Journal of Magnetics 6(1), 1-4 (2001)

Sol-Gel Synthesis and Transport Properties of $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ Granular Thin Films

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(Received 15 September 2000)

We have used acetic acid, ethanol and distilled water as a solvent to synthesize $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ (LSMFO) precursor. Crack-free LSMFO granular polycrystalline thin films have been deposited on thermally oxidized silicon substrates by spin coating. The dependence of crystallization, surface morphology, magnetic and transport properties on annealing temperature was investigated. With increasing annealing temperature, the metal-semiconductor (insulator) transition temperature and the magnetic moment decrease while the resistivity increases. The lattice constants remain almost unchanged. For LSMFO thin films, spin-dependent interfacial tunneling and/or scattering magnetoresistance were observed. Our results indicate that the annealing temperature is very important in determining the intrinsic and extrinsic magnetotransport properties.

1. Introduction

The doped manganese perovskite $Ln_{1-x}A_xMnO_3$ (where Ln is a rare-earth ion and A is a divalent ion) has stimulated interest because of its huge negative magnetoresistance [1, 2]. Double exchange [3] interaction and Jahn-Teller distortions have been used to explain qualitatively the transport phenomena observed in these perovskite oxides. The magnetic and transport properties of these samples are determined by several factors, such as the percentage of divalent ions, the ionic radii of the metal ions, the method used in the preparation of the samples, etc. [4-6] In a similar way, the replacement of Mn ions by other transition metal ions in perovskites of composition $Ln_{1-x}A_xMn_{1-y}TR^{3+}{}_yO_3$ (TR=transition metal), which show ferromagnetism and colossal magnetoresistance (CMR) at $y=0$, gives rise also to changes in the Mn^{3+}/Mn^{4+} proportion. This alters the magnetic coupling between these ions, which is reflected in a gradual weakening of the ferromagnetism as the doping level of the TR ion increases, with important modifications in the magnetic and transport properties [7]. Up to date, some authors have investigated the Fe doping effects on the structural, transport and magnetic properties of $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ [8, 9], $La_{1-x}Pb_xMn_{1-y}Fe_yO_3$ [10] and $La_{1-x}Sr_xMn_{1-y}Fe_yO_3$ [11, 12] bulk samples and found that the dopant Fe causes no structure change, but suppresses ferromagnetism and modifies magnetoresistance. As we know, there are some differences between bulk samples and thin films, such as crystal growth, microstructure etc. However, the thin film properties of Fe doped manganite has not been reported in a systematic study.

We thus report structural, magnetic, and transport properties of $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ (LSMFO) thin films, which have been prepared by a novel water-based sol-gel process. This method should be attractive since precise composition control, low-temperature synthesis, and high homogeneity are easily achieved. We have focused our effort on the preparation of thin films with a small amount of Mn replaced by Fe ions.

2. Experiments

$La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ thin films were prepared by spin-coating on Si(100) substrates with thermally oxidized to 2000 Å of SiO_2 a precursor prepared by water-based sol-gel processing. To fabricate the LSMFO precursor, we dissolved $La(CH_3COOH)_3 \cdot xH_2O$, $Sr(CH_3COO)_2$, $Mn(CH_3COOH)_3 \cdot 4H_2O$ and Fe metal (dissolved in HNO_3) in a mixed solvent (acetic acid : ethanol : distilled water = 1 : 1 : 0.5) with an appropriate molar ratio. All reactions were carried out under dry nitrogen in a glove box. Lanthanum and strontium acetates were placed in a 3-neck flask, fitted with a reflux condenser, and boiled at 110 °C for 1 hr. After cooling to room temperature, an appropriate amount of manganese acetate and dissolved iron metal was added, and the solution was refluxed for 3 h at 80 °C and then cooled. The dissolved reactant species were partially hydrolyzed with an added mixture of distilled H_2O and anhydrous ethanol. The molar ratio of H_2O to the calculated LSMFO content was 2 : 1. Then, the precursor was aged at room

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temperature for 48 hr before spin coating. Precursor solutions were generally prepared at a concentration of 0.2 M and diluted with a mixed solvent when necessary. After drying overnight, the xerogel was annealed at 800 °C in O_2 for 3 hr. Thermogravimetric (TG) and differential thermal analysis (DTA) were conducted on the powdered xerogel up to 800 °C at a heating rate of 5 °C/min.

