Structure of nanometric epitaxial films of magnetorresistive $La_{0.7}Ca_{0.3}MnO_3$ manganite

J. Rubio-Zuazo*, A. de Andrés [1], C. Prieto [1], S. Taboada [1] and G. R. Castro*[,1]

*SpLine Spanish CRG Beamline at the ESRF, ESRF- BP 220 -38043 Grenoble cedex - France. rubio@esrf.fr, spline@esrf.fr

[1]Instituto de Ciencia de Materiales de Madrid - ICMM/CSIC Cantoblanco E-28049 Madrid, Spain

Abstract

The fabrication of thin films is an easy way to obtain single crystals of magnetoresistive manganites and an unavoidable step to obtain spin-valves. Nevertheless, thin films, even for the most stable manganites (1/3 doping), are extremely susceptible to a large number of parameters as deposition temperature, annealing, oxygen atmosphere, substrate, strain effects etc.

We have grown epitaxial $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) films (thickness: 27 and 2.4 nm) and studied their structure. LCMO thin films were grown by dc sputtering technique on $SrTiO_3$ (100) substrates at room temperature and studied by GID (Grazing incidence X-Ray Scattering).Bulk LCMO is a distorted perovskite (Pbnm space group) with similar but different in-plane parameters $a \approx b <\approx a_{STO}\sqrt{2}$ and $c<\approx 2a_{STO}$. The in-plane lattice parameters a and b, of the obtained epitaxial films, matches the substrate giving rise to a square lattice. Because of the larger unit cell of the manganite, compared to STO, reflections with half integer cubic indices (referred to the $SrTiO_3$ lattice) are expected and actually detected.. The oscillations due to the finite thickness of the films are seen in the high angle diffraction peaks evidencing the high quality of the films. The samples were studied by optical interferometry revelling some defects on the surface. Between defects the roughness is about 4 Å rms. Both films adopt exactly the STO parameter in the plane of the film while the out of plane c parameter is slightly reduced. The strain of the films could be relaxed at the surface by creating such defects. Meshes around Bragg peaks were performed showing an elongated charge distribution in particular directions.

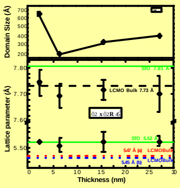
Remarkable is the disappearance of the half integer peaks in the $(1,0,\ell)$ scan and of the integer peaks in the $(1.5,0.5,\ell)$ scan for the 2.4 nm film. Simulations of the structure factor indicate that a tilt of the Mn-O octahedra and a displacement of the R ions similar to the bulk orthorhombic structure are present in the films thicker than 2.4 nm (3 unit cells). But in the thinnest film, La ions remain at regular positions of the perovskite and no tilt of the octahedra can occur. In summary, a structural phase transition has occurred when the layer thickness is reduced to 2.4 nm. Different symmetry groups were associated to such phase transition.

Grazing Incidence X-Ray Diffraction (GID)

The diffraction patterns were obtained in a 6 circles diffractometer at the ID03 beamline at the European Synchrotron Radiation Facility (ESRF), in the vertical geometry with an incident energy of 17.2 keV (λ =0.72 Å). The incidence angle was maintained at 0.3 ° so the layer signal is maximized

Epitaxial lattice parameters:

The first goal concerns with the structure determination of the grown LCMO films. The STO lattice was used as reference lattice.

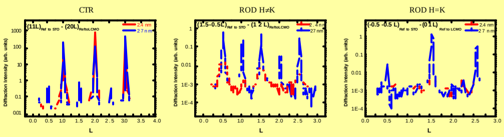


We have found signal at partial h,k,l values, which are associated to the manganite films. A first guess concludes that the films grow in a pseudomorphic way. The manganite layer adopts the lattice parameter of the substrate in the ab plane (in-plane) while the out-of-plane parameter maintains the bulk manganite parameter. **The unit cell volume changes respect to the bulk structure inducing strain in the layer.**

From the measured peak width the domain size is obtained. For films thicker than 2.4 nm the domain size increases with thickness. This behavior indicates that thicker samples are less stressed. The 2.4 nm sample show bigger domains probably caused by a structure change. The stress induced in this sample by the epitaxy is relaxed by changing the structure to a more stable phase.

When a crystal is truncated, the lattice normal to the surface is no longer periodic so the reflections instead of being punctual are continuous in this direction. Out-of-plane scans were performed in different Bragg reflections. CTR scans (Crystal Truncation ROD) correspond to reflections arising from the truncation of the crystal. Both, the substrate and the manganite layer, contributes to the CTR signal. ROD scans corresponds to the superstructure reflections which are not allowed for the substrate. Only the manganite layer contributes to the ROD signal.

Due to that the c parameter (out-of-plane) of the bulk manganite is twice the lattice parameter of the STO (substrate) reflections with half integer L indices will be present. Also due to the $\sqrt{2}$x$\sqrt{2}$R45 superstructure reflections with a,b (in-plane) half integer cubic indices (referred to the STO lattice) will be also present. So looking for the half integer peaks one can see if the sample behaves as the bulk manganite.



