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Thickness Effect on Electronic Transport in Single Crystal $La_{0.67}Ca_{0.33}MnO_3$ Thin Films*

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Abstract: $La_{0.67}Ca_{0.33}MnO_3$(LCMO) films were fabricated on (100) $SrTiO_3$(STO) and (110) $NdGaO_3$(NGO) substrates using facing-target sputtering technique. The resistivity ρ and metal-to-semiconductor transition temperature T_{MS} were studied as functions of thickness. Although lattice stresses in LCMO/NGO and LCMO/STO are substantially different as confirmed by the XRD analyses, there is no direct correlation between structure and electronic transport in LCMO films, indicating the absence of strain effects on the transport properties, for example, ρ, T_{MS} and activation energy E_a.

Key words: colossal magnetoresistance; thin film; rare earths
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Lattice strain in thin films induced by film-substrate mismatch is one source for variant magnetic and resistive behaviors especially for the manganite perovskites for which the lattice effects are well established[1~5]. It has been also reported that low-field colossal magnetoresistance (CMR) effect is due to strain-induced magnetic anisotropy[6,7]. Moreover, when the film gets thinner, surface effects become increasingly important[8]. Effects associated with surface morphology as well as structure deformation can be controlled by film thickness. Jin et al.[9] studied thickness effects on CMR in $La_{0.67}Ca_{0.33}MnO_3$, and Sun et al.[10] studied $La_{0.67}Sr_{0.33}MnO_3$ films and wanted to verify the presence of a dead layer. In this paper, the thickness dependence of structure and transport behavior of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) films was studied, and the effect of lattice strain in CMR films explored.

1 Experimental

Epitaxial LCMO films with different thickness were grown on (100) $SrTiO_3$ (STO) and (110) $NdGaO_3$ (NGO) substrates using facing-target sputtering (FTS) technique[11~13]. A mixture of high purity Ar and O_2, total pressure 10 Pa, was used as the discharge gases with the flow rates adjusted by two mass flow controllers. Prior to film deposition, the vacuum chamber was pumped down to 1×10^{-4} Pa, and then the targets were presputtered for 15 min. Immediately after each deposition, the vacuum chamber was backfilled with 100 Pa oxygen gas. The deposited film was then cooled to room temperature with the substrate heater power cut off. To optimize the oxygen stoichiometry and crystallization, post-annealing process is necessary for the as-deposited films. Our samples were post-annealed at 900 ℃ for 240 min in O_2 gas. The film structure was examined by the $\theta/2\theta$ X-ray diffraction method[11~13], and the resistance as a function of temperature was measured by standard four-probe technique.

2 Results and Discussion

XRD θ-2θ scan confirmed the epitaxial growth and high crystal quality. Taking the diffraction peak of the substrate as an internal standard, the out-of-plane lattice parameters of LCMO layer can be determined accurately. Fig. 1 shows the variation of lattice constants with film thickness d_L in LCMO/STO and LCMO/NGO. Different crystal distortions are observed. In LCMO/STO, the lattice parameters are essentially unaffected until the thickness is smaller than ~50 nm below which a sudden in-plane expansion and out-of-plane contraction of lattice take place. In contrast, deformation of the unit cell in LCMO/NGO is small.

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From 30 to 200 nm, the variation of the out-of-plane lattice constant is ~0.0056 nm for LCMO/STO and ~0.0013 nm for LCMO/NGO, respectively.

For LCMO/NGO and LCMO/STO, except for the thinnest samples, all curves exhibit typical metal-to-semiconductor transition at T_{MS} (metal-to-semiconductor transition temperature). The most triking features of present finding are the strong thickness dependent of T_{MS} and the resistivity ρ at a fixed temperature of 290 K as shown in the Fig. 2. Thickness effects are weak in films thicker than 50 nm. However, T_{MS} depends critically on thickness in ultrathin films and drops steeply from ~200 to ~50 K when the thickness varies from ~20 to 5 nm. The sharp upturn of ρ, consistent with the sudden drop of T_{MS}, suggests a close relationship between these two quantities. Early investigations of resistivity of $La_{1-x}Ca_xMnO_3$ for $T >$

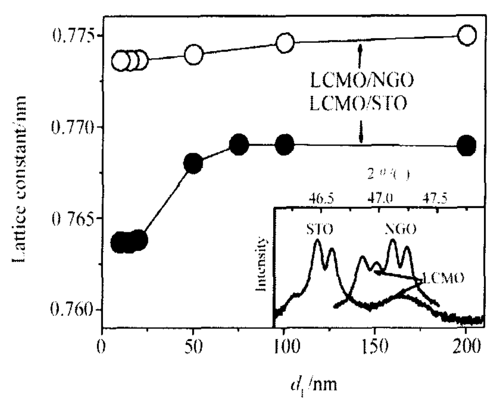

Fig. 1 Out-of-plane lattice constants of LCMO/STO and LCMO/NGO films as functions of film thickness (The solid lines are drawn as a guide to the eyes only. The inset is the XRD patterns of LCMO (200 nm)/STO and LCMO (200 nm)/NGO.)

