Journal of the Korean Ceramic Society
Vol. 43, No. 11, pp. 734~737, 2006.

Metal-to-Insulator Transitions in $La_{2/3}Sr_{1/3}MnO_3/LaMnO_3$ (LSMO/LMO) Superlattices

Sangwoo Ryu and Hyun M. Jang†

Department of Materials Science and Engineering, and Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea
(Received October 19, 2006; Accepted October 27, 2006)

ABSTRACT

A series of manganite-based superlattices composed of half-metallic $La_{2/3}Sr_{1/3}MnO_3$ and insulating $LaMnO_3$ stacking layers were fabricated by employing pulsed laser deposition method. The dc resistivity increased drastically by simply reducing the stacking periodicity. The resistivity enhancement was accompanied by a gradual decrease in the temperature (T_c) of the Metal-to-Insulator Transition (MIT). This observation was interpreted as a small decrease in the effective metallic fraction near the percolation threshold. For the stacking periodicity less than a certain critical value, there appeared another transition to an insulating state at temperatures far below T_c. This low-temperature transition seems to be closely related to the AF-type (C-type) orbital ordering in newly formed insulating domains.

***Key words*: Superlattice, Pulsed laser deposition, Metal-to-insulator transition, Stacking, Percolation**

1. Introduction

Thin films of alkaline-earth (AE)-cation-modified lanthanum maganites [$La_{1-x}AE_xMnO_3$] that exhibit 'colossal' magnetoresistivity (CMR) provide us numerous interesting potential applications.[1-5] These perovskites with an intermediate doping level of x exhibit a paramagnetic-to-ferromagnetic transition at T_c with a concomitant transition to a half-metallic state at a temperature very close to T_c.[6] Although the theoretical understanding of the CMR phenomena is still incomplete, double exchange,[7] electron-phonon coupling,[8] and orbital ordering effects[9] are commonly regarded as important ingredients to the manifestation of these peculiar effects.

Parallel to the studies based on these nondisordered atomistic models, several interesting studies have also appeared, correlating the extraordinary transport properties with an inhomogeneous local structure. Using the technique of scanning tunneling spectroscopy, Fäth and coworkers[10] made the first direct observation of an electronic phase separation into insulating and metallic ferromagnetic (FM) regions in $La_{1-x}Ca_xMnO_3$ (LCMO with $x \approx 0.3$) at near T_c. They further observed that the fraction of these metallic FM domains increased with the applied magnetic field, suggesting the formation of a magnetic field-induced percolative network of the metallic FM domains. The theoretical studies based on the Monte Carlo simulation using the random-field Ising model strongly supported this electronic phase-separated percolation scenario[11,12] and successively explained the complicated behavior of ρ_{dc} as a function of temperature.[12]

Using ^{55}Mn NMR spectroscopy, Papavassiliou and coworkers[13] further obtained an interesting evidence of the bifurcation of FM metallic phase into FM metallic and FM insulating regions in polycrystalline LCMO samples near the antiferro(AF)-type orbital ordering temperature, Too,[14] which is far below their T_c. Since this low-temperature bifurcation seems to be closely related to the AF-type (i.e., C-type) orbital ordering,[13] the formation of insulating FM domains at Too would be enhanced in a superlattice composed of alternating FM CMR (e.g., LSMO or LCMO) layers and insulating layers that exhibit the AF-type orbital ordering (e.g., LMO at $x=0$). Because of the interfacial effects, this would be especially pronounced in a superlattice having the stacking periodicity shorter than a certain critical value. Considering a percolative nature of the metallic FM domains,[10-12] we further propose that there exists a certain critical periodicity below which the Metal-to-Insulator Transition (MIT) at T_c effectively vanishes in a superlattice composed of alternating metallic FM and insulating LMO layers.

In view of the above discussion, the main purpose of the present study is to critically examine the following two propositions; (i) the disappearance of the MIT below the percolation threshold, and (ii) the formation of insulating FM domains at a low temperature in a superlattice with its stacking periodicity shorter than a certain critical value. For this purpose, we have fabricated a series of manganite-

†Corresponding author : Hyun M. Jang
E-mail : hmjang@postech.ac.kr
Tel : +82-54-279-2138 Fax : +82-54-279-2399

based superlattices composed of LSMO ($La_{2/3}Sr_{1/3}MnO_3$) and LMO stacking layers by varying the stacking periodicity and examined their structural and transport properties.

