Room temperature magnetoresistance properties in self-assembled epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$:NiO nanocomposite thin films

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ABSTRACT
Self-assembled epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$:NiO (LSMO:NiO) nanocomposite thin films were grown on (001)-oriented SrTiO$_3$ substrates by pulsed laser deposition, and their microstructures and magnetoresistance (MR) properties were investigated. The room temperature MR effect at a low magnetic field has been realized in the composite films, and the maximum MR value is 18.7% at 300 K and 1 T. The room temperature MR properties at the low magnetic field can be attributed to the special structure, which is made up of the nano-sized LSMO and NiO columns. The room temperature MR properties at low magnetic fields will facilitate its extensive room temperature applications.

IMPACT STATEMENT
The room temperature magnetoresistance properties at a low magnetic field has been realized in the self-assembled epitaxial La$_{0.7}$Sr$_{0.3}$MnO$_3$:NiO nanocomposite thin films by controlling the microstructures.

1. Introduction

Mixed-valence perovskite manganites have attracted great research interests in recent years because of their intriguing physics phenomena induced by the interactions of charge, spin, orbital, and lattice degrees of freedom [1–3]. The intrinsic colossal magnetoresistance (CMR) around the ferromagnetic-paramagnetic transition temperature ($T_C$) observed in these materials is particularly attractive as designing the memory-readers of digital device and spintronic applications [4,5]. For practical applications, it is important to obtain a large magnetoresistance (MR) value at room temperature and low magnetic fields. However, the intrinsic CMR effect can only be triggered at a high magnetic field of several Teslas and within a narrow temperature range near $T_C$. Many efforts in searching for room temperature MR properties have been focused on tuning the temperature window of CMR effect to room temperature by preparing ferromagnetic superlattices or multilayers consisting of two perovskite manganites, whose $T_C$ are below and above room temperature, respectively [6–8]. For example, the temperature window of MR effect was broadened across room temperature in the La$_{0.67}$Sr$_{0.33}$MnO$_3$/La$_{0.67}$Ca$_{0.33}$MnO$_3$ multilayers and the maximum MR value of $-66\%$ at 5 T and 295 K was obtained [8]. Although the enhanced MR properties can be achieved around room temperature in these systems, the needed applied magnetic field is so high which will obstruct the practical applications. On the other hand, the extrinsic low-field magnetoresistance (LFMR) effect, induced by spin-polarized
tunneling and scattering at grain boundaries (GBs) in polycrystalline bulk and thin-film manganites [9–11], has stimulated considerable interest as it displays a relatively strong MR effect at a low magnetic field (H ≤ 1 T). Thus, many groups have attempted to improve the LFMR properties in manganite-based composites by incorporating a secondary insulator phase to introduce the artificial GBs [12–15]. For example, a pronounced LFMR value of 21% at 20 K and 1 T in (LSMO)0.5:(CeO2)0.5 nanocomposite films [14] and a LFMR value of 12% at 77 K and 1 T in (LSMO)0.5:(ZnO)0.5 nanocomposite films [15] were obtained. Furthermore, improving the MR properties by tuning the second phase ratio in the La0.7Ca0.3MnO3:NiO [3] and LSMO:NiO [16] nanocomposite films were studied in our previous work, and the magnetotransport properties of LSMO:NiO nanocomposite films have also been investigated by Chen et al [17]. These results demonstrate that the TMI decrease rapidly to low temperatures for the nanocomposite films with excess second phase ratio (usually > 50%), which leads to the MR effect occurring only at low temperatures (< 200 K). Therefore, the ratio of second phase in the composite films should be controlled at a lower value to obtain room-temperature MR properties.

