

Effect of Tensile Strength on Phase Separated Manganites

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Abstract

The growth conditions for thin films of $(La_{1-y}Pr_y)_xCa_{1-x}MnO_3$ (LPCMO) on a $SrTiO_3$ (STO) substrate were optimized by altering the substrate temperature and oxygen partial pressure during growth. These films are strained due to the mismatch in the lattices of LPCMO and STO which allows for investigation of the effects that tensile strain has on manganites. The films were characterized using x-ray diffraction, resistivity measurements, and magnetization analysis. It was found that these films retain their magnetization even with the additional strain, but they remain in the insulating phase at low temperatures, unlike their unstrained counterparts.

1 Introduction

Manganites are materials with the chemical formula $XMnO_3$. An intriguing characteristic of manganites is that under diverse conditions they display three different phases: ferromagnetic metal, paramagnetic insulator, and charge ordered insulator. At lower temperatures, manganites usually exist in a ferromagnetic metallic state or a charge ordered insulating state. However, the material $(La_{1-y}Pr_y)_xCa_{1-x}MnO_3$ (LPCMO), demonstrates both ferromagnetic and antiferromagnetic properties at the same time, creating a phase separation. At low temperatures, LPCMO also displays a paramagnetic insulator state, making three co-existing phases.

Manganites form in the ABO_3 perovskite structure, a cubic unit cell with the A atoms at the body center, the B atoms at the corner, and the oxygen atoms, X, at the bond centers, as shown in Figure 1.

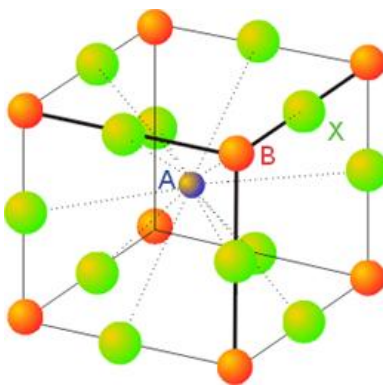


Figure 1: Schematic of the Perovskite Structure.

$SrTiO_3$ (STO), the substrate used for our studies, also has the perovskite structure. However, the lattice spacing of STO is 3.905 Å while LPCMO has a slightly smaller lattice constant of 3.84 Å. This introduces a tensile strain of 1.66% to the LPCMO being grown on the substrate. We can utilize this strain in order to analyze the effects external strain has on the phases and their separation within the thin films.

In previous studies [1], LPCMO was grown on a $NdGaO_3$ (NGO) substrate. The lattice spacing of this substrate and LPCMO are similar; therefore, little to no strain was present in the thin film. Attempts at growing smooth LPCMO films on STO in the past were not successful as clumps of the material formed on the substrate due to the high strain. Our goal in this study was to optimize the conditions for the development of smooth samples in order to compare them to their unstrained growth on NGO.

2 Thin Film Growth

Our thin films were grown using the pulsed laser deposition(PLD) technique. In this method, a substrate is placed on a heater inside a vacuum chamber while the desired material is vaporized from a target by a high power pulsed laser beam. When the pulse hits the target, a plume is ejected towards the substrate, which allows the material to be deposited on its surface. A simple illustration of this process is shown in Figure 2.

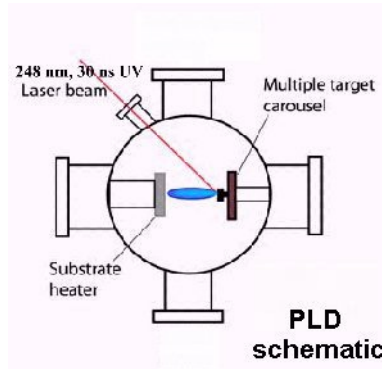


Figure 2: Pulsed Laser Deposition.

During this process, a few variables must be kept under control in order for a smooth film to be grown. The temperature of the substrate as well as the energy of the laser pulses must be monitored. Most importantly, the pressure of the background gas, such as oxygen, must be kept constant as well. These variables play a crucial role in the growth of a thin film and must be tweaked for optimization depending on the target material.

