

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

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We present a study of the effect of biaxial strain on the electrical and magnetic properties of thin films of manganites. We observe that manganite films grown under biaxial compressive strain exhibit island growth morphology which leads to a nonuniform 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 are insulating while the low strain regions are metallic. In such nonuniformly strained samples, we observe a large magnetoresistance and a field-induced insulator-to-metal transition.

Hole-doped manganites display a remarkable sensitivity to various perturbations^{1,2} and such sensitivity results in drastic changes in the sample properties depending on the form of the sample.^{3,4} Thin manganite films display properties different from those of bulk materials, and several papers have reported their anomalous properties as a function of film thickness.⁵⁻⁷ It has been argued that the difference is due to strain induced by lattice mismatch.⁸ Lattice mismatch strain is a biaxial strain which modifies the lattice parameters of the film and it has been shown that biaxial strain has an effect which is fundamentally different from that of bulk strain.⁹ Compressive bulk strain drives the lattice towards cubic symmetry whereas compressive biaxial strain further distorts the lattice. It is essential to understand the effect of substrate-induced strain on the manganite thin films to explain the behavior of the thin films and multilayers of these materials.

In this paper we present evidence that thin films of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (~ 150 Å in thickness) grown under compressive lattice mismatch strain are structurally, magnetically, and electronically nonuniform. We show that this is due to structural nonuniformity caused by the island growth mechanism. This phenomenon is well established in semiconductor heterostructures—which are also thin films grown under biaxial strain—and has been studied extensively, both experimentally and theoretically.¹⁰⁻¹⁴ Studies on the kinetics of the growth of these heterostructures have shown that the minimum energy configuration is a nonuniform strain distribution in the film resulting from a formation of islands. A continuous wetting layer of a few monolayer thickness covers the substrate first and islands are nucleated above this layer on further growth of the film. This island growth mode leads to a variation in the strain on the film, both in the direction normal to the substrate and also along the plane of the substrate, creating regions in the film which are strain relaxed (near the top of the islands) and also some regions (near the periphery of the islands) which have extremely high strain, i.e., much higher than the lattice mismatch strain.¹² This type of strain distribution limits the lateral growth of the islands resulting in uniform island size in the

entire film. This happens due to the diffusion of adatoms away from regions of higher strain as has been observed experimentally.¹⁰ All these factors can lead to structural transitions in the highly strained regions of the film due to the strain itself and/or due to the resultant migration of adatoms.¹²

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 nonuniform strain, we have grown thin films of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (~ 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 nonuniform 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 $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO), 150 Å in thickness, were grown on (001) LaAlO_3 (LAO) and (110) NdGaO_3 (NGO) substrates by pulsed-laser deposition. 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 ~ 1 Å/s. 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 superconducting quantum interference device magnetometer. The lattice parameters were measured using a Siemens D5000 diffractometer equipped with a four-circle goniometer. The in-plane lattice constant

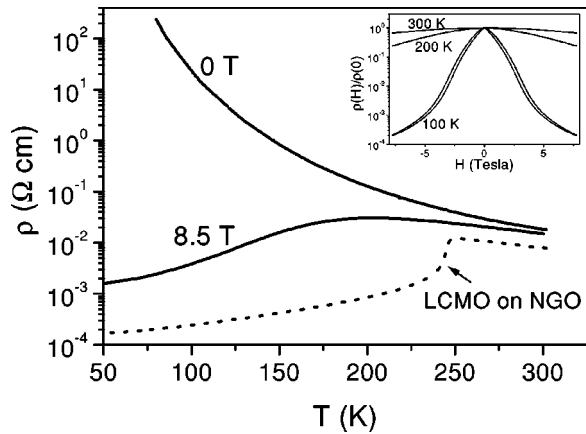


FIG. 1. The ρ vs T behavior of a 150 Å film of LCMO on LAO at 0 T and 8.5 T (solid lines). The dotted line shows the ρ vs T behavior of a 150 Å film of LCMO on NGO at 0 T. All data were taken while cooling. The inset shows the normalized ρ vs H behavior of the film of LCMO on LAO, at three different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

measurements showed that the films were on an average pseudomorphic with the substrate for this range of film thickness, i.e., the in-plane lattice constants are 3.79 Å for the film on LAO and 3.86 Å for the film on NGO. The out-of-plane lattice constant is 3.94 Å for the film on LAO and 3.86 Å for the film on NGO. This shows that the lattice parameters of the film on NGO are very close to the lattice parameters of bulk LCMO which implies that the film on NGO is relatively strain free while the film on LAO is under compressive biaxial strain. The nanostructure of the films were measured using a Nanoscope III AFM operated in the tapping mode. Cross section high-resolution transmission electron microscopy measurements were done using a JEOL 4000 EX microscope.

