Strain, spin disorder, and thickness dependence of magneto-transport in Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ films

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The correlation between the strain, spin disorder, and the thickness dependence of the magneto-transport has been investigated in as-grown and post-annealed 25-300-nm thick films of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ (SSMO) deposited on SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) substrates. In the post-annealed SSMO/LAO films, the epitaxial strain increases with a decreasing thickness; however, it is independent of the thickness of the post-annealed SSMO/STO films. In both cases, the reduction of the metal-insulator transition temperature with a decreasing thickness was observed. This behavior is attributed to an increasing compressive strain in the SSMO/ LAO films and to spin disorder effects in the SSMO/STO ones. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4728988]

Doped perovskite manganites of the composition RE$_{1-x}$A$_x$MnO$_3$ (where RE and A are the rare earth and the alkaline elements, respectively) have attracted significant interest during the past decade due to their interesting properties, such as the metal-insulator transition (MIT) and the colossal magnetoresistance (CMR). Various applications of these manganites require deposition of high quality thin films with controllable properties.

It is believed that the properties of these films are strongly influenced by the epitaxial strain, which is introduced into the film by the lattice mismatch between the film and the single crystal substrate. Lattice strain is one of key factors which modifies the physical properties of manganite films, such as the intrinsic phase separation of different magnetic phases. For example, strain affects the charge ordered insulating (COI) phase in manganite films and the MIT and its temperature. Lattice mismatch strain can be relieved by the formation of lattice defects during deposition of films at high temperatures, which may lead to the dominance of the ferromagnetic metallic (FM) phase over the COI phase.

Deposition of manganite thin films on oriented single crystal substrates induces in-plane tensile and compressive strains in these films, depending on the sign of the elastic misfit. Thin films of optimally doped manganites such as La$_{0.7}$Sr$_{0.3}$MnO$_3$ or Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ (Refs. 18 and 19) deposited on LaAlO$_3$ (LAO) or SrTiO$_3$ (STO) substrates experience a gradual suppression of the MIT temperature with decreasing thickness of the film. This suppression is generally attributed to an increasing epitaxial strain; however, recent experiments revealed that the lattice strain is not the only factor affecting the MIT in thin films.

For example, studies of the MIT in La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) films deposited on STO and LAO revealed a shift of the MIT to lower temperatures. Shift increases with a decreasing thickness of the film. For LSMO films deposited on LAO substrates, a gradual suppression of the MIT was observed as the film thickness is decreased, which has been attributed to an increase in the compressive lattice strain. However, for LSMO films deposited on STO substrates, the suppression of the MIT occurred abruptly at film thicknesses below 5 nm and this has been attributed to the symmetry breaking at the interface between the film and the substrate, producing a “dead” interface layer.

Studies of Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ (PSMO) films deposited on STO substrates showed a larger reduction of the MIT temperature with a decreasing thickness than that observed in films deposited on LAO substrates, in spite of the much weaker thickness dependence of the lattice strain in PSMO/STO. However, a decrease of the MIT temperature in these films occurs at thicknesses below 15-20 nm which is much larger than the estimated “dead” interface layer thickness of less than 5 nm for those films. These results imply that neither the lattice strain nor the film-substrate interface could be fully responsible for the drop of the MIT temperature in very thin PSMO/STO films.

The above discussion raises questions regarding the mechanism responsible for the thickness dependence of magneto-transport in such films. To address this issue, we investigated the magneto-transport in manganite films of a different composition, namely 25-300-nm thick films of Sm$_{0.55}$Sr$_{0.45}$MnO$_3$ (SSMO) deposited on STO and LAO substrates (with the in-plane lattice mismatch of $+1.6\%$ and $-1.4\%$, respectively). The SSMO films are good candidates for such a study, because the as-grown films of this...
compound are insulators which do not exhibit magneto-resistance (MR) in fields below 1 T. However, a subsequent thermal annealing at high temperatures results in a metal-insulator transition and MR in these films. By contrast, both as-grown and annealed films of other manganites, such as LSMO, PSMO, or LCMMO, show a MIT. Hence in SSMO, one can systematically investigate how the strain and magneto-transport evolve in both the insulating and the MIT configurations of the same film. The strain in the films was modified by both post-annealing and by changing the film thickness. X-ray diffraction (XRD) has been used to estimate the change of strain in these films. Our results imply that the reduction of the MIT observed in the thinnest SSMO/LAO and SSMO/STO films can be attributed to the epitaxial compressive strain and to the spin disorder effects, respectively.