In recent studies [1][2], smooth LPCMO films were grown on NGO substrates at a temperature of 780°C and an oxygen pressure between 100 and 140 mTorr. We decided to start with these values for optimizing the growth on STO substrates. Fortunately, these previous conditions worked well in producing smooth films and only small increases were needed in the background oxygen pressure.

The ablation of our thin films was performed using a Lambda Physik KrF excimer laser at an energy of approximately 400 mJ and a frequency of 5 Hz. The composition of the target was varied to obtain different Pr concentrations. As mentioned before, our samples

were grown in an atmosphere of oxygen, where the partial pressure ranged between 110 and 150 mTorr. The temperature of the substrate remained at 780° C, heated at a rate of 20° C/min. Pre-ablation was performed for five minutes in order to clean the target of possible surface impurities and the deposition time varied between 12 and 24 minutes. The partial pressure of the oxygen was kept at 440 torr during the cool down. Specific details of each film are shown in Table I.

Table I: Sample Growth Conditions

Sample Name	Composition	Temp (C)	Pressure (mTorr)	Deposition Time
061410b	$(La_{.4}Pr_{.6})_{.67}Ca_{.33}MnO_3$	780°	105	12 min
061510b	$(La_{.4}Pr_{.6})_{.67}Ca_{.33}MnO_3$	780°	115	12 min
062910a	$(La_{.5}Pr_{.5})_{.67}Ca_{.33}MnO_3$	780°	150	12 min
070610a	$La_{.67}Ca_{.33}MnO_3$	780°	105	12 min
071310a	$(La_{.5}Pr_{.5})_{.67}Ca_{.33}MnO_3$	780°	150	24 min

3 X-Ray Diffraction

After the thin films were grown, X-ray diffraction was used to confirm the growth of LPCMO. These measurements were performed on the sample by one of our lab’s graduate students, Hyuong Jeen Jeen. As seen in Figure 3, the large central peak is due to the STO substrate, while the shorter peak accompanying it is due to the LPCMO film. The large peak occurs at an angle of 46.6°. By using Bragg’s law, $n\lambda = 2d\sin\theta$, with n being 2 and λ equal to

the wavelength of the x-ray used for the diffraction (1.54 \AA), we can calculate the lattice spacing of the substrate. This value falls around 3.90 \AA which is close to the observed value mentioned above for STO. The shorter peak gives a lattice spacing of 3.80 \AA for LPCMO. This is smaller than 3.84 \AA because the out-of-phase lattice constant is reduced when the in-plane lattice constants are stretched due to tensile strain from the STO substrate.

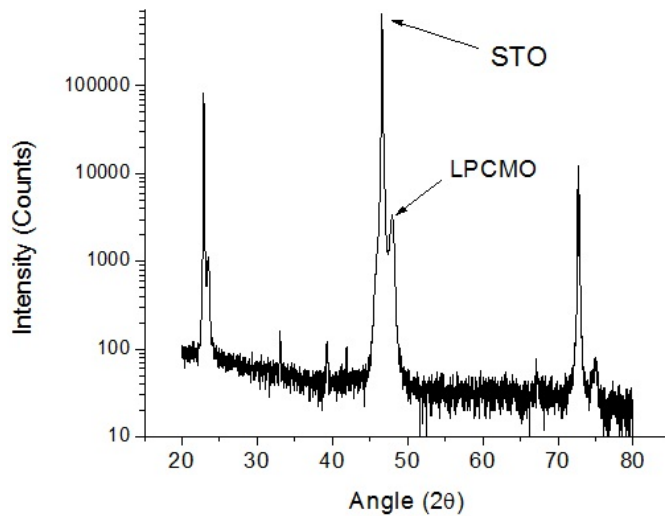


Figure 3: X-ray diffraction for sample 061410b, showing peaks for STO and LPCMO.

