The effect of substrate induced strain on the charge-ordering transition in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films

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We report the synthesis and characterization of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films grown by the Pulsed Laser Deposition technique on 100 -oriented LaAlO$_3$ substrates. X-ray diffraction (XRD) studies show that the films are 101 -oriented, with a strained and quasi-relaxed component, the latter increasing with film thickness. We observe that transport properties are strongly dependent on the thickness of the films. Variable temperature XRD down to 100 K suggests that this is caused by substrate induced strain on the films.

Hole-doped manganites, with the general formula RE$_{1-x$A$_x$}O$_3$ (RE=rare earth, A=alkaline earth) exhibit a rich phase diagram as a function of the doping concentration $x$. For certain values of $x$ and the average A-site cation radius ($< r_A >$), the metallic state below $T_c$ becomes unstable and the material goes to an insulating state. This is due to the real space ordering of the Mn$^{3+}$ and Mn$^{4+}$ ions in different sublattices. Such a charge ordering (CO) transition is associated with large lattice distortions. This phenomenon has been observed in Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ where $< r_A > = 1.236$ Å. However, most of the work published up to now has been on single crystals or ceramic samples. One study on Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films has been reported in which no CO behavior was observed. Epitaxial thin films have properties similar to those of single crystals and are also important for potential device applications. We have investigated growth of thin films of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and their structural and physical properties. The properties of these films are significantly different from those observed in single crystals of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. We have proposed a model to explain these differences.

Thin films of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ were grown using the pulsed laser deposition (PLD) technique. The target used had a nominal composition of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. The substrates were [100] LaAlO$_3$ (LAO), which has a pseudocubic crystallographic structure with $a=3.79$ Å. The laser energy density on the target was about 1.5 J/cm$^2$, and the deposition rate was 10 Hz. The LAO substrate was kept at a constant temperature of 820 C during the deposition which was carried out at a pressure of 400 mTorr of flowing oxygen. After deposition, the samples were slowly cooled to room temperature at a pressure of 400 Torr of oxygen. Further details of the target preparation and the deposition procedure are given elsewhere.

The structural study was done, at room temperature, by X-ray diffraction (XRD) using a Rigaku diffractometer. Low temperature XRD experiments were performed with a Siemens kristalloflex X-ray diffractometer. DC resistivity was measured by a four-probe method and magnetization was measured using a Quantum Design MPMS SQUID magnetometer. The composition analysis, by Rutherford Backscattering spectroscopy (RBS), indicate a stochiometric composition within error limits.

Fig.1 shows the $\theta - 2\theta$ scan of the films for different thicknesses in the region 45$^\circ$-50$^\circ$. A peak is observed at 46.5$^\circ$ for all thicknesses which corresponds to an out-of-plane parameter of 1.955 Å. Another diffraction peak appears gradually for thicknesses above 1000 Å. This latter peak corresponds to a lattice parameter of 1.92 Å for a 2000 Å film. These two peaks correspond to two phases which we will call phases A and B (where A indicates the phase with the larger lattice parameter). The structure of bulk Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ is orthorhombic (Pnma) with $a=5.43153$ Å, $b=7.63347$ Å and $c=5.47596$ Å. The out-of-plane parameter of the B-phase is equal to the $d_{202}$ of bulk Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. Since this phase, which corresponds to the bulk value, appears for larger thicknesses, we assume that it is the relaxed part of the film with less influence from the substrate. The A-phase is always present, even in the thinnest film, which strongly suggests that it represents the strained phase of the initial layers of the film. The B-phase appears as the thickness is increased, which implies that the film is relaxed after a critical thickness of about 500 Å (see inset of Fig. 1). Moreover, the film is [101]-oriented, i.e. with the [101] axis perpendicular to the substrate plane, which is similar to an a-axis orientation according to the cubic perovskite cell. Note, that this orientation has already been seen in (Pr$_{0.7}$Ca$_{0.3}$)$_2$Sr$_2$MnO$_7$ thin films grown by magnetron sputtering. Detailed studies by Transmission Electron Microscopy are in progress to confirm these results.

The resistivities of three films with different thicknesses are shown in Fig. 2. The 200 Å film is insulating at all temperatures. This layer is formed due to non-uniform distribution of the strain over the film and oxygen defects. On increasing the thickness of the film, the resistivity shows the metal-insulator transition ($T_{MI}$) near 200 K, which is significantly lower than the $T_{MI}$ observed in the bulk compound. This is an effect which has been observed in as-grown thin films of other CMR materials and is attributed to the substrate induced strain on
the rise in the resistivity is not as sharp as observed in single crystals of Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) for different thicknesses. The inset depicts phases A and B which are the strained and the quasi-relaxed phases, respectively (see text). Peaks labeled * and S are due to the sample holder and LaAlO\(_3\) substrate.