2. Experimental Procedure

$La_{1-x}Sr_xMnO_3$ (x=0 and 1/3) single-layer films (100 nm thick) and superlattices with alternating stacking layers composed of x=1/3 and x=0 were fabricated by employing pulsed laser deposition method. KrF excimer laser (λ=248 nm) pulses were focused on each stoichiometric target at an energy density of 2.5 J/cm^2. The deposition was carried out on a single-crystal $LaAlO_3$ substrate at 700°C while keeping 200 mTorr oxygen pressure. The layer-by-layer growth of LSMO and LMO was contolled by monitoring the Reflection High-Energy Electron Diffraction (RHEED) patterns. Six superlattices with different stacking periodicitis but with essentially the same overall thickness were fabricated : $[125/125]_1$, $[63/63]_2$, $[31/31]_4$, $[12/12]_{10}$, $[5/5]_{25}$, and $[2/2]_{62}$. In a notation of $[M/N]_n$, M and N respectively indicate the number of LSMO and LMO atomic layers whereas n denotes the number of repeated units in the LSMO/LMO stacking. X-Ray Diffraction (XRD) was carried out by a four-circle diffractometer with Cu Kα and synchrotron radiation source at Pohang Light Source (PLS). Magnetic transport properties were measured by employing the four-probe method at a magnetic field up to 7 Tesla applied along the film plane.

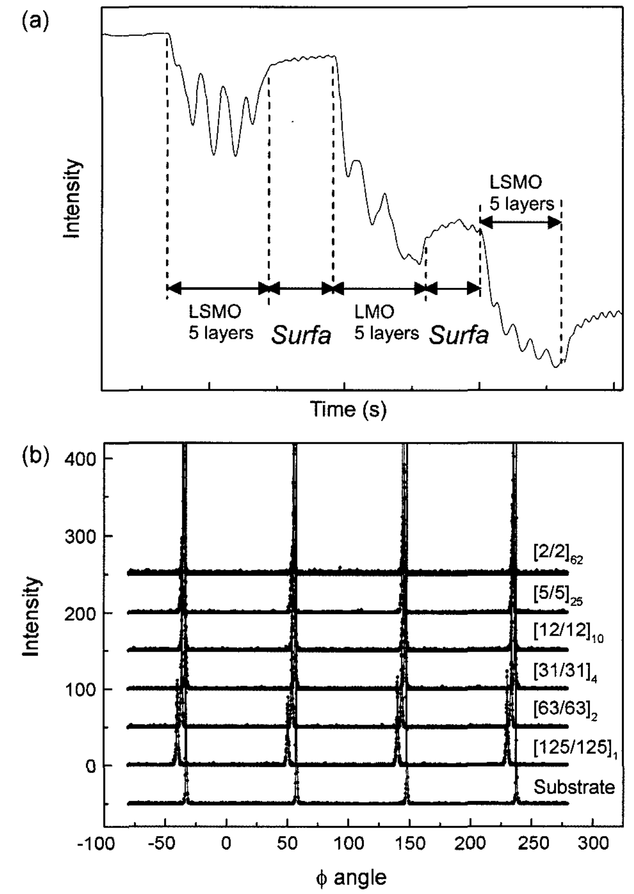

Fig. 1. (a) RHEED oscillation pattern obtained during the deposition of the $[5/5]_{25}$ superlattice, indicating a layer-by-layer growth of each constituent layer. Peaks and plateaus respectively correspond to the layer growth and the surface recovery and (b) XRD in-plane Phi scan around (011) plane of the LSMO layer, indicating an epitaxial growth of all six distinct superlattices.

3. Results and Discussion

Fig. 1(a) shows the RHEED oscillation pattern of the $[5/5]_{25}$ superlattice, demonstrating the layer-by-layer growth. The XRD phi scan data presented in Fig. 1(b) indicate an epitaxial growth of each constituent layer for a wide range of the stacking periodicity. In order to examine whether these superlattices had well-defined interfaces or not, we further carried out more detailed XRD experiments using the BL3C2 synchrotron beamline at PLS.

Fig. 2 compares the experimental XRD pattern of the $[12/12]_{10}$ superlattice with the calculated pattern based on the