4 Atomic Force Microscopy

In order to determine the smoothness of our thin films, we utilized tapping mode atomic force microscopy (AFM). AFM consists of a cantilever with a very fine tip that has a curvature on the order of nanometers. Like most setups, our AFM incorporates a laser beam deflection

system. The laser beam is reflected off the back of the cantilever and is analyzed by a position-sensitive detector. In the tapping mode, the cantilever is oscillated near the surface, where it encounters the various forces generated by its proximity to the sample. The amplitude of the cantilever's oscillation changes accordingly, and the deflection of the laser light is recorded, generating an image of the surface of the desired sample. Figure 4 illustrates the difference between one of our smooth films and an earlier attempt at producing one, which shows many island-like clumps.

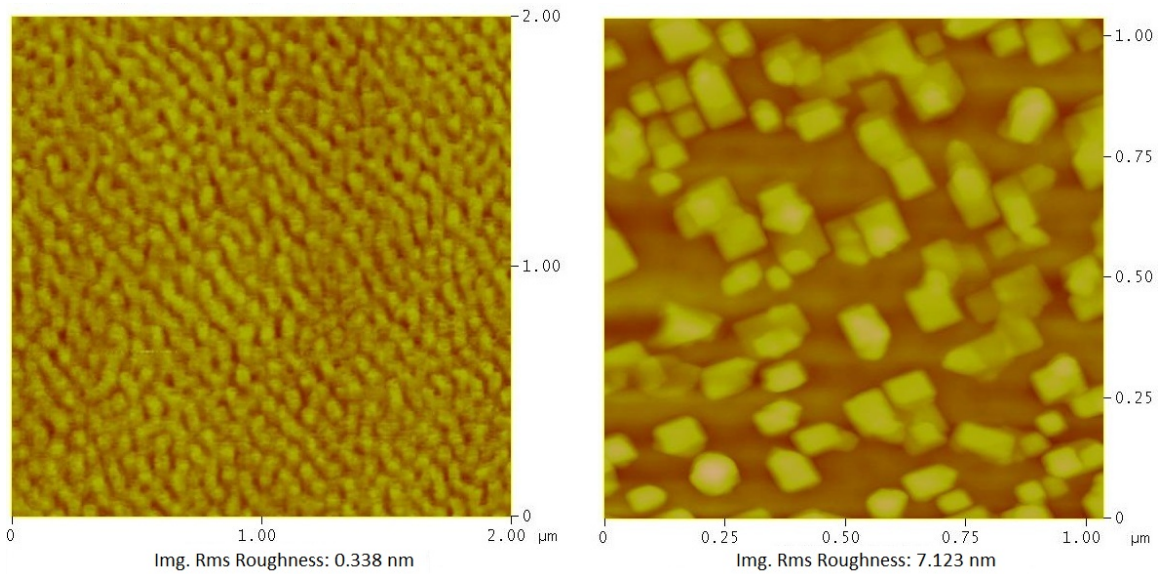


Figure 4: AFM done on LPCMO films. Left image is the result of this project, while the right image is an earlier result.

AFM can also be used to determine the thickness of the film. First, the film is etched by covering a portion of the sample with a protectant. The sample is then exposed to a chemical, which destroys the thin layer on top of the substrate that is not covered. Using

this method, we measured the thickness of the film by scanning the boundary with the AFM. The thickness of our LPCMO films deposited for 12 min was measured to be approximately 280 Å. On previous NGO substrates, this thickness was roughly 310 Å. The slight change of thickness between the substrates is most likely due to the way they adhere to the surface upon deposition, which varies for each substrate. The strain introduced by STO also stretches the film, decreasing its thickness.

5 Resistance vs. Temperature Measurements

After creating acceptable films, we ran them through various procedures in order to determine their characteristics. The simplest of these methods was a resistivity vs. temperature measurement. After carefully placing contacts on the outside of the thin film, our samples were placed in a dewar where the temperature was lowered and the resistivity was measured at different increments. The curve produced by this measurement can identify whether the thin film is insulating, metallic, or possibly a mixture of the two.

