Strain study of ultrathin epitaxial films of $La_{0.66}Ca_{0.33}MnO_3$ on $SrTiO_3$

J.Rubio-Zuazo[1], A.de Andrés[2], S.Taboada[2], C.Prieto[2], J.L.Martinez[2] and G.R.Castro[1,2]

[1] *Spanish CRG beamline at the European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble,France.* rubio@esrf.fr
[2] *Instituto de Ciencia de Materiales de Madrid, Consejo Sup. de Investigaciones Científicas.Cantoblanco E-28049, Madrid, Spain.*

It is well known that compounds of mixed valence manganites with a perovskite structure $La_{1-x}Ca_xMnO_3$ present colossal magnetoresistance properties (CMR) accompanied by a combined paramagnetic-ferromagnetic and insulator-metal (IM) transitions. Several models as the double exchange mechanism or a strong electron-phonon Jahn-Teller distortion are usually used to explain the behavior of such compounds in bulk form. However, when these compounds are grown in thin film form, the properties of these materials change drastically obtaining larger MR at lower temperatures [1]. Recent publications have shown that the changes of the thin film properties respect to the bulk are highly sensitive to the preparation method, i.e, deposition technique, deposition recipe and chosen substrate [2,3]. These changes are usually attributed to structural disorder effects, as partial strain relaxations or dislocations formations, but remains still more unclear than in bulk compounds. In the present work we present a detailed study of ultrathin epitaxial films of $La_{0.66}Ca_{0.33}MnO_3$ (LCMO), with thicknesses between 2.4 nm and 27 nm, grown on $SrTiO_3$ (001) substrates. Bulk LCMO is a distorted perovskite (Pbnm space group) with similar but different in-plane parameters with a lattice mismatch of ~1% respect to the STO in the ($\sqrt{2}$x$\sqrt{2}$R45) superstructure. The in-plane lattice parameters, a and b, of the obtained epitaxial films, matches the substrate giving rise to a square lattice. The samples were grown by dc sputtering technique at room temperature in an atmosphere of Ar and O_2 (ratio 4:1) at a rate of 4.5 Å min. The films were annealed at 800 ^{0}C for 10 minutes in an O_2 flux. The thicknesses of the films were obtained by low angle X-Ray diffraction. 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 is constant except for the 2.4 nm sample where it drops drastically. Our X-Ray diffraction measurements show a change in the crystal structure for the 2.4 nm sample while the bulk structure remains for thicker films. If the samples are completely pseudomorphic then they should be completely strained which could influence the magnetic behaviour of the samples. It is clear that a detailed structural study should be made taking special attention to strain effects induced by the epitaxial character of the samples and possible ways of relaxation, as the formation of facets or dislocation in order to elucidate if the changes in the magnetic properties are due to strain effects or due to a crystal structure change.

In this work we present a detailed X-Ray diffraction study performed at the insertion device beamline ID03 at the ESRF. The diffraction patterns were obtained in a six-circle diffractometer in vertical geometry with an incident energy of 17.2 KeV (λ=0.72 Å). The incident angle was fixed at 0.3^0 so the layer signal is maximized. Reciprocal space maps for three different reflections, (1 1 0.8), (1.5 –0.5 0.5) and (2.5 1.5 0.5) in the notation of the cubic STO, were performed for the 2.4 nm sample and for a thicker sample (27 nm).

Both substrate and film will contribute to the diffracted intensity of the (1 1 0.8) reflection while in the superstructure reflections (1.5 –0.5 0.5) and (2.5 1.5 0.5) will only contribute the manganite layer. From the shape of the diffracted peak obtained in these maps the layer in-plane lattice parameter distribution is obtained. If the epitaxial samples were fully strained with in-plane lattice parameters equal those of the substrate then a circular peak shape with width given by the domain size will be obtained. If the samples were partially relaxed then differences in the peak shape will be obtained. The reciprocal space maps performed for both samples clearly shows a uniformly elongated peak in direction to the (00) for all reflections measured. The elongation is about 1% respect to the STO lattice parameter (in the $\sqrt{2}x\sqrt{2}R45$ notation). This elongation covers the range from the (STO) substrate lattice parameter to the LCMO bulk lattice parameter. This is attributed to a change in the in-plane lattice parameters due to a partial strain relaxation. The ratio of intensities of the three reflections is different in both samples. A code has been developed in order to simulate the diffraction line shape (in single scans or H-K maps) and the CTR/ROD intensities. This programme code takes into account the diffractometer resolution, i.e., broadening induced by the diffractometer slits and polarization factor. It also includes the effects of domains sizes, different atomic positions and occupancies over the film thickness, changes in lattice parameters, roughness as steps in the surface, etc. The reflection intensity ratios for the thinnest sample (2.4 nm) could not be simulated using the Pbnm crystallographic space group while the 27 nm sample is perfectly simulated using the bulk structure, which is in agreement with the previous reported work. For the 2.4 nm the strain relaxation is in accordance with a model where the lattice parameter changes from the epitaxial lattice parameter for the interface with the substrate layer up to the bulk lattice parameter for the outmost layer. The 27 nm sample could be simulated with the same model but using the Pbnm crystal structure. In this sample we cannot distinguish if in the first layers of the interface is present the 2.4 nm sample structure. Compounds with lower Ca doping reduce the lattice mismatch with the substrate [5] giving rise to Ca segregation to the surface favouring the lattice parameter change. According to this segregation model the first layers of the sample will grow pseudomorphic and a change in its lattice parameter will occur while increasing the thickness up to the bulk lattice parameter. In this simple model the sample is relaxed all over the layer. With this model one can then associate the change of the magnetic behaviour to the crystal structure change. This segregation model is in agreement with angle resolved photoemission measurements performed elsewhere [6].

[1] *H.W.Zandbergen, S.Freisem, T.Nojima, and J.Aarts. Phys.Rev.B 60,14 (1999) 10 259*
[2] *T.Y.Koo, S.H.Park, K.B.Lee and Y.H.Jeong. Appl. Phys. Lett 71, 7 (1997) 977-979*
[3] *J.H.Song, J.H.Park, Y.H.Jeong and T.Y.Koo. Phys. B 312-313 (2002) 729-731*
[4] *A. de Andres, J. Rubio, G.R.Castro, S.Taboada, J.L.Martinez and J.M.Colino. Appl. Phys. Lett 83, 4 (2003) 713-715*
[5] *S.J.Hibble, S.P.Cooper, A.C.Hannon,I.D.Fawcett and M.Greenblatt. J.Phys.: Condens. Matter 11 (1999) 9221-9238*
[6] *J.Choi, J.Zhang, S.H.Liou, P.A.Dowben and E.W.Plummer. Phys.Rev.B 59, 20 (1999) 13453*