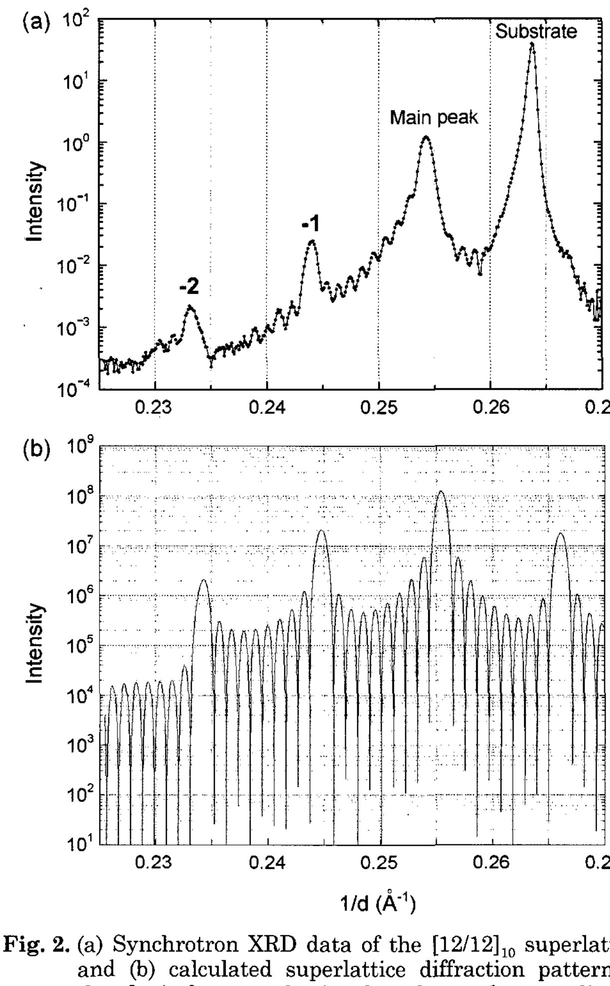

Fig. 2. (a) Synchrotron XRD data of the $[12/12]_{10}$ superlattice and (b) calculated superlattice diffraction pattern of the $[12/12]_{10}$ superlattice based on the one-dimensional step model.

one-dimensional step model.[15-17] In conventional θ-2θ scan with the scattering vector normal to the film plane ($\boldsymbol{k}=\boldsymbol{k}_f-\boldsymbol{k}_i$), both the main peak and the satellite peaks associated with (00l) planes of a superlattice structure are observed. The satellite peaks denoted as '−1' and '−2' in Fig. 2(a) come from the superlattice modulation of $[12/12]_{10}$ along the growth direction. Because of the broadness of the substrate peak, the satellite peaks with their 1/d (= | $\boldsymbol{k}$ |) values higher than the one corresponding to the substrate are not shown. The superlattice intensity $I(\boldsymbol{k})$ as a function of the scattering vector was theoretically estimated,[17] and the results for the $[12/12]_{10}$ are presented in Fig. 2(b). Comparing these two patterns, one can conclude that the compositional profile at the LSMO/LMO interface is abrupt with a well-defined structure and the c-axis lattice parameter is regularly modulated along the growth direction with $d_{LSMO}=3.83$ Å and $d_{LMO}=4.02$ Å.

Fig. 3 presents the temperature dependence of the electrical resistivity of six distinct superlattices under various magnetic fields. As shown in the figure, the dc resistivity changes drastically by simply varying the stacking periodicity. This resistivity enhancement is accompanied by a gradual decrease in the MIT temperature. The MIT characteristics finally disappear for the stacking periodicity shorter than a certain critical value (for $M=N<5$), and thus the $[2/2]_{62}$ superlattice is insulating for a wide range of temperature. In other words, as the half-metallic LSMO layer is confined along the growth direction, the LSMO/LMO superlattice eventually becomes insulating with a concomitant disappearance of the MIT characteristics.

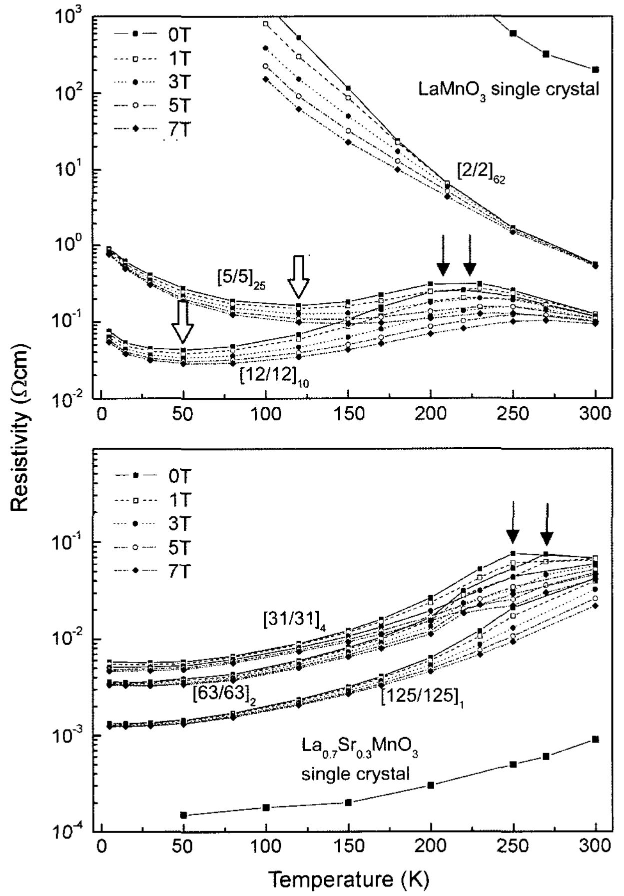

Fig. 3. Temperature dependence of the dc electrical resistivity of six different superlattices under various magnetic fields. The filled arrows indicate the metal-to-insulator transition at T_c.