Prior to spin coating, the substrates were cleaned with acetone, methanol, and distilled H_2O. LSMFO films were deposited by spin-coating at 4000 rpm for 30 s and films were pyrolized on a hot plate at 80 °C, 200 °C, and 300 °C, respectively, for 3 min between each coating. The LSMFO-coated films were placed in on alumina boat and annealed in O_2 at temperatures in the range of 500~850 °C. Crystallographic structures were examined using a thin-film X-ray diffractometer with CuKα radiation. The surface morphology was observed by using a tapping mode atomic-force microscope (TM-AFM). Magnetic property measurements were carried out with a vibrating sample magnetometer (VSM) in fields up to 1.0 Tesla at room temperature. High-field magnetotransport properties were measured from 77 K to 310 K in fields up to 1.0 Tesla using a standard four-probe technique. In the transport -property measurements, the field was applied parallel to the film surface.

3. Results and Discussion

The thermal decomposition and transformation characteristic of the gel system with temperature were studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The thermolysis behavior of LSMFO gel containing Fe that had been pre-dried at 120 °C is shown in Fig. 1. The weight loss of the bulk gels obtained from the precursor solutions takes place in two distinct steps defined by two temperature intervals. The first step of weight loss is between 40 and 290 °C, and the major weight loss step between 150~290 °C, minor loss is 600 °C and weight loss was completed about 600 °C. It can be seen that the gel exhibited approximately 53 % weight loss in the temperature range 100 °C to 600 °C due to the elimination of adsorbed water and solvents, and the decomposition of organic by-products. The DTA curves show a series of exothermic peaks. The peaks between 200 °C and 400 °C are associated with the weight losses noted above. For all systems, an exothermic peak is observed at ~290 °C, which has been associated with decomposition of organics and crystallization of manganese perovskite.

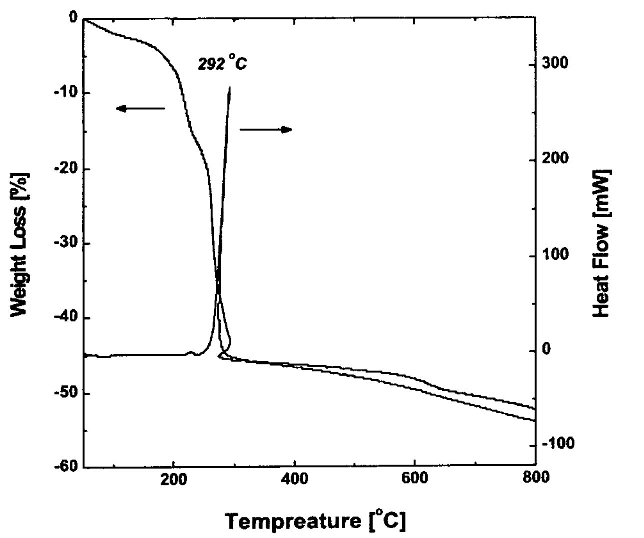

Fig. 1. TGA-DTA curves for $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ xerogel.

The x-ray diffraction (XRD) spectra of thin films after annealing at increasing temperatures are shown in Fig. 2. Pure perovskite peaks of LSMFO begin to appear in the sample annealed at 300 °C and the phase is fully developed at temperatures above 500 °C. No peaks other than those of the cubic perovskite phase were observed, which indicates the highly homogeneous nature of the developed phase. The XRD spectra were indexed by assuming a pseudocubic structure. The lattice constants were found to be 3.8747 and 3.8724 Å for $x = 0.0$ and $x = 0.01$, respectively. Studies by Ajan *et al.* [11] showed that the lattice parameter of bulk $La_{0.8}Sr_{0.2}Mn_{1-x}Fe_xO_3$ is nearly independent of x, 3.8790 Å for $x = 0.0$ and 3.8811 Å for $x = 0.1$. This indicates that doping with Fe has hardly any influence on lattice parameter. This could be because of the identical ionic size of Fe^{3+} and Mn^{3+} [13]. These results imply that a homogeneous thin film of manganite was synthesized at temperatures lower than that required by conventional ceramic solid-state synthesis.

