Two-phase behavior in strained thin films of hole-doped manganites

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We present evidence that thin films of La_{1-x}Ca_{x}MnO_{3} (\sim 150 Å in thickness) grown under compressive strain exhibit island growth morphology which leads to a non-uniform distribution of the strain. Transport and magnetic properties of these films suggest the coexistence of two different phases, a metallic ferromagnet and an insulating antiferromagnet. We suggest that the high strain regions of the film due to the strain itself and/or due to the resultant migration of adatoms

Motivated by the idea that the high sensitivity of the properties of manganites to changes in structure and stoichiometry should result in interesting effects when these materials are subjected to a large non-uniform strain we have grown thin films of La\textsubscript{0.67}Ca\textsubscript{0.33}MnO\textsubscript{3} (\sim 150 Å) with different amounts of lattice mismatch with the substrate and have studied the resulting differences in the growth morphology, magnetization and transport. Conductivity and magnetization measurements indicate that the film grown under compressive strain due to lattice mismatch is a mixture of ferromagnetic (metallic) and antiferromagnetic (insulating) regions. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) experiments confirm the island growth of the strained film and a non-uniform distribution of strain over the film. We suggest that the high strain regions are at the edges of the islands and are insulating and the low-strain regions are at the top of the islands and are metallic. The difference in properties may be either a direct effect of the strain on the electronic properties or due to strain induced cation diffusion.

Thin films of La\textsubscript{0.67}Ca\textsubscript{0.33}MnO\textsubscript{3} (LCMO), 150 Å in thickness, were grown on (001) LaAlO\textsubscript{3} (LAO) and (110) NdGaO\textsubscript{3} (NGO) substrates by pulsed laser deposition (PLD). On LAO there is a compressive lattice mismatch strain of \sim 2% for a film of LCMO while on NGO this strain is negligible. The films were grown at a rate of \sim 1 Å/sec. The substrate temperature was 820°C. The films were grown in an oxygen atmosphere of 400 mTorr. The thicknesses were measured by Dektak IIA profilometer. The resistivities were measured by the conventional four-probe method and the DC magnetization was measured using a SQUID magnetometer. The lattice parameters were measured using a Siemens D5000 diffractometer.
equipped with a four circle goniometer. The in-plane lattice constant measurements showed that the films were pseudomorphic with the substrate for this range of film thickness. The nanostructure of the films were measured using a JEOL 4000 EX microscope.

Figure 1 shows the resistivity behavior of a 150 Å film of LCMO on NGO at 0 T and 8.5 T (solid lines). The dotted line shows the \( \rho \) vs. \( T \) behavior of a 150 Å film of LCMO on NGO at 0 T. All data were taken while cooling. The inset shows the normalized \( \rho \) vs. \( H \) behavior of the film of LCMO on NGO, at three different temperatures.

A striking feature of our data is that application of a strong magnetic field causes the low temperature insulating state to become metallic in the strained film. In figure 1 we show that the resistivity of the LCMO film on NGO at 8.5 Tesla has an insulator to metal transition near 200 K. The inset in figure 1 shows the \( \rho \) vs. \( H \) behavior of the film at 5 K. The value of \( M_{\text{sat}} \) is \( \approx 1.8 \mu_B \).

Figure 2 shows the magnetization of the strained film grown on NGO as a function of temperature. The magnetization (\( M \)) starts rising around 250 K but this rise is much slower than what is observed in thicker films of LCMO on NGO[2]. The inset shows the \( M \) vs. \( H \) curve for the film on NGO at 5 K. The saturation value of \( M \) (\( M_{\text{sat}} \)) is \( \approx 1.8 \mu_B \) which is about 50% of the expected \( M_{\text{sat}} = 3.67 \mu_B \) for this compound. This shows that about half the volume of the film is not ferromagnetic at low temperatures. The magnetization of the film on NGO could not be measured due to the paramagnetic nature of the substrate, however, the correspondence of the resistivity behavior to that of the bulk compound suggests that the magnetization will be the same as the bulk material.

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FIG. 3. (a) A 2 \( \mu \text{m} \times 2 \mu \text{m} \) AFM image of the 150 \( \text{Å} \) film of LCMO on LAO showing the formation of islands on the film. (b) An enlarged portion of the image. The profile of the image along the white line is shown in (c). The distance shown by the two arrowheads in (c) shows the typical distance between two islands.

 FIG. 4. (a) A 2 \( \mu \text{m} \times 2 \mu \text{m} \) AFM image of the 150 \( \text{Å} \) film of LCMO on NGO showing the step flow type growth mode. (b) An enlarged portion of the image. The profile of the image along the white line is shown in (c). The two arrowheads define an atomic step of \( \sim 4\text{Å} \).