Epitaxial SSMO films have been deposited on STO (001) and LAO (001) substrates at 750 °C by off-axis DC magnetron sputtering at 50 W in an oxygen-argon mixture, with O2 and Ar pressures of 100 mTorr and 20 mTorr, respectively. After the deposition, the samples were cooled down to 650 °C at a rate of 20 °C/min and subsequently annealed for 3 h at this temperature after the chamber was filled with pure oxygen at atmospheric pressure. This was followed by cooling the samples down to room temperature at a rate of 20 °C/min. The samples were then cut into two pieces. One piece was post-annealed in air at 900 °C for 24 h, then cooled to room temperature at a rate of 30 °C/min. The other piece was used as a reference sample and was not post-annealed. These films have smooth surfaces (<1 nm RMS roughness in a 1 x 1 μm² scanning area), as confirmed by atomic force microscopy.

The resistivity ρ in a magnetic field of 1.1 T (applied parallel to the current direction) and in zero field was measured at temperatures between 10 K and 300 K. The measurement in 1.1 T was as follows: first, a field of 1.1 T was applied at 300 K and ρ was measured during field cooling (FC) to 10 K. The field was then reduced to zero at 10 K and the sample was warmed up to 300 K, and subsequently zero field cooled (ZFC) down to 10 K. Then a 1.1 T field was applied at 10 K and ρ was measured in this field during warming to 300 K. The measurement of ρ in a zero field was done using the same cooling/warming route but in a field of 0 T.

All the as-grown SSMO/STO and SSMO/LAO films are insulating over the measured temperature range between 10 and 300 K and do not show any MR in fields up to 1.1 T. Post-annealing produces the MIT and MR in some of these films. The temperature dependence of ρ of the post-annealed SSMO/STO and SSMO/LAO films is plotted in Figures 1 and 2. In zero field, the SSMO/STO films thicker than 25 nm exhibit the MIT. However, the SSMO/LAO films show the MIT only when the film thickness is larger than 50 nm. All these films except the 25-nm-thick SSMO/STO film exhibit MR in a field of 1.1 T.

The insulating as-grown and annealed 25 nm thick SSMO/LAO films have the same resistivities as well as ρ(T). This implies that all our SSMO films have the same optimum oxygen concentrations, and the observed changes in ρ(T) due to annealing are caused by other factors, such as modification of the strain, lattice defects, etc. Also post-annealing in air at 900 °C for longer than 24 h did not change the magneto-transport properties of these films, ruling out the effects of oxygen deficiency on these properties.

The SSMO/STO and SSMO/LAO films are epitaxial with a dominant (001) c-axis orientation, as confirmed by x-ray diffraction. To investigate the changes in the lattice strain in these films, we measured the in-plane and out-of-plane lattice constants using XRD. The lattice parameters along the c-axis...
were calculated from the position of (001) and (002) reflections with an error of ±0.004 Å. We have calculated the in-plane lattice constants using the measured reciprocal space maps from (206) reflections of the films. The lattice strain along the c-axis (out-of-plane) and a-axis (in-plane) directions have been defined as \( \epsilon_{c}(\%) = [(\epsilon_{\text{film}} - \epsilon_{\text{bulk}})/\epsilon_{\text{bulk}}] \times 100 \) and \( \epsilon_{a}(\%) = [(\alpha_{\text{film}} - \alpha_{\text{bulk}})/\alpha_{\text{bulk}}] \times 100 \).24

The dependence of \( \epsilon_{a} \) and \( \epsilon_{c} \) on the film thickness for as-grown SSMO/STO and SSMO/LAO films, which are all insulators, are shown in Figure 3. The 25 and 50-nm-thick as-grown SSMO/STO films are strained with the tensile in-plane strain \( \epsilon_{a} \approx 0.9\% \) and the compressive out-of-plane strain \( \epsilon_{c} = 1.2\text{-}1.6\% \), \( \epsilon_{a} \) and \( \epsilon_{c} \) in thicker films are reduced down to about 0.30% and 0.75%, respectively. On the other hand, the 25 and 50-nm-thick as-grown SSMO/LAO films exhibit higher compressive in-plane strain \( \epsilon_{c} \) and tensile out-of-plane strain \( \epsilon_{a} \) of about 1.3%-1.6% and 2.1%, respectively, \( \epsilon_{a} \) and \( \epsilon_{c} \) in thicker films are reduced down by a small amount to about 1.1% and 2.0%, respectively.

The decrease of \( \epsilon_{c} \) and \( \epsilon_{a} \) with an increasing thickness implies that if the thickness of SSMO films is kept small enough, the elastic strain energy is below the formation energy of defects that are able to release the strain in the film. For example, 25 and 50 nm strained as-grown SSMO/STO and SSMO/LAO films are thermodynamically stable against defect formation. The elastic energy increases with an increasing film thickness. At thicknesses larger than the “critical thickness” of about 100 nm, this energy exceeds the defect formation energy, and lattice defects such as misfit lattice dislocations are formed, leading to strain reduction.

