Enhanced Magneto电阻 of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ Thin Films by Reaction with Substrates

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(Received Oct. 6, 2000; Accepted Jan. 24, 2001)

Magnetic and magnetotransport properties of polycrystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) thin films annealed at high temperatures were investigated. The reaction of the LSMO thin films with YSZ substrates effectively induces enhancement of low-field MR up to 13.8% at 78 K for the film annealed at 1350°C. The results are consistently explained by the formation of potential barriers at grain boundaries by the annealing.

**Key words:** perovskite manganite, colossal magnetoresistance, polycrystalline $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, low-field magnetoresistance, spin-polarized intergranular tunneling, annealing

1. Introduction

The doped perovskite manganite $\text{La}_{1-x}\text{A}_x\text{Mn}_2\text{O}_4$ (A: Ca, Sr, Ba etc.) exhibits colossal magnetoresistance (CMR) near the Curie temperature $T_C$ owing to the double-exchange coupling between the localized moments of manganese and conduction electrons. This system has been expected for the application of high sensitive magnetic sensors. However, the magnetic fields of several tesla is necessary to show CMR. Therefore, enhancement of low-field magnetoresistance (MR) has been required for the application to high sensitive sensors. For this purpose, the use of tunnel type MR is effective for the enhancement of low-field MR, since the perovskite manganites have high spin polarization of conduction electrons. Recently, polycrystalline perovskite manganites have been studied considering the magnetotransport nature similar to the giant magnetoresistance (GMR) granular system. Hwang et al. interpreted that the sharp low-field MR of polycrystalline perovskite manganite is due to spin-polarized intergranular tunneling between adjacent grains. It has been also reported that this sharp low-field MR depends on the grain size in the manganite.

In this study, we employ another approach to achieve further enhancement of low-field MR. High temperature thermal treatment could control the reaction between LSMO and YSZ substrate, which produces some insulating phases at grain boundaries as reported elsewhere. The insulating phases may be effective barriers for the intergran spin-polarized tunneling. Indeed, large enhancement of low-field MR is demonstrated in this manner.

2. Experimental

Polycrystalline LSMO thin films were deposited on (100)-oriented YSZ substrates by rf sputtering at 700°C. The composition of sputtering target was $\text{La}_2\text{Sr}_2\text{Mn}_3\text{O}_{12.5}$ and the films were deposited under $\text{Ar}/\text{O}_2 = 2$ atmosphere at 1.7 Pa. The thickness of all-as-deposited films was about 2000 Å. After the deposition, each film was annealed at temperatures from 1050°C to 1350°C for 2 hours in O$_2$ atmosphere to produce insulating phases at grain boundaries. The composition of the films was confirmed to be $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{3-3x}\text{O}_7$ by ICP emission spectrometry. Crystal structures of all the films were characterized by x-ray diffraction (XRD). Observation of surface morphology of the films was performed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The zero field resistivity and the MR at 78 K were measured by a standard four-point method in the field in-plane and parallel to current direction. The MR ratio is defined as $\text{MR} = [(R_{\text{MR}} - R_{\text{bulk}})/R_{\text{bulk}}] \times 100$, where $R_{\text{MR}}$ is the resistance in zero field and $R_{\text{bulk}}$ is the resistance in a field of H. Magnetization measurements were also performed at temperatures from 5 K to 400 K using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and Discussion

Figures 1 show x-ray diffraction patterns of LSMO thin films on (100)-oriented YSZ substrate annealed at (a) 1050°C and (b) 1300°C. Only LSMO phase was found for the films.
annealed at temperatures from 1050°C to 1150°C. On the other hand, the other phases were detected for the films annealed above 1200°C as in Fig.1 (b). It was confirmed that the other phases were insulating La$_2$Zr$_2$O$_7$ (LZO) and Sr$_2$Zr$_2$O$_7$ (SZO) resulted from the progressive reaction of LSMO with YSZ substrate at high temperatures. The volume of the products is increased with increasing annealing temperature.

The film annealed at 1050°C possesses uniformly sized grains of ~100 nm, while large grains ~1 μm and smaller grains ~100 nm coexist in the film annealed above 1200°C. The large grains are deduced to be LZO and SZO based on XRD patterns. Figure 2 shows the SEM image of the surface morphology of the LSMO thin film annealed at 1300°C around the region with small grains, which is typical of the films annealed above 1200°C. It is plausible that the small grains with the size of about 100 nm is LSMO and the intergrain phase is the insulator in similar to the previously reported LCMO/STO and LSMO/CeO$_2$. Thus, the geometry in which LSMO is surrounded by the insulator could be realized, although direct information about identification of the phases is still lacking.

