Effect of Fe doping on high field magnetoresistance and low field magnetoresistance at zero field in polycrystalline La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ (x=0–0.12) thin films

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Polycrystalline La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ thin films, with x=0–0.12, have been prepared on (001)-Si substrates using pulsed laser deposition. The films consist of fine grains with an average size of 60–80 nm. For those films, the metal–insulator transition temperature, $T_p$, is much lower than the Curie temperature, $T_C$. The high field magnetoresistance, HFMR, is nearly temperature independent for $x<0.08$, whereas the extrapolated low field magnetoresistance at zero field, LFMR*, decreases rapidly with increasing temperature. Moreover, Fe doping significantly decreases LFMR* and enhances HFMR at low temperatures. We propose that for the Fe-doped films, both the reduced spin polarization of conduction electrons and the increased spin-flip scattering are responsible for the decrease of LFMR*, while the weakened ferromagnetic spin interaction at the grain boundaries is responsible for the enhanced HFMR. © 2001 American Institute of Physics. [DOI: 10.1063/1.1358344]

Recently, extensive studies have been focused on the extrinsic magnetoresistance (EMR) in polycrystalline manganites due to its high sensitivity to a small magnetic field. On application of an external magnetic field, a sharp decrease in resistivity in the low field region and a slow linear decrease in resistivity in the high field region are shown in those polycrystalline samples. Accordingly, EMR can be separated into two parts, namely, the nonlinear low field magnetoresistance (LFMR), and the linear high field magnetoresistance (HFMR). The spin dependent tunneling (SPT) mechanism has been used to describe the LFMR. In those models, the LFMR is correlated to the relative orientation of the magnetizations of the neighboring grains. On the other hand, the HFMR is believed to be related to the disordered spins at the grain boundaries (GB) or the interface layers. Nevertheless, controversy remains. For example, Evetts et al. have proposed a mesoscopic magnetoresistance (MR) model and suggested that a rather thick surface layer with suppressed magnetic Curie temperature, $T_C$, is responsible for the EMR in both the low and high field region. Obviously, more experimental explorations are still needed to enhance our understanding on EMR.

At present, studies of EMR for various types of GB have shown that the LFMR is pronounced only for the films with a large angle GB. The investigation on the grain size dependence of the EMR has shown that decreasing grain size enhances both the LFMR and HFMR. However, the effect of ion doping on the EMR is less addressed. A systematic examination of ion doping on the EMR, where the HFMR and LFMR have been considered separately, is still open. In this article, the effect of Fe doping on the LFMR and HFMR in polycrystalline La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Fe$_x$O$_3$ (LSMFO) thin films, with x=0–0.12, has been systematically studied.

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The polycrystalline LSMFO thin films were deposited on (001) oriented Si substrates of 5×10×0.5 mm$^3$ in size using pulsed laser deposition (PLD). The PLD experiment was performed utilizing a KrF excimer laser of 248 nm in wavelength and 30 ns in pulse width. The optimized laser fluency of 1.80 J/cm$^2$ and a rate of 5 Hz were used. The thin films of ~300 nm in thickness were deposited on the substrates at a temperature of 680°C. The oxygen ambient pressure was 0.5 mbar during deposition and was increased to 400 mbar while cooling down at a rate of 15 K/min to room temperature. The ceramic LSMFO disks with x=0, 0.02, 0.05, 0.08, and 0.12, respectively, were chosen as targets. The targets were made using the standard ceramic synthesis technique. The microstructure of the samples was checked by x-ray diffraction (XRD). The morphology and the magnetization distribution were checked by atomic force microscopy (AFM) and magnetic force microscopy (MFM). The interdiffusion between film and substrate was checked by a secondary ion mass spectrometer (SIMS). The electro- and magnetotransport properties were evaluated using a four-probe method. The magnetoresistance was measured with a field applied parallel to the current direction. The magnetic properties were characterized using an Oxford superconducting vibrating sample magnetometer (VSM).

XRD measurements verified that all the LSMFO (x =0–0.12) films were polycrystalline with a single-phase perovskite structure. No apparent structural change due to Fe doping was identified. The reason is that Fe$^{3+}$ and Mn$^{3+}$ have the same ionic radius and Mn$^{3+}$ ions are replaced directly by Fe$^{3+}$ ions. However, Fe doping causes great changes in resistivity and magnetism of the thin films. This is clearly seen in Fig. 1, where resistivity and magnetization are plotted as a function of temperature for films with various Fe concentration x. With increasing x, the resistivity at low temperature increases by more than two orders in magnitude and the metal–insulator transition temperature, $T_p$, shifts...
to resistivity is greatly enhanced, thus making the metal–insulator transition broad and causing $T_p$ to shift down to a lower temperature. $T_C$ is less affected since it is governed by the ferromagnetism of grains. For the films with $x \neq 0$, the effect of Fe doping on $T_p$ must be considered as well. It was reported that Fe doping also downshifts $T_p$ in bulk materials, although the effect is less significant than that observed in films. It seems that the Fe doping and grain size are cooperating together to lower $T_p$ for the Fe-doped films with fine grains.

