no. 7, pp. 07D721, 2012.