Interestingly, it is worth noting that the enhanced so-called LFMR properties have been observed near TC in several epitaxial nanocomposite thin films [16–19]. Although the MR properties were obtained under low magnetic fields (≤ 1 T), it might not be appropriate to take them as the conventional LFMR effect. Because the temperature window of MR effect is closely related to the metal–insulator (M-I) transition temperature (TC) and the enhanced MR properties can be explained by the mechanism of enhanced spin-fluctuation depression, which is similar to that of CMR effect [16–20]. Therefore, it is possible to adjust the MR following TC at low magnetic fields to room temperature if the TC can be tuned effectively. The self-assembled epitaxial nanocomposite thin films are one of the optimal candidates, because their TC can be tuned by the microstructures [21,22]. In this work, we deposit self-assembled epitaxial La0.7Sr0.3MnO3:NiO (LSMO:NiO) nanocomposite thin films on (001)-oriented SrTiO3 (STO) substrates by pulsed laser deposition (PLD). To obtain the MR properties near room temperature, we select the LSMO:NiO compositions with low NiO ratios (L:N = 1:0.6 and 1:1) and attempt to adjust MR properties by controlling microstructures. The results show that the room temperature MR properties at a low magnetic field can be realized, which can be attributed to the nano-sized artificial electronic phase separation in the nanocomposite thin films.

2. Experimental details

The LSMO:NiO composite thin films were grown on the (001)-oriented STO substrates by PLD using a KrF (λ = 248 nm) excimer laser, with a flux of approximately 1.4 J cm −2 and a repetition rate of 5 Hz. The substrate temperature and process oxygen pressure were kept at 700°C and 30 Pa. During the deposition process, the LSMO:NiO ratios were controlled by the deposition time of the LSMO and NiO. The fabricated samples were cooled down to room temperature at 10°C/min under an oxygen pressure of 5 × 104 Pa. For convenience, the LSMO:NiO composite films with the LSMO:NiO ratios of 1:0.6 and 1:1 are defined as sample 1 (S1) and sample 2 (S2), respectively. For comparison, pure LSMO films were also grown on the STO substrates with the same conditions. Crystal structures of the films were determined by X-ray diffraction (XRD; Rigaku, D/max-2000, Cu Kα radiation) analysis. Microstructures were studied by transmission electron microscopy (TEM) (F20, Tecnai). Magnetization measurements were performed from 10 K to 360 K using a superconducting quantum interference device (SQUID) magnetometer along the in-plane direction. Transport properties were measured by the standard four-terminal method using a physical property measurement system (PPMS) and the current was performed in the plane.

3. Results and discussions

Figure 1(a) shows XRD patterns of the pure LSMO film and the composite films S1 and S2 on the (001)-oriented STO substrate. The LSMO phase in both the pure LSMO film and the composite films only exhibits (00 l) diffraction peaks, and only a prominent peak of NiO (200) is detected in the composite films. This indicates that LSMO and NiO phases in the composite films have grown epitaxially on the STO substrate. The local XRD patterns around the (002) diffraction peaks are illustrated in Figure 1(b), showing that the LSMO(002) diffraction peak shifted to the left side of the STO(002) diffraction peak compared to the pure LSMO film, while the position of NiO(002) diffraction peak is almost the same. For the pure LSMO film, the lattice parameter along the out-of-plane direction (d(001)LnSrTiO3), is determined to be 3.860 Å, and is smaller than the bulk value of 3.870 Å, indicating a compression state in the out-of-plane direction. Because the LSMO film has grown epitaxially on the STO substrate, the larger lattice parameter of STO (d(100)STO = 3.905 Å) made the LSMO film in a tensile stress state in the plane. In contrast, the d(001)LSMO value for the composite films S1 and S2 is determined to be 3.903 Å and 3.942 Å, respectively, which are larger than
Figure 1. (a) XRD patterns of the LSMO: NiO composite films S1 and S2, and the pure LSMO film. (b) An enlarged XRD scan around the STO (002) peak.