Our results show that LPCMO grown on STO stays insulating at lower temperatures, unlike on NGO. As can be seen in Figure 5, the curve for the thin film on NGO has a smooth transition from insulating to metallic, while the curve for the film on STO maintains its high resistance at lower temperatures. We attempted to force this insulating phase into a metallic one by applying a magnetic field on the samples. This was done by slowly ramping up the magnetic field to 8 Tesla and observing the current across the sample. A drastic jump in

the current would have suggested this shift. However, we did not observe this increase in current; therefore, the STO films retained their insulating phase even in the presence of a high magnetic field.

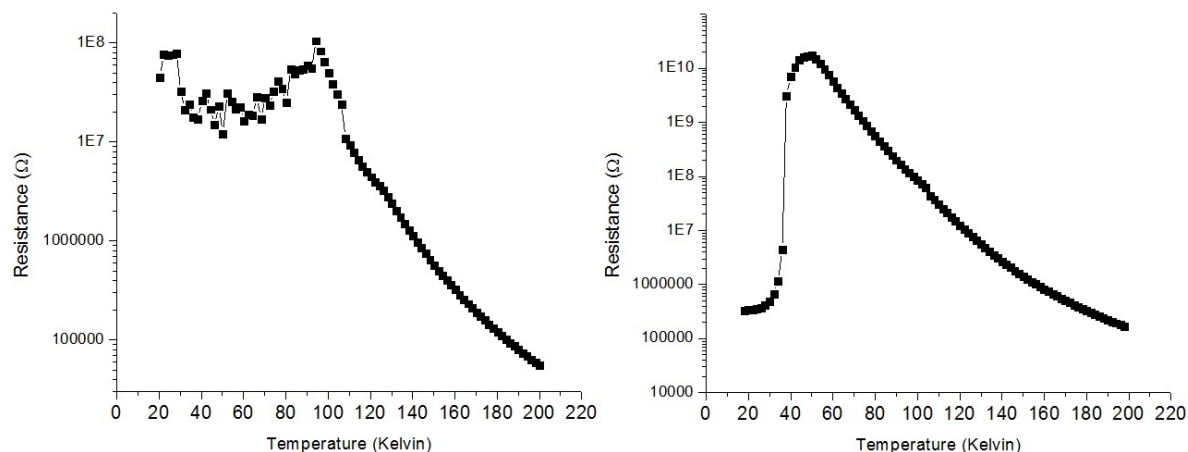


Figure 5: Left: Curve of strained LPCMO, showing high resistivity at low temperatures (Instability in measurement at high resistance), Right: Curve of LPCMO on NGO, showing a smooth transition into a metallic phase at low temperatures

We made another attempt to alter the phase of our LPCMO films through annealing. Annealing is a heat treatment that is done by increasing the temperature of the sample above the recrystallization value. This temperature is then maintained for a set time and then the sample is cooled. Annealing has numerous effects on different materials, such as relieving internal stress and refining the structure. Sometimes adverse effects can occur and other times annealing leaves the film unchanged. We broke one of our LPCMO films into two sections and placed them in the annealing tube for 30 and 90 min. We maintained a temperature

of 550° C during this time frame and after cooling, we placed contacts on each sample in order to measure their resistance at low temperatures. Unfortunately, the insulating phase was impervious to the annealing. The annealing also increased the roughness of the thin film.

One last test was to measure the interface between the substrate and the thin film. In previous studies [3], it has been suggested that the interface between a non-polar substrate and a polar film could create a different phase from the rest of the film. In our scenario, where the substrate and the film are both insulating, it has been proposed that due to polar catastrophe, the interface could become metallic. We tested this theory on our LPCMO films first by scratching down to the substrate and applying the contacts in these dug out areas. We also tried another method, by cleanly breaking off the film's edges and applying contacts here instead of on top of the film. For each of these situations, we were unable to measure a metallic interface.

