Strain state evolution and thickness-dependent properties of epitaxial Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ films

S. W. Jin,$^{1,2}$ G. Y. Gao,$^1$ Z. Z. Yin,$^1$ Z. Huang,$^1$ X. Y. Zhou,$^2$ and W. B. Wu,$^{1,*}$

$^1$Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

$^2$Department of Modern Physics, University of Science and Technology of China, Hefei 230026, China

(Received 11 March 2007; published 5 June 2007)

Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ (NSMO) films 7–300 nm thick have been grown on (001)(LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) and (001)SrTiO$_3$ (STO) substrates, with lattice mismatches of 0.33% and 1.29%, respectively. The strain state evolution was examined fully by x-ray reciprocal space maps, in order to clarify its impact on the thickness-dependent properties of the films. It was found that all NSMO/LSAT films are coherently strained, having almost the same Curie ($T_C$) and peak resistivity ($T_p$) temperatures at fixed thicknesses, while the NSMO/STO films evolve from being fully strained to relaxed, showing inhomogeneous magnetic transitions and lower or higher $T_C$ than their counterparts at 7–60 nm. The results underline that $T_C$ ($T_p$) and phase separation are all controlled by the strain states of the films.

DOI: 10.1103/PhysRevB.75.212401 PACS number(s): 61.10.Nz, 68.55.Jk, 75.47.Lx, 75.70.Ak

Since the discovery of colossal magnetoresistance (CMR) in doped manganites,$^4$ much effort has been devoted to the fabrication of manganese-based heterostructures for device applications.$^{2–4}$ To improve the device performance, the thickness-dependent properties of epitaxial CMR films have been widely explored in recent years.$^{5–13}$ The films usually exhibit magnetic and transport properties different from those of the bulk materials at fixed doping levels, e.g., strong magnetic anisotropy and reduced Curie (peak resistivity) temperature $T_C$ ($T_p$). As the film thickness decreases the difference can become more dramatic. The effects have been ascribed to a variety of factors, mainly substrate-induced strains, dimensional effects, and oxygen deficiencies.$^{5–13}$ Millis et al.$^5$ reported, based on theoretical analyses, that $T_C$ of a CMR film is extremely sensitive to the biaxial strain and a 1% strain would cause a 10% shift in $T_C$ due to the Jahn-Teller term in the lattice distortion.$^3$ However, this relation between $T_C$ and strain has rarely been observed for films of various thicknesses.$^{7,13}$ Also, it was believed that the decrease of $T_C$ is not due to strain but to the dimensional nature of the films or charge depletion at the interface.$^{10–12,14}$ So the thickness effects in epitaxial CMR films are not fully understood yet.

Among all the mechanisms proposed, the biaxial strain is surely an important ingredient and its role in phase separation, as well as the shift in $T_C$, needs to be further clarified.$^{15}$ Apart from the lattice mismatch and thickness, the strain state can also be affected by some extrinsic factors such as oxygen deficiency, making the problem intricate. In this Brief Report, well-oxygenated Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ (NSMO) films 7–300 nm thick and under lattice mismatches of 0.33% and 1.29% were grown on (001)(LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) and (001)SrTiO$_3$ (STO) substrates and studied comparatively. The NSMO is chosen for its small angle mismatch with the cubic substrates,$^{16}$ which will simplify the strain relaxation processes.$^6,11$ To scrutinize the strain states, asymmetric x-ray reciprocal space mapping (RSM) on (103) reflections from all the films was performed. The magnetic and transport measurements demonstrated that the shifts in $T_C$ and phase separation at the interface could all be attributed to the strain state evolution of the NSMO films.

The NSMO films were grown concomitantly on (001)LSAT and (001)STO substrates by laser ablation under optimized parameters, as described previously.$^{17}$ The films were annealed in situ at 10 Torr of O$_2$ for 20 min before being cooled down in the same ambient. To optimize the oxygen content and to facilitate the comparison, all films were further annealed ex situ at 750 °C for 2 h in flowing O$_2$ and in one batch. As such, they become well oxygenated and the highest $T_C$ was obtained even for those 13 nm thick.$^{15}$ The x-ray diffraction (XRD) was performed using Cu Ka$_1$ radiation ($\lambda=1.5406$ Å), and the temperature dependence of

![FIG. 1. (Color online) XRD linear scans and $\omega$-scan RCs around the NSMO(001) reflections. The sharp peak at $2\theta=22.984^\circ$ can be indexed as LSAT(001). The dashed lines are guidance for eyes for the shift of NSMO(001) peaks and the background for the RCs.](image)
magnetization \((M-T)\) and resistivity \((R-T)\) were measured on a superconducting quantum interference magnetometer.

Figure 1 shows XRD 2\(\theta\)-\(\omega\) scans around the (001) reflections and \(\omega\)-scan rocking curves (RCs) on the NSMO(001) peaks. The films grown on LSAT (left panels) and STO (right panels) substrates were labeled as L1–L7 and S1–S6 according to their thicknesses, as denoted. Those simultaneously deposited (e.g., L3 and S3) show almost the same thicknesses as determined by the interference fringes.\(^{1,13}\) The appearance of the fringes and the narrow full width at half maximum of the RCs indicate that the films are smooth and of high crystallinity. Based on the NSMO(001) reflection and those at higher orders (not shown), the out-of-plane lattice constant of each film on LSAT or STO was calculated. As the film thickness is increased from 10 to 165 nm, it changes slowly from 3.827 to 3.836 Å for the former, but fast from 3.806 to 3.845 Å for the latter. They are all smaller than the lattice parameter (3.855 Å) of the pseudocubic NSMO bulk,\(^{16}\) indicating that all the NSMO films are under tensile stress and those on STO were strained more highly but relaxed faster.