Figure 2. (a) A cross-sectional TEM image of the film S1. (b), (c) HRTEM images of the film S1. ‘L’ stands for LSMO phase and ‘N’ stands for NiO phase. (d) A HRTEM image of the film S2. (e) A HRTEM image of the LSMO/NiO interface, and (f-g) its corresponding intensity line profiles of two neighboring LSMO and NiO (indicated in the HRTEM images). (h), (i) The Fast Fourier Transformation (FFT) patterns transformed from the HRTEM image of (b) and (d).

that of the pure LSMO film. The results indicate that the strain state of LSMO in the composite films switches from compression state to tension state in the out-of-plane direction. Namely, the LSMO lattice is elongated in the out-of-plane direction, which is possibly to match the larger lattice of NiO ($d_{(001)\text{NiO}} = 4.170 \text{Å}$). In addition, the $d_{(001)\text{LSMO}}$ value of the film S2 is larger than that of the film S1, which is attributed to the difference of microstructures between them. The following TEM results on microstructures show a nano-sized columns structure has been formed in both films S1 and S2, and the interface-to-volume ratio in the film S2 is larger, which is responsible for the greater interface strain in the film S2.

Microstructures of the composite films S1 and S2 were studied by TEM, and the partial results are shown in Figure 2. Figure 2(a) shows a cross-sectional low-magnification TEM image of film S1, demonstrating self-assembled growth of the LSMO and NiO columns on the STO substrate. The well-ordered LSMO and NiO columns are observed to fill the entire film. The high resolution TEM (HRTEM) images in Figure 2(b–d) reveal
that the diameter of LSMO and NiO columns in the films S1 and S2 is in nanometer scale. Thus, the LSMO matrix has been divided to nanometer in size by NiO. The cross-sectional structures were further investigated by STEM with EDS line profiles and the results also show that the composite films are consisted of the alternate LSMO and NiO phases (not shown here). The HRTEM images also indicate the formation of a well-ordered superlattice structure along the in-plane direction. The corresponding FFT patterns with the regular superlattice spots are shown in the Figure 2(h–i). Additionally, as shown in Figure 2(e–g), the out-of-plane d-spacing of the LSMO phase is determined to be 0.390 nm for film S1, which is corresponding to the XRD result, indicating the existence of interface strain. From the HRTEM images shown in Figure 2(b–d), the unit structure period width defined as the two neighboring LSMO and NiO columns is around 2.8 nm and 2.2 nm for the films S1 and S2, respectively. The results indicate that the interface-to-volume ratio in the film S2 is larger than that in the film S1, which leads to a larger interfacial strain in the film S2. It can be speculated that the films S1 and S2 will show different magnetic and MR properties due to the difference in microstructures.

Figure 3 shows the magnetic properties of the LSMO: NiO composite films and the pure LSMO film. Figure 3(a) presents the temperature dependence of the field-cooled magnetization with a magnetic field of 500 Oe. The magnetization decreases with increasing temperature, and the PM-FM transition is observed in all the films. The transition temperature $T_C$ can be obtained from the peak in the dM/dT-T curve as shown in the inset in Figure 3(a), and is 318 K, 300 K and 270 K for the pure LSMO film and the composite films S1 and S2,

Figure 4. (a) Temperature dependence of the resistivity at 0 T and 1 T for the LSMO: NiO composite films S1 and S2, and the pure LSMO film, (b) MR values of the LSMO: NiO composite films S1 and S2, and the pure LSMO film under the external magnetic field of 1 T.
respectively. Thus, the $T_C$ of the composite films has been successfully adjusted to room temperature, which will give chance to obtain room temperature MR properties. The recent studies have shown that the interface strain has a significant effect on the $T_C$ of the manganite-based composites films [22,23]. In this study, the interface strain between the LSMO and NiO nanocolumns causes the LSMO to be in a tensile strain state along the out-of-plane direction, resulting in the change in the length and angle of Mn-O-Mn bonds. The electron transfer integral of the Mn$^{3+}$-O-Mn$^{4+}$ is decreased and the double-exchange interaction is weakened, leading to the decrease of the $T_C$. The magnetic hysteresis loops recorded after field cooling of 500 Oe from 360 K down to 10 K are shown in Figure 3(b). The saturation magnetization ($M_s$) of the composite films is smaller than that of the pure LSMO film, which may be attributed to the weakened double-exchange interaction and the spin disorders at interfaces. Comparing the film S2 with S1, the $M_s$ was also decreased by the increased interface strain and spin disorders because the interface-to-volume ratio in the film S2 is larger than that in the film S1, which is similar to the reported results of the $(La_{0.7}Sr_{0.3}MnO_3)_{0.7}:(Mn_3O_4)_{0.3}$ composite films [24]. The above results indicate that the magnetic properties of manganite nanocomposite films can be strongly influenced by the microstructures.