Figure 1 shows the resistivity behavior of a 150 Å film of LCMO on LAO. The figure also shows the resistivity behavior of a 150 Å film of LCMO on NGO (dashed line). This figure clearly shows the drastic effect of lattice mismatch strain on the transport properties. The film of LCMO on LAO is insulating. In contrast the film of the same thickness on the lattice matched substrate NGO shows a resistivity behavior very close to that of the bulk.

Figure 2 shows the magnetization of the strained film grown on LAO 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 LAO.¹⁵ The inset shows the M vs H curve for the film on LAO at 5 K. The saturation value of M (M_{sat}) is $\sim 1.8\mu_B$ which is about 50% of the expected $M_{sat} = 3.67\mu_B$ 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.

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 Fig. 1 we show that the resistivity of the LCMO film on LAO in a field of 8.5 T has an insulator to metal transition near 200 K. The

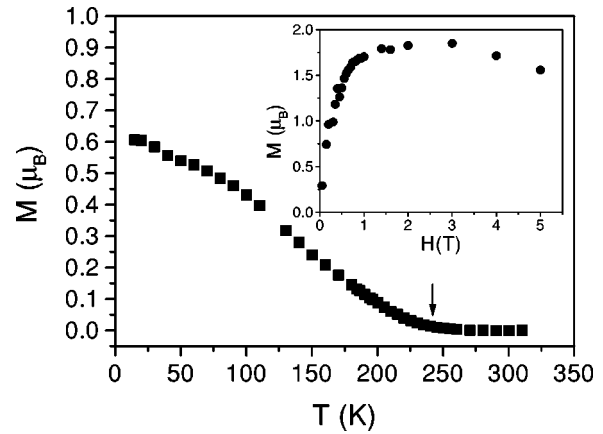


FIG. 2. The M vs T behavior of the 150 Å film of LCMO on LAO in a field of 1000 G. The arrow marks the temperature region where the magnetization starts increasing gradually. The inset shows the M vs H behavior of the film at 5 K. The value of M_{sat} is $\sim 1.8\mu_B$.

inset in Fig. 1 shows the ρ vs H behavior of the film on LAO at three temperatures. At 100 K, ρ drops by about 4 orders of magnitude in a field of 8 T. There is also a significant hysteresis in the ρ vs H curve at 100 K. This behavior of the ρ with H is both quantitatively and qualitatively different from the magnetoresistance behavior of bulk ceramic $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. In the latter the presence of grain boundaries causes a small but sharp drop in the resistivity at low fields followed by a gradual decrease in the resistivity at higher fields.^{3,4} Our ρ vs H data is also different from the low-field magnetoresistance observed in strained ultrathin films of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ which was attributed to domain-wall scattering.⁵ On the other hand, the magnitude of the magnetoresistance and the hysteresis in the ρ vs H curve at low temperatures are similar to that observed in materials which exhibit charge ordering.¹⁶ Our data also resembles that seen in the compound $(\text{La,Pr,Ca})\text{MnO}_3$, now believed to consist of a two-phase coexistence of ferromagnetic metallic and charge-ordered insulating phases,¹⁷ where the field-driven insulator-to-metal transition is induced by a change of the metal volume fraction through a percolation threshold. On the basis of this similarity and the magnetic and transport data discussed above, we argue that the biaxially strained thin film of LCMO grown on LAO exhibits two-phase coexistence whereas the film grown on the lattice matched substrate NGO does not. The origin of the large magnetoresistance in the strained film is due to this phase separation—the magnetic field drives the insulating phase to a metallic phase leading to a metallic conduction path in the film. We emphasize that for this composition of LCMO ($x=0.3$), a highly insulating state due to phase separation has not been observed in the bulk form.

So the important question is: What is the origin of the two-phase coexistence observed in the film grown under biaxial strain which results in properties far removed from the properties of the bulk form of this compound? To answer this we take AFM images of our films as shown in Figs. 3 and 4. At the outset we stress that discontinuities in the film are not the cause. From the AFM micrographs, we have calculated the roughness of the film on LAO to be about 15 Å