The figure above shows as example one CTR and two ROD´s taken from the recorded database based on 50 different reflections (CTR's and ROD's). Clearly we distinguish different behaviour for the two samples. We found systematic extinctions characteristic from the bulk structure in the 2.4 nm sample. Remarkable is the disappearance of the half integer peaks in the CTR's scans and of the integer peaks in the ROD's scans with H≠K for the 2.4 nm film. In the ROD's scans H=K (superstructure crystallography axis) no peaks were found for the 2.4 nm film.

Based on the extinction of these reflections joined to the sudden increase of the domain size for the 2.4 nm sample we conclude that a **different phase occurs for layer thickness below 2.4 nm**

The table resumes the conditions limiting possible reflections obtained from the systematic extinctions. The 2.4 nm film could be associated to different space groups (either tetragonal or orthorrombic) by inspection of the International Tables for X-Ray crystallography:

- Tetragonal: I4/mcm, $P4_2bc$, I4cm, I4c2, $P4_2/nbc$, $P4_2/ncm$
- Orthorhombic: Ibam, Iba2, Pbcn

Conditions limiting possible reflections (Not Forbidden)

2.4 nm	27 nm
hkL: h+k+L=2n h0L: h=2n-1,L=2n h=2n,L=2n-1,L=2n 0kL: L=2n,2n-1	h0L: h=2n,L=2n-1 0kL: k=2n,L=2n-1

Structure Factor

The diffracted intensity is proportional to the square of the structure factor which includes the atomic position for the unit cell atoms. The 2.4 nm film phase could be determined by evaluating the structure factor expression so conditions limiting possible reflection are fulfilled. The bulk manganite structure is Orthorhombic with space group Pbnm (D_{2h}^{16}). The structure factor for this space group is

$$F_{hkL}Mn(q) = f_n(q)Mn\left[e^{i\pi h} + e^{i\pi k} + e^{i\pi(h+L)} + e^{i\pi(k+L)}\right]$$

$$F_{hkl}La/Ca(q) = \left\{1 + e^{i\pi[h+k(-4y+1)+L]} + e^{i\pi[h(-4X)+k(-4y)+L]} + e^{i\pi[h(-4X+1)+k]}\right\}\sum_{n}^{4} f_n La/Ca(q) e^{i2\pi\left(hX+ky+\frac{L}{4}\right)}$$

$$F_{hkl}O_1(q) = \left\{1 + e^{i\pi[h+k(-4y+1)+L]} + e^{i\pi[h(-4X)+k(-4y)+L]} + e^{i\pi[h(-4X+1)+k]}\right\}\sum_{n}^{4} f_n O(q) e^{i2\pi\left(hX+ky+\frac{L}{4}\right)}$$

$$F_{hkl}O_2(q) = \left\{1 + e^{i\pi[h+k(-4X+1)+L(-4Y)]} + e^{i\pi[h(-4X)+k(-4y)+L]} + e^{i\pi[h(-4X+1)+K+L(-4Z+1)]} + e^{i\pi[h(-4X)+k(-4Y)+L(-4Z)]} + e^{i\pi[h(-4X+1)+k]} + e^{i\pi[L(-4Y+1)]} + e^{i\pi[h+k(-4y+1)+L]}\right\} f_n O(q)\sum_{n}^{8} e^{i2\pi(hX+kY+LZ)}$$

Evaluating the structure factor expressions we obtain that:

- **The 27 nm sample behaves as the Pbnm predicts** with the Mn at 4a, La/Ca ans O(1) atoms at 4c position and O(2) atoms placed at 8d position. **The 27 nm sample presents bulk like structure.**
- **The 2.4 nm sample could not be explained with the bulk like structure.**

Structure models

- **The 27 nm sample shows the behavior characteristic of Pbnm space groups where the R ions displaces from the cubic position and the Mn-O octahedra tilts and distorts.**
- **The 2.4 nm sample** shows a different behavior where some reflections characteristic of the Pbnm space group are not present. Evaluations of the structure factor indicates that **the R ions remains at the regular position of the perovskite and no tilt of the Mn-O octahedra can occur**. The octahedra can be distorted in two ways: **A rotation of the basal plane of the octahedra can occur accompanied by a rotation of the above and below octahedra (model 1). Or a Q_2 distortion can occur in the Mn-O octahedra so the just below and above octahedras distorts -Q_2 (model 2)**

Introduction

Strain effects in epitaxial films are usually claimed to explain the reduction of T_C by more than 100 K compared to bulk values. But the further reduction of T_C, down to about 60-100 K, as thickness is reduced, cannot be related to changes in the strain of the epitaxial films since their in plane lattice parameter is constant by "construction". The weakening of the double exchange interaction [1] or changes in the composition, as self-doping by vacancies, as the thickness is reduced have been used to explain it. Ziese et Al.[2] report that the slight decrease of T_C in relaxed films is in agreement with the finite size scaling theory [3] while its drastic reduction in films grown on $SrTiO_3$ (STO) is related to strain effects.