The dependence of both \( \epsilon_{a} \) and \( \epsilon_{c} \) on thickness in these two systems is different after post-annealing. \( \epsilon_{c} \) of the post-annealed SSMO/STO films drops to 0.5% while the \( \epsilon_{a} \) takes a value of around 0.25%. Notice that both out-of-plane and in-plane strains weakly depend on the film thickness. On the other hand, \( \epsilon_{c} \) and \( \epsilon_{a} \) of the post-annealed SSMO/LAO films are much higher than those found for the post-annealed SSMO/STO films (see Figure 3).

The post-annealed SSMO/LAO films less than 100-nm-thick remain insulating in zero applied field but those with larger thicknesses now exhibit an MIT as shown in Figure 2. Therefore in these films, the lattice strain (which increases with a decreasing thickness) seems to be the main factor suppressing this transition. In particular, highly strained films are insulating while films with a reduced strain exhibit a MIT.

This is not, however, the case for SSMO/STO films where the in-plane strain is relatively small (around 0.2%-0.3%) and almost independent of film thickness. Although the strain changes little with the film thickness, only films thicker than 50 nm show a well developed MIT. Films thinner than 50 nm remain insulating. The lack of a correlation between the presence of a MIT and the values of the strain implies that strain is not the sole parameter governing the observed changes in the thickness dependence of the MIT in SSMO/STO films. The question is therefore what mechanism is responsible for the suppression of conductivity in the thinnest films.

The dependence of \( \epsilon_{a} \) and \( \epsilon_{c} \) on film thickness in SSMO/STO films before and after annealing (see Figure 3) implies that during the post-annealing of the 25 and 50 nm thick films, strain-relieving arrays of structural defects (such as misfit dislocations/grain boundaries) are created in these films that results in a large reduction of the internal strains. Such defects could be also responsible for spin disorder in manganites.25 Grain boundary-induced quenched spin disorder (spin-glass-like state) was found by Martinez et al.26 to produce a splitting/irreversibility at low temperatures (below

FIG. 2. Thickness dependence of resistivity \( \rho \) vs temperature for post-annealed SSMO/LAO films.
about 40 K) in the temperature dependence of $\rho$ measured in granular manganites under FC and ZFC conditions.

In order to confirm the presence of such phenomena in our films, we performed the measurements of $\rho(T)$ of SSMO films according to the experimental procedure mentioned above, i.e., in zero field (for cooling and warming) and in a field of 1.1 T (under FC and ZFC conditions). The results are shown in Figures 1 and 2.

Measurements in zero field show a warming/cooling hysteresis in both SSMO/STO and SSMO/LAO films that exhibit the MIT. Application of a magnetic field reduces the width of this hysteresis. This type of thermal hysteresis has been observed previously and is consistent with the first order type transition in a system with two-phase coexistence or phase separation between FMM and COI phases.27 The magnetic field melts the COI state and significantly reduces the thermal hysteresis.27,28

The spin-disorder phenomenon is revealed in the measurements of the temperature dependence of the ZFC-FC resistivity in our SSMO films at 1.1 T. In 25-nm and 50-nm-thick SSMO/STO films, the results show very large splitting/irreversibility in the ZFC-FC resistivity at low temperatures, suggesting the presence of a spin-glass-like state in these samples. In thicker SSMO/STO films and in all SSMO/LAO films, this splitting is minimal.

According to the discussion above, a large splitting/irreversibility in $\rho(T)$ measured under FC and ZFC conditions is an indicator of the quenched spin disorder/spin-glass-like state caused by the arrays of structural defects. A large density of such defects must be formed in the 25 and 50 nm thick SSMO/STO films in order to reduce the in-plane lattice strain down to 0.2%-0.3%.

The splitting/irreversibility in $\rho(T)$ is still visible in the 50-nm-thick SSMO/LAO film, but it is much smaller than the corresponding one in the SSMO/STO films. This could be due to a much smaller density of structural lattice defects in these films after post-annealing, compared to that in the SSMO/STO films, as mentioned above. It is known that LAO substrates are twinned and this could promote the formation of grain boundaries in SSMO films grown on LAO. Grain boundaries are however, effective in blocking the motion of misfit dislocations, thus reducing the density of strain-relieving extended lattice defects that could be created in the films during post-annealing. This could explain our results which show that post-annealing of the as-grown SSMO/LAO films does not reduce the strain as much as in the SSMO/STO films.

In summary, we investigated the correlation between the lattice strain, the defect-induced spin disorder, and the thickness dependence of magneto-transport of SSMO/LAO and SSMO/STO films. The results show that the suppression of the MIT and an increase of resistivity with a decreasing thickness of these films is the outcome of two different processes. In SSMO/LAO films, it is driven by the lattice strain. However, in SSMO/STO films, where the strain is thickness independent, it could be attributed to the defect-induced spin disorder (spin-glass-like state). These findings may also apply to the thickness dependence of magneto-transport properties of other manganite films deposited on STO and LAO substrates, such as PSMO (Ref. 19) or SCMO.15

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