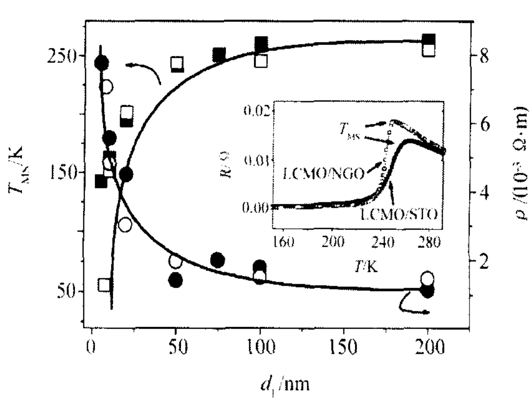

Fig. 2 Thickness dependence of resistivity at 290 K and metal-to-semiconductor transition temperature (T_{MS}) of LCMO/STO (solid points) and LCMO/NGO (open points) films (The solid lines are drawn as a guide to the eyes only. The inset is the temperature dependence of resistance of LCMO (200 nm)/STO and LCMO (200 nm)/NGO)

T_{MS} indicate that resistivity increases roughly exponentially with inverse temperature in semiconductor regime. The nature of conduction mechanism is ascribed to variable range hopping, or a nearest-neighbor hopping model based on small polaron. By fitting the semiconductor part (high temperature regime) of ρ-T curve to small polaron model ($\rho = \rho_0 T\exp(E_a/k_B T)$, where ρ_0 is resistivity at 0 K, k_B is Boltzmann constant), the activation energy for small polaron conduction (E_a) is deduced from the slope of each curve. As shown in Fig. 3, E_a has a well-defined correlation with T_{MS}, and increase monotonically from 0.086 to ~0.125 eV corresponding to a decrease of T_{MS} from ~260 to ~50 K. In special, E_a is independent of the substrate.

From our results, although lattice stresses in LCMO/NGO and LCMO/STO are substantially different as confirmed by XRD analyses, there is no direct correlation between structure and resistivity in our LCMO films, indicating the absence of strain effects on transport properties.

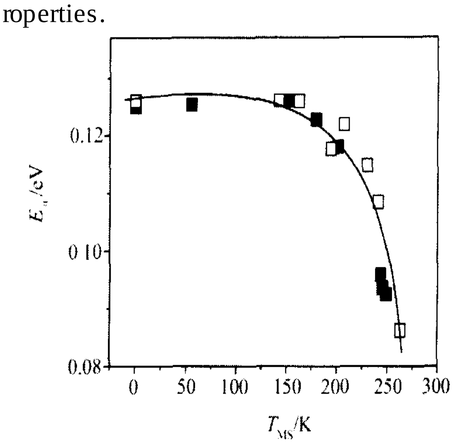

Fig. 3 Correlation between E_a and T_{MS} of LCMO/STO (solid points) and LCMO/NGO (open points) films (The solid line is as a guide to the eyes only)

3 Conclusion

The resistivity ρ and metal-to-semiconductor transition temperature T_{MS} were studied as functions of thickness in LCMO/NGO and LCMO/STO films. Although lattice stresses in LCMO/NGO and LCMO/STO are substantially different as confirmed by XRD analyses, there is no direct correlation between structure and electronic transport in LCMO films, indicating the absence of strain effects on transport properties, for example, ρ, T_{MS} and activation energy E_a.

References:

[1] Fontcuberta J, Martinez B, Seffar A, et al. Colossal

magnetoresistance of ferromagnetic manganite: structural tuning and mechanisms [J]. Phys. Rev. Lett., 1996, 76(7): 1122.
[2] Tokura Y, Kuwahara H, Moritomo Y, et al. Supercurrent noise in quantum point contacts [J]. Phys. Rev. Lett., 1996, 76(20): 3814.
[3] Blasco J, Garcia J, Teresa J M de, et al. A systematic study of structural, magnetic and electrical properties of $(La_{1-x}Tb_x)_{2/3}Ca_{1/3}MnO_3$ perovskites [J]. J. Phys.: Condens. Matter, 1996, 8(40): 7427.
[4] Kamegashira N, Nakano H, Chen G, et al. Phase behavior of rare earth manganite [J]. J. Rare Earths, 2004, 22(5): 582.
[5] Cui M S, Li M L, Zhang S L, et al. Preparation and physicochemical characterization of $La_{1-x}Ce_xCoO_3$ perovskite catalyst and its methane catalytic combustion [J]. J. Rare Earths, 2004, 22(5): 623.
[6] Wang H S, Li Qi, Liu Kai, et al. Low-field magnetoresistance anisotropy in ultrathin $Pr_{0.67}Sr_{0.33}MnO_3$ films grown on different substrates [J]. Appl. Phys. Lett., 1999, 74(15): 2212.
[7] Zeng X T, Wong H K. Anisotropic transport properties of single-crystal (La, Ca) MnO thin films [J]. Appl. Phys. Lett., 1998, 72(6): 740.
[8] Park J H, Vescovo E, Kim H J, et al. Magnetic properties at surface boundary of a half-metallic ferromagnet $La_{0.7}Sr_{0.3}MnO_3$ [J]. Phys. Rev. Lett., 1998, 81(9): 1953.
[9] Jin S, Tiefel T H, McCromark M, et al. Thickness dependence of magnetoresistance in La-Ca-Mn-O epitaxial films [J]. Appl. Phys. Lett., 1995, 67(4): 557.
[10] Sun J Z, Abraham D W, Rao R A, et al. Thickness-dependent magnetotransport in ultrathin manganite films [J]. Appl. Phys. Lett., 1999, 74(20): 3017.
[11] Zeng X T, Wong H K. Epitaxial growth of single crystal (La, Ca) MnO_3 thin films [J]. Appl. Phys. Lett., 1995, 66(24): 3371.
[12] Zhao K, Zhou L Z, Leung C H, et al. Epitaxial growth of oxide films (La-Ca-Mn-O and Y-Ba-Cu-O) by the facing-target sputtering technique [J]. J. Cryst. Growth, 2002, 237 - 239(Part1): 608.
[13] Zhao K, Wong H K. Epitaxial growth of platinum thin films on various substrates by facing-target sputtering technique [J]. J. Cryst. Growth, 2003, 256(3 - 4): 283.