In a previous work[4] **a magnetic study of the samples were made showing a drastically decrease of T_C when thickness is reduced while the remanent magnetization was constant except for the 2.4 nm sample where it drops drastically.**

A detailed structural study of ultrathin manganites films is necessary to explain the magnetic behavior of the epitaxial samples, especially for the 2.4 nm film.

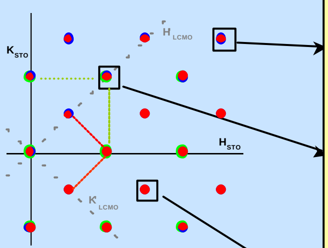
LCMO thin films were grown by dc sputtering technique on STO (100) at room temperature in an atmosphere of Ar and O_2 (ratio 4:1) at a rate of 4.5Å min. The films were annealed at 800ºC for 10 min in an O_2 flux. The thickness of the samples were obtained by low angle X-Ray diffraction. A detailed structural study of the samples was made by performing GID experiments and phase interferometry measurements.

Possible mechanism of relaxation

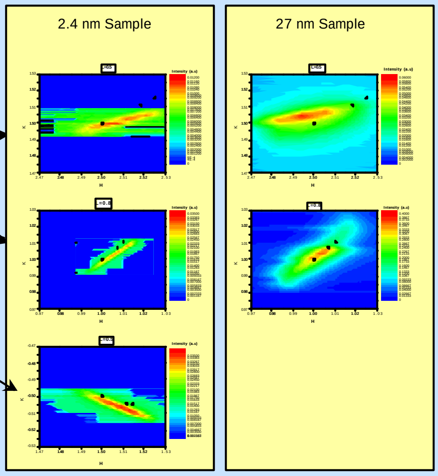
The unit cell volume changes respect to the bulk structure inducing strain in the layer. The samples could be relaxed by different mechanism.

- **Facets formation:** One possible mechanism for relaxing a system is the formation of facets. We have looked for them, but **no Facets were found**
- **Relaxation of the lattice parameters:** The strain layer will try to relax to its ideal structure, so a change in the lattice parameter will occur. We have performed reciprocal space maps around CTR reflections and ROD reflections so the peak profiles could be obtained.

Bulk LCMO is a distorted perovskite (Pbnm space group) with similar but different in-plane parameters $a \approx b <\approx a_{STO}\sqrt{2}$ and $c<\approx 2a_{STO}$. The in-plane lattice parameters a and b, of the obtained epitaxial films, matches the substrate giving rise to a square lattice. Because of the larger unit cell of the manganite, compared to STO, a superstructure rotated 45º is created $\sqrt{2}$x$\sqrt{2}$R45.



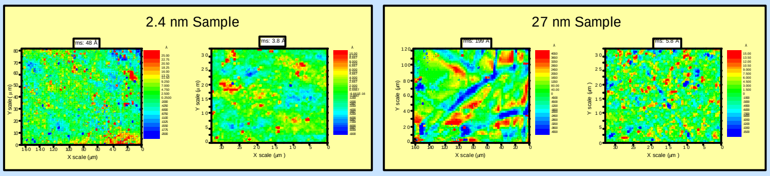
In this figure the square lattice is drawn as both domains of the Orthorrombic phase (Manganite bulk structure)



The reciprocal space maps show clearly that **the lattice parameter is elongated in direction of the relaxation to the orthorhombic structure.** The elongation contains the lattice parameter of the substrate evidencing the epitaxial behavior of the samples.

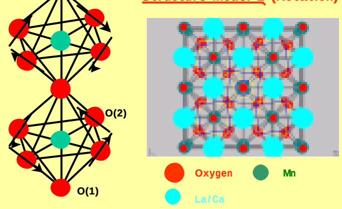
In the 27 nm film the elongation is larger than in the 2.4 nm film. A relaxation to the bulk structure can occur where as thicker is the layer more relaxed it is.

- **Phase shift interferometry:** The phase shift interferometer uses a reference beam to create fringe interference patterns, or interferograms. From these patterns a 3D roughness map is obtained. A Micromap 512 profiler was used

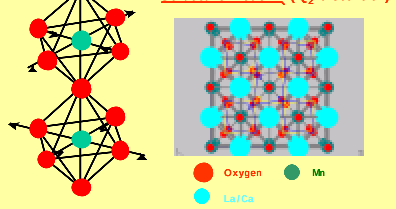


The samples presents defects on the surface which could be the way how the strain is relaxed. In smaller areas ~ 30 μm x 30 μm a roughness of few amstrongs is obtained

Structure model 1 (Rotation)



Structure model 2 (Q_2 distortion)



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