Next, we examine the correlation between the temperature dependence of resistivity $\rho$ and the formation of the insulator. Figure 3 shows the zero field $\rho$-$T$ curves of the

![Figure 3](image)

**Fig. 3** $\rho$-$T$ curves in zero field. Inset shows annealing temperature $T_a$ dependence of $T_p$. The vertical arrow indicates the shoulder.

![Figure 4](image)

**Fig. 4** Temperature dependent magnetizations normalized by the values at 5 K.

![Figure 5](image)

**Fig. 5** Low-field MR profiles and magnetization curves of LSMO thin films annealed at (a) 1050°C and (b) 1350°C.
films annealed at 1050°C and 1350°C. Inset shows the annealing temperature dependence of $T_p$, where $T_p$ is the temperature that the resistivity shows maximum in the $\rho$ - $T$ curves. The $\rho$ - $T$ curve of the film annealed at 1050°C shows maximum at 335 K accompanied with a shoulder around 250 K. On the other hand, the resistivity of the film annealed at 1350°C possesses only a maximum around 250 K. Recently, Gross et al. have precisely investigated the $\rho$ - $T$ curves of the film with bicrystal grain boundary junction [11]. They observed clear double maxima in the $\rho$ - $T$ curve of the film with grain boundaries in spite of a single maximum for the film with no junction. Thus, they attributed the additional maximum to the grain boundary. In this sense, it is most likely that the shoulder observed in the $\rho$ - $T$ curve of the film annealed at 1050°C is due to the grain boundaries. Further, when the film is annealed at higher temperatures, the contribution of the grain boundaries to the resistivity becomes dominant and the maximum in the $\rho$ - $T$ curve at 335 K is smeared out. Thus the decrease $T_p$ with the annealing temperature can be explained by the pronounced grain boundary resistivity. In addition to the decrease in $T_p$ due to grain boundary contribution, the temperature of the maximum at 335 K should intrinsically shift toward low temperatures with annealing temperature for the film annealed at 1050°C, since the Curie temperature is decreased in the film annealed at higher temperatures as shown in Fig. 4.

Figures 5 show the low-field MR profiles and the magnetization curves of the films annealed at (a) 1050°C and (b) 1350°C. The MR of the film annealed at 1050°C exhibits an abrupt drop in 50 Oe corresponding to rapid magnetization reversal shown in Fig. 5 (a). In contrast, the MR curve of the film annealed at 1350°C becomes somewhat gradual. This may be due to the change in magnetization process from domain wall movement to magnetization rotation with increasing annealing temperature. Noted that the MR is enhanced by a factor of 3 by annealing.

We measured high field MR of the films annealed at (a) 1050°C and (b) 1350°C as shown in Fig. 6 to get clear insight into the magnetotransport nature. Both the films show rapid increase in the MR in the low field region followed by the moderate one, although the magnitude is different. Taking into account that the rapid and moderate increases originate from the grain boundaries and the intrinsic double exchange coupling [11], respectively, it is obvious that the grain boundary contribution becomes significant with increasing annealing temperature. Further we plot the differential MR ($dMR/dH$) above 3 T and the low field MR obtained by extrapolation of the high field region between 0.5 T and 1 T as a function of temperature (Figs. 7). The $dMR/dH$ of the film annealed at 1350°C is larger than that of the film annealed at 1050°C, and also shows maximum around 250 K in contrast to the temperature independent behavior of the film annealed.
at 1050°C. If we consider that the $dMR/dH$ is associated with grain boundaries, this feature is in agreement with the results for the granular perovskite \(^{(3)}\) and the LSMO with artificial grain boundaries \(^{(12)-(14)}\). Therefore, we believe that the enhancement of magnetotransport is attributed to the formation of the potential barrier at grain boundaries by the reaction with YSZ substrate. Recent our study on the I-V characteristics also supports this picture \(^{(15)}\).

The enhancement of the low-field MR as a function of annealing temperature is clearly demonstrated in Fig. 8. Hence, the low-field MR* is tentatively defined to be \([R_{20C}[R_{20C} - R_{100C}] \times 100\), where \(R_{20C}\) denotes the field showing positive peak in the MR profiles. The MR* increases gradually up to 1250°C and changes the increment more steeply above 1250°C. The resistivity at 78 K also shows a sharp increase above the annealing temperature of 1250°C, suggesting the formation of insulating phases invoked for spin-polarized tunneling at grain boundaries. Consequently, the enhanced MR caused by the annealing becomes significant above 1250°C.

**4. Conclusion**

We presented another approach to achieve further enhancement of low-field MR. At the annealing temperatures above 1250°C, the potential barrier for the spin polarized tunneling is formed at grain boundaries by the reaction of LSMO grain with YSZ substrate, and consequently the low-field MR is increased. This picture consistently explains the magnetic and magnetotransport properties obtained in this study.

**Acknowledgments**  This work was supported in part by the SRC (Storage Research Consortium) and The Murata Science Foundation.

**References**

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