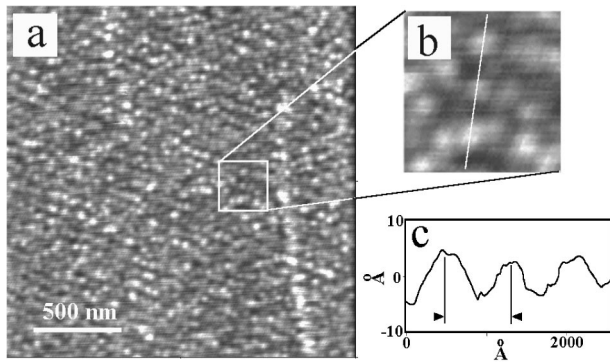


FIG. 3. (a) A $2 \mu\text{m} \times 2 \mu\text{m}$ AFM image of the 150 \AA film of LCMO on LAO showing the formation of islands on the film. (b) An enlarged portion of the image. The profile of the image along the white line is shown in (c). The distance shown by the two arrowheads in (c) shows the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

which is much smaller than the thickness of the film. This and the fact that a magnetic field drives the film metallic at low temperatures, show that the film on LAO is continuous. It is clear from Figs. 3 and 4 that there are significant differences in the nanostructure depending on the strain. The film of LCMO on NGO has negligible substrate-induced strain and the film shows a step flow growth mode. The height of each step is marked in Fig. 4(c). The ρ vs T of this film is very close to that of bulk LCMO, as shown earlier. The film of LCMO on LAO which has about 2% strain, has an island growth mode. As shown in Fig. 1, this film is insulating down to the lowest temperatures. As discussed earlier, island growth leads to a highly nonuniform distribution of the strain. Such a variation of strain in the film may also lead to the migration of the constituent atoms resulting in a compositional inhomogeneity on the scale of the variation of the strain. The large strain at the edge of the islands leads to insulating, and perhaps charge-ordered regions due to structural and/or compositional variations. As mentioned earlier the top of the islands are relatively strain free and these regions are ferromagnetic (metallic) but are separated by the insulating regions at the periphery of the islands. Our resistivity data in a field of 8.5 T suggests that enough of the insulating regions are driven metallic at this field that a metallic path is formed in the sample joining the ferromagnetic

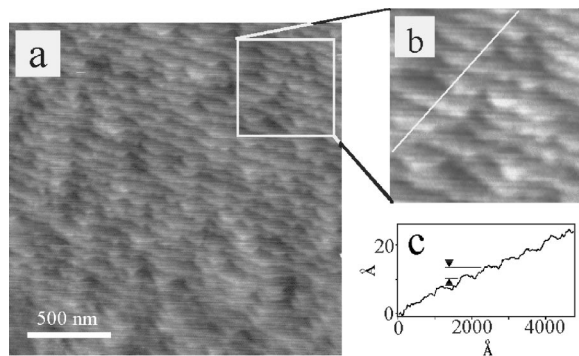


FIG. 4. (a) A $2 \mu\text{m} \times 2 \mu\text{m}$ AFM image of the 150 \AA film of LCMO on NGO showing the step-flow-type growth mode. (b) An enlarged portion of the image. The profile of the image along the white line is shown in (c). The two arrowheads define an atomic step of $\sim 4 \text{ \AA}$.

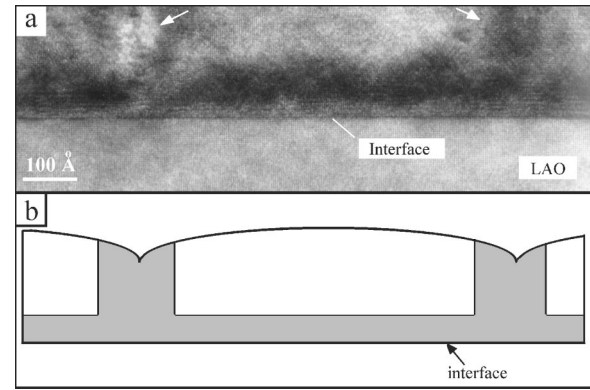


FIG. 5. (a) A high-resolution XTEM image showing the initial layers ($\sim 200 \text{ \AA}$) of a 1500 \AA film of LCMO on LAO. The white arrows show the edges of the islands where there is a large variation in the image contrast showing a variation in the strain and/or stoichiometry. (b) A schematic representation of the regions of low strain (white regions) separated by regions of high strain (shaded gray regions).

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° for 10 h, the film on LAO has the resistivity behavior and lattice parameters found in thicker films of LCMO on LAO, i.e., similar to the resistivity behavior of the LCMO film on NGO shown in Fig. 1, 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 \AA 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 \AA of this sample is the same as the 150 \AA film on LAO. Figure 5(a) shows that on the scale of the distance between two islands [as estimated from the AFM images in Fig. 3(c)] 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 Fig. 3(c) (i.e., $\sim 500 \text{ \AA}$). Figure 5(b) 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 $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ultrathin films grown on LAO and NGO substrates revealed a surface and interface related “dead layer” of about 30–50 Å depending on the substrate.⁶ 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.*¹⁸ observe a reduced saturation magnetization and a large magnetoresistance at low temperatures in their ultrathin 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. In a recent paper Fäth *et al.*¹⁹ 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. A LCMO film grown on STO is under tensile biaxial strain and should result in a nonuniform distribution of the strain. The nonuniformity 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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