The ferromagnetic metallic regions in the film and consequently there is a large drop in the resistivity of the sample upon the application of a magnetic field.

The magnetization measurements at 5 K show that the film on LAO has a saturation magnetization value of \( \sim 1.8 \mu_B \) and the expected \( M_{sat} \) for this composition is 3.67\( \mu_B \) which suggests that a significant part (\( \sim 50 \% \)) of the film is not in the ferromagnetic state at low temperatures. The saturation magnetization approaches 3.67\( \mu_B \) as the thickness of the films on LAO is increased i.e., the effect of the substrate induced strain becomes less. Another observation is that on annealing in flowing oxygen at a temperature of 850\( ^\circ \)C for 10 hours, the film on LAO has the resistivity behavior and lattice parameters found in thicker films of LCMO on LAO and a saturation magnetization of 3.4 \( \mu_B \). The AFM images suggest a significant increase in the size of the islands but more controlled experiments are required. This strengthens our claim that the insulating behavior is due to strain induced structural and compositional variations which are removed by annealing the film in oxygen.

To get a better picture of the variation of the strain and composition over the film on LAO, cross sectional TEM (XTEM) studies were performed on a 1500 \( \text{Å} \) film of LCMO on LAO. A thicker film was used for reasons of sample preparation for the XTEM studies. We assume that the first 150 \( \text{Å} \) of this sample is the same as the 150 \( \text{Å} \) film on LAO. Figure 5a shows that on the scale of the distance between two islands (as estimated from the AFM images in figure 3c) there is a significant variation in the contrast of the image. The arrows mark the regions where there is a clear demarcation between two regions of similar contrast. These are the edges of the islands and the distance between the regions marked by the arrows is of the order of the distance between islands as seen from the profile of the AFM image shown in figure 3c (i.e., \( \sim 500 \text{Å} \)). Figure 5b is a schematic diagram showing the expected regions of low and high strains. The variation in
the contrast shows a variation of strain and/or stoichiometry in the film, both of which are expected in the growth of these thin films on lattice mismatched substrates. The properties of hole-doped manganites are sensitive to both these factors. The structure and the stoichiometry affect the transport of the material by tuning the number and mobility of carriers and the bandwidth.

Although very large changes in stoichiometry are required for producing an effective Ca doping of \(x < 0.2\) or \(x > 0.5\), this gives us a possible mechanism for having charge ordered (insulating) regions in the film corresponding to the regions of very high strain i.e. at the edges of the islands. There is also a significant variation of the contrast in the image very near the substrate which reveals the initial wetting layer of the film. An earlier study of the near-interface transport properties of \(La_{0.67}Ca_{0.33}MnO_3\) ultra-thin films grown on LAO and NGO substrates revealed a surface and interface related “dead layer” of about 30 - 50 Å depending on the substrate. This “dead layer” could arise due to this wetting layer. We would like to add here that the effect of tensile strain on the magnetic and transport properties of LCMO is similar to what is observed here. Zandbergen et al. observe a reduced saturation magnetization and a large magnetoresistance at low temperatures in their ultra-thin films of LCMO grown on SrTiO\(_3\) (STO). These properties are attributed to the distortions induced in the film due to the lattice mismatch as inferred from high resolution XTEM experiments. These films, grown under tensile strain, remain insulating at low temperatures even upon application of a field of 8 T. In a recent paper Fäth et al. have shown scanning tunneling spectroscopy data on thin films of LCMO grown on STO substrates which suggests a two phase behavior in the film. On the application of a magnetic field the metallic phase grows at the expense of the insulating phase and the authors show a correspondence between this and the colossal magnetoresistive properties of the material. An LCMO film grown on STO is under tensile biaxial strain and should result in a non-uniform distribution of the strain. The non-uniformity in the strain is a likely origin of the observed two-phase behavior based on our results discussed here.

In conclusion, we propose the following model to explain the properties of LCMO grown on LAO, a film which is under compressive biaxial strain. The film grows in the form of islands. The edges of the islands are regions of high strain and are insulating due to changes in structure and/or stoichiometry. The top of the islands are relatively strain free and only these parts are ferromagnetic and conducting at low temperatures and thus a two-phase state is formed. This explains the reduced saturation magnetization at low temperatures. The insulating regions separating the islands makes the film insulating, down to the lowest temperatures. The insulating regions are driven to a metallic state upon application of a magnetic field which results in a large decrease in the resistivity of the film. For a direct measure of the magnetization in different parts of the film low temperature magnetic force microscopy measurements in the presence of a magnetic field are underway.

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