Atomic force microscopic images of LSMFO thin films annealed between 500 and 800 °C are displayed in Fig. 3. The LSMO thin films were composed of uniformly distrib-

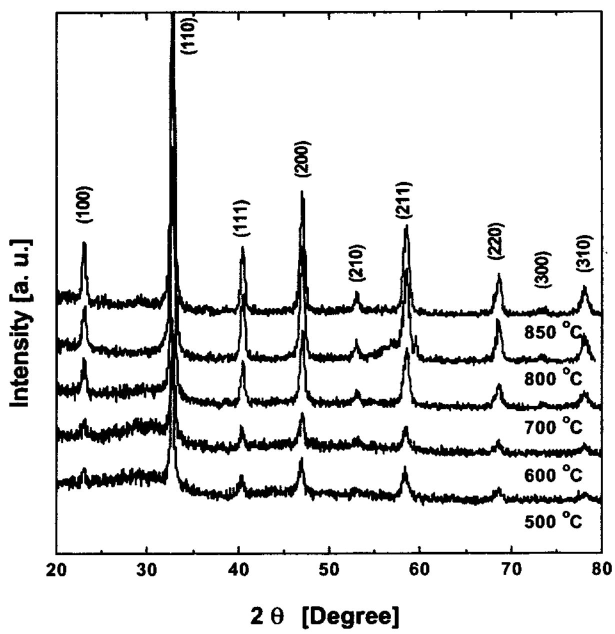

Fig. 2. Thin film XRD normal scans of $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ thin films deposited on SiO_2/Si(100) substrate with annealing temperature.

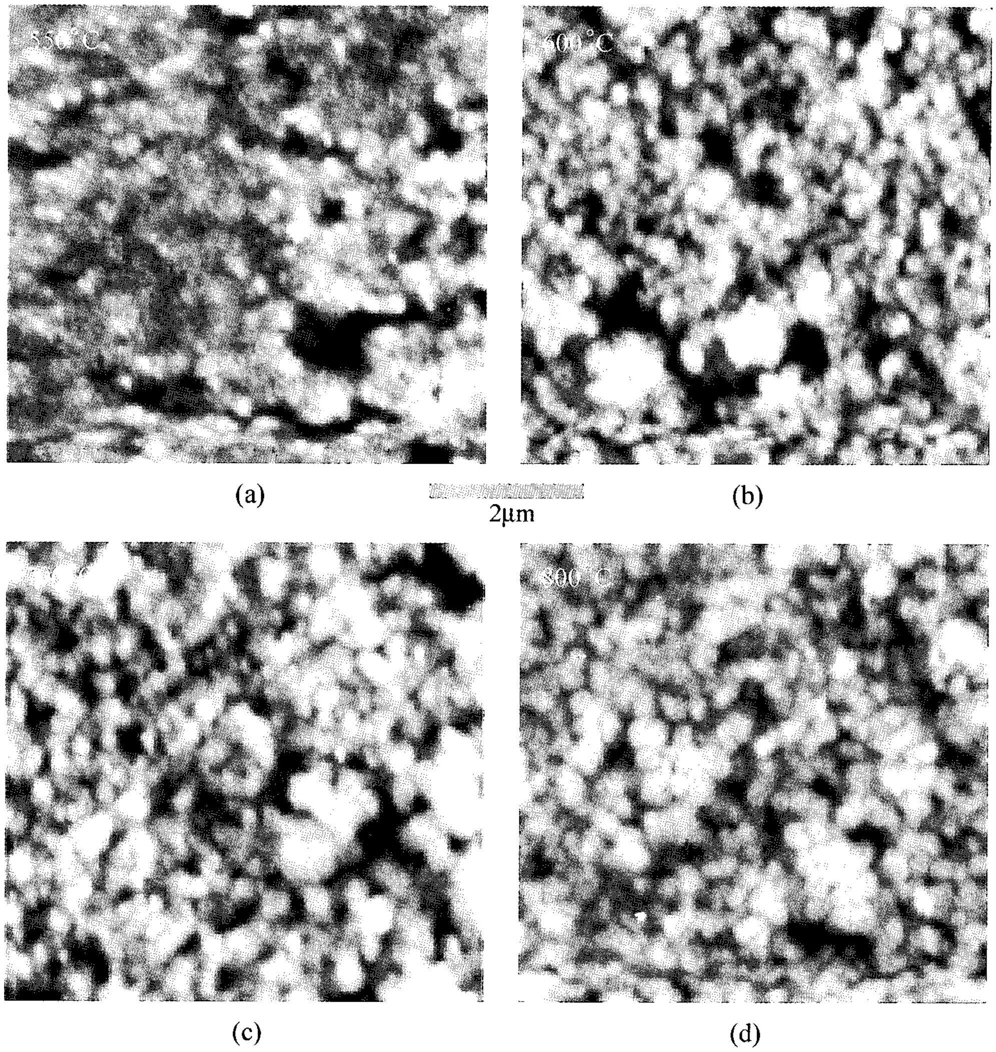

Fig. 3. AFM photographs of $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ thin film deposited on SiO_2/Si(100) substrate for different annealing temperatures; (a) 500 °C (b) 600 °C (c) 700 °C (d) 800 °C.