Figure 4(a) shows the temperature dependence of resistivity $\rho(T)$ for the composite films S1 and S2, and the pure LSMO film under applied field (1 T) and zero field, respectively. The insert is a zoom-in image for the pure LSMO film around room temperature. Compared with the pure LSMO film, the composite films show the increased resistivity due to the existence of the insulator NiO. In addition, with increasing the temperature, the composite films display an M-I transition behavior. The $T_{MI}$ defined as the temperature at the maximum resistivity in $\rho(T)$ data is 342 K and 336 K for the films S1 and S2, respectively, which are above room temperature. The magnetic field strongly affects the resistivity around the $T_{MI}$, especially for the composite films, giving rise to the MR effect. The MR value is defined as $MR\% = (\rho(H, T) - \rho(0, T))/\rho(0, T)) \times 100\%$, where $\rho(H, T)$ and $\rho(0, T)$ are the temperature dependent resistivity values under applied field (1 T) and zero field. As shown in Figure 4(b), the composite films show excellent MR properties at room temperature. The maximum MR value is about 11.2% and 18.7% at 300 K for the films S1 and S2, respectively. Moreover, the MR effect of the composite films locates in the broadened temperature range (250 K to 350 K) cross over room temperature. The results show that the room temperature MR properties at a low magnetic filed have been realized in the LSMO: NiO nanocomposite films. For most of the manganite-based composite films, the $T_{MI}$ is decreased greatly and is far lower than $T_C$, so that the LFMR effect is triggered at low temperatures [12–15]. By contrast, in this work, the $T_{MI}$ is close to the $T_C$ and is near room temperature. The room temperature MR effect shows a much higher temperature window than that of the LFMR effect and the MR values at low temperatures can be negligible. Therefore, for the LSMO: NiO nanocomposite films, the mechanism of the room-temperature low-field MR effect is different from that of the LFMR effect, and is similar to that of the CMR effect.

On the mechanism of the CMR effect, the theoretical research results [25,26] and experimental evidences [27–29] have demonstrated that the electronic phase separation is common in the doped manganites. The electronic phase separation can be considered as that the metallic FM phase is separated in the insulating regions with sub-micrometer scale. The competition between the two electronic phases with temperature leads to the M-I transition behavior, and the CMR effect can be explained by the percolative transport through the FM phase. When applying a magnetic field, the metallic FM phases will enlarge and the resistivity of the system will be reduced due to the formation of the metallic percolative transport paths, resulting in the CMR effect. Usually, the intrinsic electronic phase separation for the CMR effect in pure doped manganites always exists in sub-micrometer scale. However, in this study, the alternate nano-sized columns of LSMO and NiO forms a chemical phase separation, leading to an artificial electronic phase separation of metallic phase LSMO and insulator phase NiO in nanometer scale. The magnetizations can be easily aligned parallel to the external magnetic field in the nano-sized FM phase compared to bulk manganites [24]. Therefore, the room temperature MR effect can be triggered at a low magnetic field, which is crucial to facilitate their extensive room-temperature applications.

4. Conclusions

In this study, the self-assembled epitaxial LSMO: NiO nanocomposite films were grown on the (001)-oriented SrTiO$_3$ substrates by PLD, and their microstructures and magnetic properties have been investigated. The results show that the MR properties of the LSMO: NiO nanocomposite films can be tuned by the microstructures. The room temperature MR properties at a low magnetic field of 1 T have been achieved. In the LSMO: NiO nanocomposite films, the chemical phase separation due to the alternate nano-sized columns of LSMO and NiO leads to an artificial electronic phase separation in nanoscale. The LSMO: NiO nanocomposite films featuring a large room-temperature MR value at a low magnetic
field will facilitate their extensive applications, especially at room temperature.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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