6 SQUID Magnetometer

A SQUID magnetometer was used to measure the magnetic moment of the samples as a function of temperature and an external magnetic field. A SQUID consists of two superconductors separated by thin insulating layers to form Josephson junctions. This setup allows for great sensitivity in measuring changes in a magnetic field. After the sample is loaded into the SQUID, the magnetic field generated by the sample is measured.

Due to time constraints on the SQUID, we performed this magnetization measurement on two of our samples. The results are shown in Figure 6. Although our previous measurements demonstrate that these samples maintain an insulating phase at low temperature, it is worthwhile to check their magnetization in order to evaluate the presence of ferromagnetic properties. Interestingly enough, both of our tested samples follow a hysteresis curve, which confirms that they retain some ferromagnetic characteristics even with the added external strain.

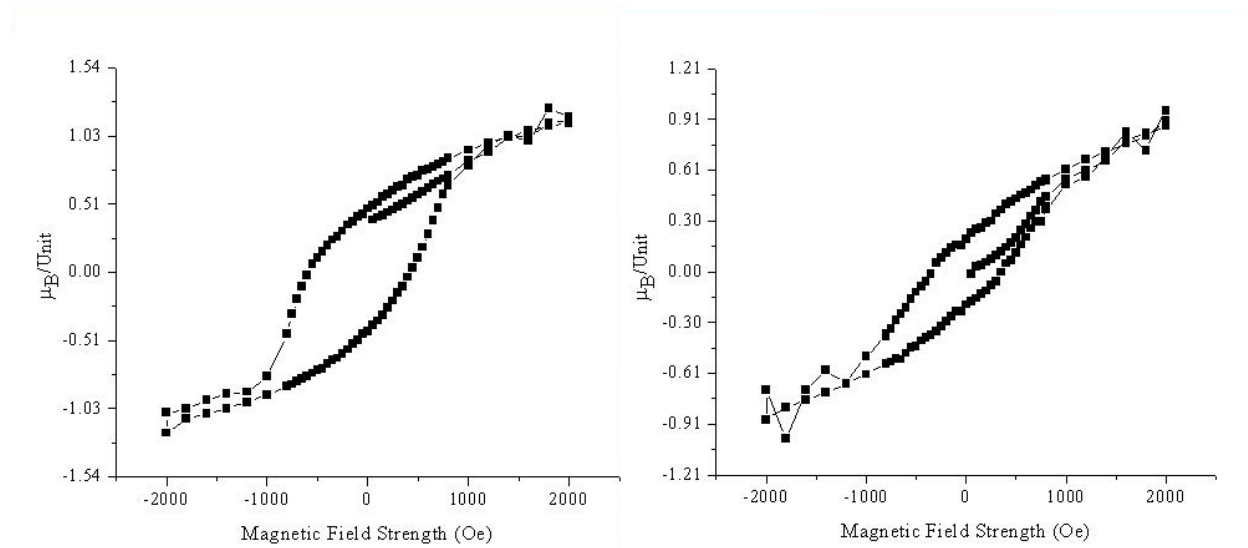


Figure 6: LPCMO films showing hysteresis loop. Left: LP6 (061410b) Right: LP5 (062910a)

7 Conclusion

As has been detailed, the effect of the external strain introduced by the STO substrate has a major effect on the phase of the film. Even after exposure to a high magnetic field and

annealing procedures, the LPCMO films remain insulating. These same films grown on NGO show a metallic behavior. The ability to switch between these two phases by applying tensile or compressive strain is a pleasing idea in physics and is an exciting opportunity for future applications. This study will be extended by applying direct external strain to these various films and observing the changes from the metallic to insulating states [4]. Also, additional LPCMO films will be grown on STO with higher oxygen pressures in hopes of developing a metallic phase that exists in the presence of the tensile strain.

8 Acknowledgements

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References

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