uted grains, and the grains grew with increasing annealing temperature. The abnormally grown grains observed in LSMFO thin film annealed at 500 °C may be due to the lower annealing temperature. The surface roughness was ~135 Å in the film annealed at 500 °C and 117 Å in the film annealed at 800 °C. The maximum peak to peak and valley-to-valley were 950 Å and 960 Å, respectively.

To explore the effect of the annealing temperature on the magnetic properties in detail, we studied the magnetic hysteresis loops of $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3/SiO_2$/Si(100) thin films as a function of annealing temperature. Gutierrez *et al.* [10] already reported some of the magnetic properties of the Fe-doped manganese composition. From these magnetic measurements it is inferred that there is a transition from ferro- to antiferromagnetic behavior as the Fe content in the bulk sample increases. The sample with $x = 0.01$ Fe doping content is still ferromagnetic. Notably, both coercivity (H_c) and magnetization (M) are strongly dependent on annealing temperature.

The zero-field temperature dependence of normalized [R(T)/R(300 K)] resistance for the LSMFO thin films with different annealing temperature is shown in Fig. 4. All samples show a metal-semiconductor (insulator) transition temperature (T_{MS}) and T_{MS} is much lower than the Curie temperature (T_C). T_{MS} shifts to lower temperature with increasing annealing temperature (increasing grain size). At low temperature, for all the samples, the resistance curve tends to flatten. The transition temperature is found to be strongly dependent on the annealing temperature. Zhang *et al.* [14] suggested that the broad resistance peak results from a spin-dependent interfacial tunneling and scattering, which stems from the difference in magnetic state between the grain boundary and the grain. For 850 °C annealed thin films, two resistance transition peaks were observed. It was suggested that the peak at lower temperature arises from spin dependent interfacial tunneling and scattering, and the other peak at higher temperature is related to the usual ferromagnetic transition due to the double exchange interaction of Mn^{3+}-O-Mn^{4+}.

As an example, the magnetoresistance data at T=77 K for

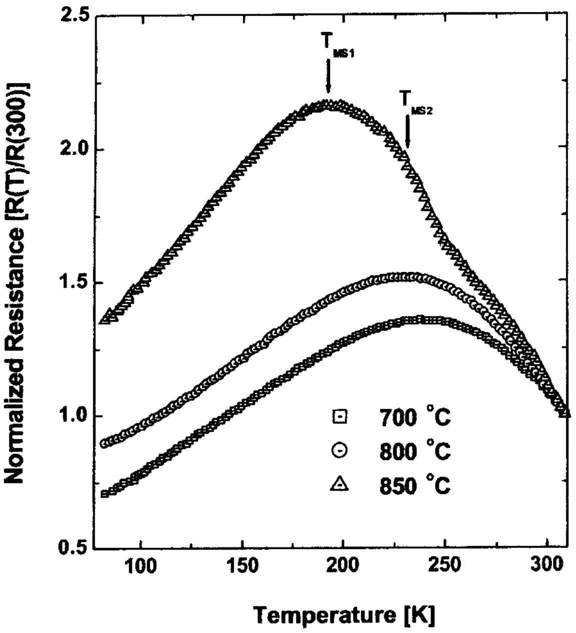

Fig. 4. Temperature dependence of normalized resistance of $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ thin films deposited on SiO_2/Si(100) substrate at various annealing temperature.