FIG. 2. Resistivity vs. temperature of films with different thicknesses. Arrows indicate the T\(_{CO}\) transition.

the film [9]. Also, around 170K, the resistivity starts increasing with decrease in temperature. This is a typical signature of a charge ordering transition (T\(_{CO}\)), but the rise in the resistivity is not as sharp as observed in single crystals of Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\). The effect of a magnetic field on the resistivity is shown in figure 3. A field of 8 T shifts the T\(_{CO}\) to 140 K and also shifts the T\(_{MI}\) to higher temperatures. There is a large reduction of the resistivity for the entire temperature range. These features are qualitatively similar to the behavior observed in single crystals of Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\). When the thickness of the film is increased to 2000 Å, the T\(_{MI}\) shifts to a higher temperature of 240 K as found in bulk. This is a signature of a reduction of the strain on the film [17]. But now the CO transition is suppressed and the resistivity shows a metallic behavior down to the lowest temperatures. This is unexpected since, as the substrate induced strain reduces, the properties should have approached those of the bulk whereas we find film sample is semiconductor below T\(_{CO}\).

The small deviation of composition between the film and the ideal composition, Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\), is not enough to explain the difference between the thin film and the bulk compounds. Two main features need to be clarified:

(1) Why does the 500 Å film show a CO-like behavior whereas the thicker 2000 Å film is metallic at low temperatures?

(2) Why is the transition seen in the 500 Å film not as sharp as seen in bulk?

The thickness dependence of the properties suggests that strain plays an important role in determining these properties. The substrate induced strain can be expected to play an important role especially for the x=0.5 composition. In single crystals of Nd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\), there is an abrupt change of the lattice parameters in the orthorhombic structure which accompanies the CO transition [8]. Is this abrupt change seen in a thin film?

To answer these questions, we performed variable temperature XRD down to 100K in order to check the behavior of the out-of-plane parameter as the temperature is lowered below the bulk T\(_{CO}\). Fig.4 shows the evolution of the d\(_{202}\) between 110 K and 260 K for a 2000 Å film. We also indicate in this graph the evolution of the 202 reflection of a single crystal at low temperatures, according to ref. [8] (at room temperature the 202 reflection of the bulk coincides with that of phase B). From these data, we can see that neither of the film phases has the bulk value of the lattice parameters, below T\(_{CO}\) of the bulk. Thus, it seems impossible to have a sharp CO-transition in the films since the lattice parameters show no sharp change at T\(_{CO}\) nor do they have the same values as the bulk. In other words, the lattice is constrained by the substrate and is unable to change to the low temperature structure observed in single crystals.

The distortion of the lattice is essential for the CO transition, as this decreases the Mn-O-Mn angle and thus the hopping probability, which results in the insulating behavior. The strain does not allow the Mn-O-Mn angle to change significantly in a thin film. However, the A-phase should exhibit a resistivity behavior close to that of a single crystal at low temperatures because the d\(_{202}\) is close to the value of the single crystal below T\(_{CO}\). It can be seen in fig. 2 that the 500 Å film does show a behavior resembling a charge-ordering transition, with the low temperature resistivity similar to the resistivity behavior of a charge-ordering single crystal under a hydrostatic pressure of about 1.5 GPa [4]. It is known that the pressure induced by the substrate is of this order of magnitude. Indeed, it is possible to stabilize in thin film form compounds similar to those synthesized by high-pressure methods [17]. The 2000 Å film is metallic.
FIG. 3. Magnetic field dependence of the resistivity of the 500 Å film and the magnetization as a function of temperature measured in a field of 2000 Oe.

FIG. 4. Temperature dependence of $d_{202}$ for a 2000 Å film. Solid squares and circles refer respectively to phases A and B (see text). Dotted line corresponds to the parameter of a single crystal calculated from Ref.[8].

because of the phase B which forms the top layer of the thicker films. The phase B is the quasi-relaxed phase at room temperature and has an out-of-plane parameter close to that of the bulk at room temperature. This is reflected in the fact that the $T_{MI}$ of the 2000 Å film is close to that of the single crystal. But when the temperature is lowered the lattice parameters of the phase B do not change as in a single crystal as seen (see Fig. 4). This keeps the film in a metallic state. The overall resistivity behavior of the film is due to the parallel combination of the phase A and phase B. When the thickness of phase B exceeds a certain critical value, it changes the current distribution in the film, effectively shorting out the underlying phase A. The effect of phase A can still be seen in the resistivity curve of the 2000 Å film, as marked by the arrow.

In conclusion, we have grown Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films by PLD on [100] LAO substrates. We found that the transport properties depend on the thickness of the film. We show that for intermediate thickness, it is possible to obtain a charge-ordering like behavior. However, thicker films lead to a metallic behavior. This anomalous behavior is due substrate induced strain on the film in the whole temperature range. Further investigations are in progress, in particular, growing films on different types of substrates, to confirm these results.

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