Figure 2 shows the reduced MR hysteresis loops $[\rho(H)/\rho(H_s)–H$ curves] at 77 K for LSMFO thin films with various Fe concentration $x$. Here $\rho(H_s)$ denotes the resistivity at coercivity field, $H_s$. In a field up to 10 kOe, MR curves can be well divided into LFMR and HFMR components. Significant modification on the LFMR and HFMR by Fe doping is found. In order to quantify these changes, we first backextrapolate the high field linear curves to find the zero field intercept. Then one minus this quantity is denoted as LFMR*. HFMR can be defined as

$$\text{HFMR} = d[\rho(H)/\rho(H_s)]dH.$$  

(1)

For LSMFO thin films, the calculated LFMR* and HFMR values at various temperatures ($T$) are shown in Fig. 3. For the film with $x = 0$, the LFMR* decreases rapidly with increasing $T$, whereas the HFMR is almost $T$ independent in the whole $T$ range. This agrees well with the reported EMR behavior on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ceramics without Fe doping. This trend (constant HFMR) does not change by low Fe-doping. The HFMR of the films are nearly independent as $x < 0.08$, as revealed in Fig. 3. For $x = 0.08$, the HMR is constant only at $T < 150$ K but drops as $T$ further increases. Nevertheless, the most striking feature for these films is that Fe doping significantly damages the LFMR* and enhances the HFMR at low temperatures. At 77 K, the LFMR*HFMR are (20%)/(4.6 $\times$ 10$^{-3}$/kOe), (16%)/(5.6 $\times$ 10$^{-3}$/kOe), (11%)/(9.2 $\times$ 10$^{-3}$/kOe), and (9%)/(14.7 $\times$ 10$^{-3}$/kOe) for $x = 0.02$, 0.05, and 0.08, respectively. Hwang et al.$^1$ first correlated LFMR* to the field alignment of magnetizations between the neighboring grains in a...
spin polarized tunneling (SPT) process. In their pioneer work, spin flip was not considered. However, recent theoretical studies have shown that the inelastic spin-flip scattering process also plays an essential role in determining the magnitude of the LFMR*. To explain the decrease of the LFMR* by Fe doping, we recall a recent SPT model proposed by Lyu et al., in which

$$\Delta p / p(H) = \frac{(1 - \tilde{\gamma})}{1 + \tilde{\gamma}} \rho^2 M^2,$$

(2)

where $\tilde{\gamma}$ is the parameter to characterize the inelastic spin-flip scattering. $P$ is the electron polarization, $M(0 = 0.01)$ is the magnetization reduced by its saturation value. Although there is a small difference between $\Delta p / p(H)$ and the LFMR*, qualitatively they will change together since the LFMR* $\sim 1 - [\Delta p / p(H) + 1]^{-1}$. Thus without any transformation, we adopt Eq. (2) to discuss the lowering of the LFMR* by Fe doping. At a certain $T$ where $\tilde{\gamma}$ and $P$ are fixed, the model predicts $\Delta p / p(H) \propto M^2$. This roughly agrees with the experiment results. Comparing Fig. 2 and its inset, we find that the sharp decrease of $\rho$ indeed exists as the magnetization is saturated at $H \sim 1500$ Oe. Furthermore, one notes that the reduced magnetization loops resemble with each other for different $x$ as long as $x \leq 0.08$, as shown in the inset of Fig. 2. Despite $H_c$ is slightly lowered from $-190$ Oe for $x = 0$ to $-140$ Oe for $x = 0.08$. This indicates that the variation of $M$ by Fe doping does not contribute much to the decrease in the LFMR*. Therefore, it is possible to attribute the decrease in the LFMR* to the variation of $P$ and $\tilde{\gamma}$. For $x = 0$, the conduction electrons is well known to be nearly 100% polarized at 77 K. For Fe-doped samples, as the De interaction is weakened by the increasing Fe doping, the electron normalized magnetization and $P$ decreases accordingly. In addition, it has been shown that the collective excitations of local spins at GB is also responsible for the decay in the LFMR*. In LSMFO thin films, due to the competition between Fe–Mn antiferromagnetism and Mn–Mn ferromagnetism, statistically more spin flip excitation (increase of $\tilde{\gamma}$) is expected during the tunneling process, which subsequently lowers the LFMR*.

To explain the HFMR, the spin susceptibility of the GB state, $\chi_{gb}$, is always of key importance for various models. For example, Guinea has calculated the magnetococonductance for spin-polarized tunneling via a paramagnetic impurity. Ziese pointed out that generalizing his result by taking into account magnetic correlations in a mean field approach yields

$$\text{HFMR} \propto - \chi_{gb} M_{gb},$$

(3)

where $M_{gb}$ denotes the grain boundary magnetization. This result is identical to that obtained by Evetts et al. through a different approach. If one assume that GB is paramagnetic in nature, which gives $M_{gb} = \chi_{gb} H$ and $n_{gb} \propto 1/T$, HFMR $\propto 1/T^2$ is predicted, which is contradictory to our experimental results (Fig. 3 upper panel). This clearly indicates that spin interactions exist at the GB. The spin interaction at the GB is different from that in grains due to the reduced coordination and surface distortions, etc. However, it still can be modified by Fe doping as Fe doping weakens the DE interactions between Mn ions. Therefore, the enhanced HFMR by Fe doping can be explained by reduced ferromagnetic interactions at the boundary states. The HFMR increases monotonically with increasing Fe concentration. According to Eq. (3) this indicates that $\chi_{gb}$ is enhanced by Fe doping and $M_{gb}$ should be lowered. For $x = 0.08$, the enhancement of $\chi_{gb}$ dominates at the low temperatures and the enhanced HFMR is shown; as $T$ increases, the decrease in $M_{gb}$ dominates and the HFMR is lowered. However, VSM measurements were unable to detect the small changes in $\chi_{gb}$ due to Fe doping. Future experiments are still needed to further confirm the earlier picture.


FIG. 3. (a) The high field magnetoresistance, HFMR = \(\Delta \rho(H) / \rho(H)\), and (b) the extrapolated low field magnetoresistance at zero field, LFMR*, are plotted against temperature for the La0.7Sr0.3Mn1–xFe0.08O3 films with $x = 0$ to 0.08.