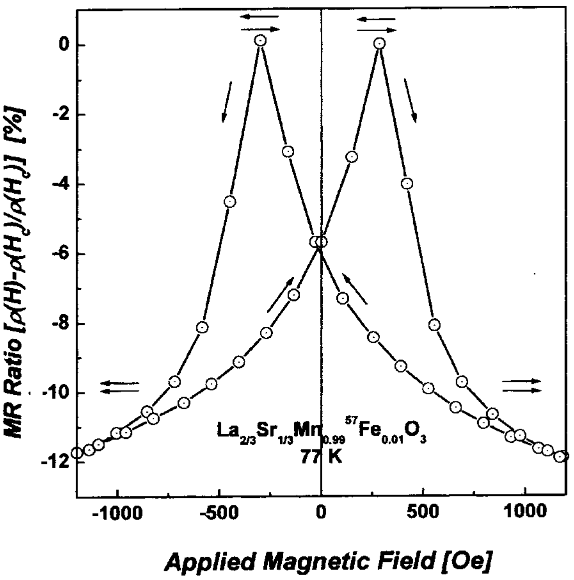

Fig. 5. Normalized magnetoresistance [R(H)-R(max)/R(max)] ratio at T=77 K of $La_{2/3}Sr_{1/3}Mn_{0.99}{}^{57}Fe_{0.01}O_3$ thin film deposited on SiO_2/Si(100) substrate annealed at 800 °C in O_2 for 3 hr.

the thin film annealed at 800 °C are presented in Fig. 5. The nonlinear [R(H)-R(max)/R(max)] response is very similar to that for polycrystalline sample where spin-dependent tunneling and/or spin-dependent scattering are responsible for the nonlinearity [15]. These results provide evidence that the underlying mechanism responsible for the MR effect may be a spin-dependent sequence like spin-dependent tunneling and/or scattering.

In summary, LSMFO granular polycrystalline thin films were successfully synthesized by a water-based sol-gel process. This sol-gel method has potential advantages over the ceramic route, not only for achieving homogeneous mixing of components on the atomic scale easily, but also for controlling the microstructure. We found that the lattice constant of LSMFO does not change with annealing temperature. The metal-semiconductor transition temperature was found to decrease with increasing annealing temperature. The annealing temperature can govern the microstructure, surface morphology, and magnetic properties. Our results also indicate that the annealing temperature is very important in determining the intrinsic and extrinsic magnetotransport properties.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (97-0702-0401-5) and by the Brain Korea 21 Program.

References

[1] P. V. Vanitha, R. S. Singh, S. Natarajan, and C. N. R. Rao, J. Solid State Chem., **137**, 365 (1998).
[2] G. Ji, X. J. Fan, J. H. Zhang, C. S. Xiong, and X.-G. Li, J. Appl. Phys., **31**, 3036 (1998).
[3] C. Zener, Phys. Rev., **82**, 403 (1951).
[4] A. Maignan, F. Damay, C. Martin, and B. Raveau, Mater. Res. Bull., **32**, 965 (1997).
[5] L. Righi, P. Gorria, M. Insausti, J. Gutierrez, and J. M. Barandiaran, J. Appl. Phys., **81**, 5767 (1997).
[6] J. Gutierrez, J. M. Barandiaran, M. Insausti, L. Lezama, A. Pena, J. J. Blanco, and T. Rojo, J. Appl. Phys., **83**, 7171 (1998).
[7] M. Pissas, G. Kallias, E. Devlin, A. Simopoulos, and D. Niarchos, J. Appl. Phys. Rev., **81**, 5770 (1997).
[8] S. B. Ogale, R. Shreekala, Ravi Bathe, S. K. Date, and S. I. Patil, B. Hannoyer, F. Petit, and G. Marest, Phys. Rev., **57**(13), 7841 (1998).
[9] B. Hannoyer, G. Marest, J. M. Greneche, Ravi Bathe, S. I. Patil, and S. B. Ogale, Phys. Rev., **B61**(14), 9613 (2000).
[10] J. Gutierrez, A, Pena, J. M. Barandiaran, J. L. Pizarro, T. Hernandez, L. Lezama, M. Insausti, and T. Rojo, Phys. Rev., **B61**(13), 9028 (2000).
[11] A. Ajan, N. Venkataramani, S. Prasad, S. N. Shringi, A. K. Nigam, and R. Pinto, J. Appl. Phys., **83**(11), 7169 (1998).
[12] J. H. Zhang, X. J. Fan, C. S. Xiong, X.-G. Li, Solid State Comm., **115**, 531 (2000).
[13] R. D. Shannon, Acta Crystallogr., Sect., **A32**, 751 (1976).
[14] N. Zhang, W. P. Ding, W. Zhang, D. Y. Xing, Y. W. Du, Phys. Rev., **B56**, 8138 (1997).
[15] P. Raychaudhuri, K. Sheshadri, P. Taneja, S. Bandyopadhyay, P. Ayyub, A. K. Nigam, and R. Pinto, Phys. Rev., **B59**, 13919 (1999).