The pronounced stacking periodicity-dependent resistivity characteristics are very similar to the MC simulation results of the metallic fraction (p)-dependent ρ_{dc} near the percolative regime ($0.4<p<0.5$).[12] As the stacking periodicity decreases, the resistivity of the half-metallic LSMO layer is increasingly affected by the adjacent insulating LMO layers because of the increase in the number of LSMO/LMO interfaces. Thus, the effective metallic fraction (p) is expected to be slightly decreased with decreasing periodicity (M or N) in $[M/N]_n$-type superlattices. According to the MC simulation, the dc resistivity increases drastically with a small decrease of p near the percolation threshold.[12] This suggests that the percolation threshold exists in a superlattice with N (periodicity) between 2 and 5. The observed disappearance of the MIT for N (=M) less than 5 also seems to reflect that for N less than the critical value, the metallic connectivity in an insulating matrix[12] is strongly inhibited by the confinement along the growth direction.

Another prominent feature of the result shown in Fig. 3 is that there appears an interesting low-temperature metal-to-insulator transition in a superlattice with N between 2 and 31, as marked with open arrows. This low-temperature transition corresponds to the bifurcation of FM metallic phase into FM metallic and FM insulating regions.[13] As discussed previously, the formation of the FM insulating domains is closely related to the AF-type orbital ordering in newly formed insulating domains, which is enhanced by the decrease of x in $La_{1-x}AE_xMnO_3$.[14] Because of the interfacial

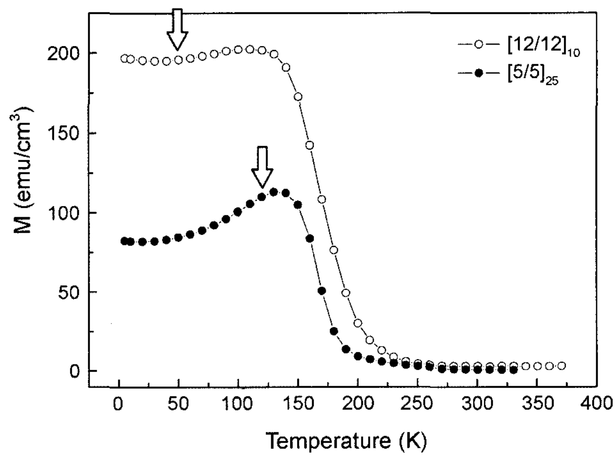

Fig. 4. Magnetization-temperature (M-T) curves of the two superlattices that exhibit a low-temperature transition to an insulating state. The open arrows, as obtained from Fig. 3, correspond to the onset of transformation to this low-temperature insulating phase.

effect from the insulating LMO layer having the AF-type orbital ordering, the formation of insulating FM domains at Too is expedited in a LSMO/LMO superlattice with the stacking periodicity shorter than a critical value. In the present case, this critical *N* value seems to be less than 31 but is more than 12.

As presented in Fig. 4, the temperature-dependent magnetization of the two superlattices does not change abruptly at this 2^{nd} MIT temperature. This suggests that either the newly formed insulating domains are still ferromagnetic or the metallic FM domains do not completely transform to insulating domains even below this transition temperature. According to the previous NMR study,[13)] both possibilities are valid, i.e., a coexistence of FM metallic and insulating regions. However, the resistivity data (Fig. 3) indicate that the metallic connectivity is effectively destroyed below this 2^{nd} MIT temperature.

4. Summary

A series of manganite-based superlattices composed of half-metallic $La_{2/3}Sr_{1/3}MnO_3$ and insulating $LaMnO_3$ stacking layers were fabricated to critically examine the following two propositions : (i) the disappearance of the MIT below the percolation threshold, and (ii) the formation of insulating FM domains at a low temperature in a superlattice with its stacking periodicity shorter than a certain critical value. The dc resistivity increased drastically by simply reducing the stacking periodicity. The resistivity enhancement was accompanied by a gradual decrease in the temperature (T_c) of the Metal-to-Insulator Transition (MIT). This observation was interpreted as a small decrease in the effective metallic fraction near the percolation threshold. For the stacking periodicity less than a certain critical value, there appeared another transition to an insulating state at temperatures far below T_c. This low-temperature transition seems to be closely related to the AF-type (C-type) orbital ordering in newly formed insulating domains.