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Preparation and Compressive Stress Effect of Polymer Matrix RE-Fe Giant Magnetostrictive Composite

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Abstract: Polymer matrix RE-Fe giant magnetostrictive composite (GMPC) was prepared using bonding and magnetic field forming technique, and magnetostriction of samples was measured for different compressive stress. The experimental results show that there is certain compressive effect in GMPC. And the influence of compressive stress on magnetostriction of sample was investigated. It offers essential reference for application and device design of GMPC.

Key words: magnetostriction; polymer matrix; composites; GMPC; compressive stress effect; rare earths

(See J. Chin. RE. Soc. (in Chin.), 2005, 23(6): 727 for full text)

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Zhao Kun *, Yeung Chunfai, Wong Hongkuen

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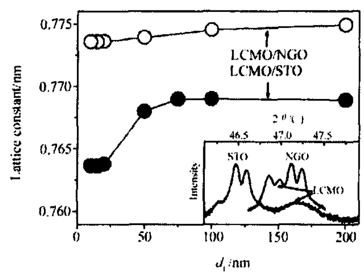
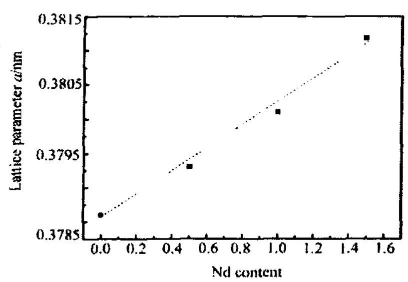


Out-of-plane lattice constants of LCMO/STO and LCMO/NGO films as functions of film thickness (The solid lines are drawn as a guide to the eyes only. The inset is the XRD patterns of LCMO (200 nm)/STO and LCMO (200 nm)/NGO.)

724 In-Situ High Temperature X-Ray Diffraction Study of Structure and Phase Transformation of Nd-FePt Alloys

Cheng Gang *, Gu Zhengfei, Zhou Huaiying, Wang Zhongmin, Zou Ruiping, Yuan Songliu

J. Rare Earths, 2005, 23: 724～726

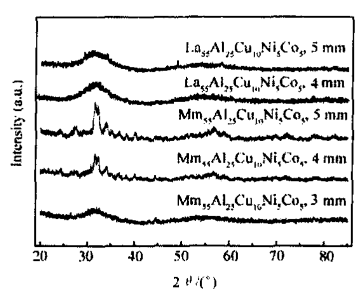


Lattice parameter of FCC for $Nd_xFe_{60.5-x}Pt_{39.5}$ alloys vs. Nd content

727 Preparation and Mechanical Properties of Misch Metal Based Bulk Metallic Glasses

Wu Xiaofeng *, Qiu Keqiang, Meng Likai, Zhao Wei, Suo Zhongyuan

J. Rare Earths, 2005, 23: 727～731

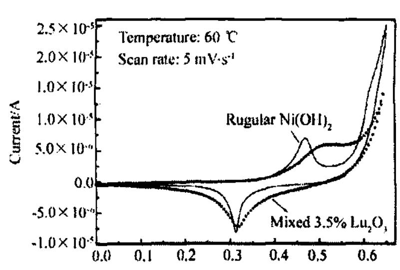


XRD patterns taken from the cross-section of as-cast rods with different diameters for $La_{55}Al_{25}Cu_{10}Ni_5Co_5$ and $Mm_{55}Al_{25}Cu_{10}Ni_5Co_5$ alloys

732 Effect of Lu_2O_3 on Charge/discharge Performances of Spherical Nickel Hydroxide at High Temperature

Ren Junxia, Wang Xiaojian, Li Yuzhan, Gao Xueping, Yan Jie *

J. Rare Earths, 2005, 23: 732～736



Cyclic voltammetric of regular Ni $(OH)_2$ and that mixed with 3.5% Lu_2O_3