To fully examine the strain states, RSM on (\(\bar{1}03\)) reflections from all the films was performed, as shown in Fig. 2. Due to the size effect the thinner films such as L1 (10 nm) show NSMO(\(\bar{1}03\)) more elongated along the out-of-plane direction. For NSMO/LSAT, as the film thickness increases the out-of-plane lattice constant \(e=\lambda/2Q^*_x\) increases more slowly than their counterparts, consistent with the results shown in Fig. 1. The in-plane lattice constant \((a=\lambda/2Q^*_x)\) of the films at 10–165 and even at 300 nm (not shown) matched perfectly that of the LSAT substrate, implying that they were all grown coherently. It was also noted that for this series at 60 nm and above, the NSMO(\(\bar{1}03\)) reflections are a little broadened along the \(Q^*_x\) direction, indicating that the constant \(a\) of the films fluctuates slightly from that of the substrate. This structural relaxation may be ascribed to the domain formation due to the angle mismatch,\(^{6}\) implying that even for those grown coherently, the thinner films are more highly strained. In contrast, for NSMO/STO only S1 was fully strained. The NSMO(\(\bar{1}03\)) reflections from the other films move gradually along the \(-Q^*_x\) direction. At 15 or 30 nm the films are partially relaxed, where the reflections from the parts grown coherently and relaxed are defined. At above 60 nm the films are fully relaxed since the scattering from the fully strained fraction becomes negligible. Thus,
one may conclude that the larger lattice mismatch has induced not only a faster release of the biaxial strain but also more pronounced structural inhomogeneities in the films.

Figures 3(a) and 3(b) show the derivatives of the $M$-$T$ curves measured from the films of various thicknesses. The magnetization was recorded (field cooling) with a magnetic field of 0.1 T applied in plane. For both series, $T_C$ decreases gradually as the film thickness decreases, and, strikingly, those on STO show broader magnetic transitions than their counterparts, especially in the range below 30 nm. Surely this broadening can be traced to the inhomogeneous strain states of the films. The samples S2 and S3 are partially strained and the volume fractions of the relaxed and fully strained are comparable, resulting in a much wider ferromagnetic transition for the films. $T_C$ versus thickness is plotted in Fig. 3(c). Before being fully relaxed at 60 nm the films on STO show lower $T_C$ than their counterparts, which can be well explained by the biaxial strain due to lattice mismatch. The larger strain induced lower $T_C$. At 60 nm and above, the films have higher $T_C$ than their counterparts, however. It is also determined by the strain states. The NSMO/STO films are then strain relieved, while the NSMO/LSAT films, with a larger critical thickness, are strained persistently. The cross-plotting clearly manifests that the change of $T_C$ is correlated with the strain state evolution. As shown in the inset to Fig. 3(c), for the strained films $T_C$ decreases almost linearly with the reduction of the $c/a$ ratio, indicating that the change of $T_C$ is very sensitive to the lattice distortion.

Figure 4 shows $M$-$T$ and $R$-$T$ curves measured from the typical films of 10, 15, and 60 nm thick. As aforementioned, S1 (S2) shows a much lower $T_C$ than L1 (L2), and S4 has a higher $T_C$ onset than L4. The magnetization at 10 K of the strained thin films depends strongly on the substrates and film thicknesses, i.e., the strain states. For all NSMO/LSAT films, due to the small lattice mismatch $T_p$ is almost the same as the onset $T_C$. However, for NSMO/STO films, when fully relaxed (S4), $T_p$ equals also the $T_C$ onset, when partially strained (S2), $T_p$ is lower than $T_C$, and when fully strained S1 is insulating in the whole range above 50 K, although it showed a weak ferromagnetic transition at about 100 K. This means that for NSMO/STO films under the larger lattice mismatch, phase separation and charge depletion can be more readily induced by the strain. For fully strained films, with decreasing film thickness the $c/a$ ratio can decrease further, and according to Konishi et al. their magnetic and electronic phases can be affected drastically, leading to an orbital ordering. This may be true for the NSMO/STO film at 7 nm, since a very uniform biaxial strain and nonferromagnetic insulating behavior have been observed, as shown in Fig. 5, though the magnetic structure is not clear at present. The phase separation usually exhibited by CMR films with strain distribution in plane, such as the sample S2, was also observed for the completely strained thin films, implying that it might be intrinsically strain induced or arise from the strain field possibly along the film normal direction. So, for NSMO films, the shift in $T_C$, inhomogeneous ferromagnetic transitions, and phase separation at the interface could all be controlled by the strain states.

In summary, the strain state evolution of NSMO films grown on LSAT and STO substrates has been fully examined by asymmetric RSM. It was demonstrated that the biaxial strain has a direct impact on properties of the films at various thicknesses, underlining that the shift in $T_C$ and phase separation at the interface could all be correlated with the strain states of the NSMO films.

This work was supported by the Chinese Natural Science Foundation Grants No. (50325206 and 50421201), and the National Basic Research Program of China Grant No. (2006CB922005).