REFERENCES

1. Y. Lu, X. W. Li, G. Q. Gong, G. Xiao, A. Gupta, P. Lecoeur, J. Z. Sun, Y. Y. Wnag, and V. P. Dravid, "Large Magneto-tunneling Effect at Low Magnetic Fields in Micrometer-scale Epitaxial $La_{0.67}Sr_{0.33}MnO_3$ Tunnel Junctions," *Phys. Rev. B*, **54** R8357 (1996).
2. N. D. Mathur, G. Burnell, S. P. Isaac, T. J. Jackson, B.-S. Teo, J. L. MacManus-Driscoll, L. F. Cohen, J. E. Evetts, and M. G. Blamire, "Large Low-Field Magnetoresistance in $La_{0.7}Ca_{0.3}MnO_3$ Induced by Artificial Grain Boundaries," *Nature (London)*, **387** 266 (1997).
3. J.-M. Liu, J. Li, Q. Huang, L. P. You, S. J. Wang, C. K. Ong, Z. C. Wu, Z. G. Liu, and 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** 2286 (2000).
4. H. Yamada, M. Kawasaki, Y. Ogawa, and Y. Tokura, "Perovskite Oxide Tricolor Superlattices with Artificially Broken Inversion Symmetry by Interface Effects," *Appl. Phys. Lett.*, **81** 4793 (2002).
5. J. Jiang, L. L. Henry, K. I. Gnanasekar, C. Chen, and E. I. Meletis, "Self-Assembly of Highly Epitaxial (La,Sr)MnO_3 Nanorods on (001) $LaAlO_3$," *Nano Lett.*, **4** 741 (2004).
6. M. Imada, A. Fujimori, and Y. Tokura, "Metal-Insulator Transitions," *Rev. Mod. Phys.*, **70** 1039 (1998).
7. C. Zener, "Interaction between the d-Shells in the Transition Metals. II. Ferromagnetic Compounds of Manganese with Perovskite Structure," *Phys. Rev.*, **82** 403 (1951).
8. A. J. Millis, "Lattice Effects in Magnetoresistive Manganese Perovskites," *Nature*, **392** 147 (1998).
9. R. Maezono, S. Ishihara, and N. Nagaosa, "Phase Diagram of Manganese Oxides," *Phys. Rev. B*, **58** 11583 (1998).
10. M. Fäth, S. Freisem, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, "Spatially Inhomogeneous Metal-Insulator Transition in Doped Manganites," *Science*, **285** 1540 (1999).
11. A. Moreo, M. Mayr, A. Feiguin, S. Yunoki, and E. Dagotto, "Giant Cluster Coexistence in Doped Manganites and Other Compounds," *Phys. Rev. Lett.*, **84** 5568 (2000).
12. M. Mayr, A. Moreo, J. A. Vergés, J. Arispe, A. Feiguin, and E. Dagotto, "Resistivity of Mixed-Phase Manganites," *Phys. Rev. Lett.*, **86** 135 (2001).
13. G. Papavassiliou, M. Fardis, M. Belesi, T. G. Maris, G. Kallias, M. Pissas, and D. Niarchos, "^{55}Mn NMR Investigation of Electronic Phase Separation in $La_{1-x}Ca_xMnO_3$ for $0.2 \le x \le 0.5$," *Phys. Rev. Lett.*, **84** 761 (2000).
14. Y. Endoh, K. Hirota, S. Ishihara, S. Okamoto, Y. Murakami, A. Nishizawa, T. Fukuda, H. Kimura, H. Nojiri, K. Kaneko, and S. Maekawa, "Transition between Two Ferromagnetic States Driven by Orbital Ordering in $La_{0.88}Sr_{0.12}MnO_3$," *Phys. Rev. Lett.*, **82** 4328 (1999).
15. T. Shinjo and T. Takada , Metallic Superlattices; Elsevier, Amsterdam, 1987.
16. T. Hahn, International Tables for Crystallography; Kluwer Academic Publishers, Boston, 1995.
17. M. E. Vickers, M. J. Kappers, T. M. Smeeton, E. J. Thrush, J. S. Barnard, and C. J. Humphreys, "Determination of the Indium Content and Layer Thicknesses in InGaN/GaN Quantum Wells by X-Ray Scattering," *J. Appl. Phys.*, **94** 1565 (2003).