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Application for beam time at ESRF – Experimental Method

Template for ESRF Standard proposals, CRG proposals, MX Rolling Crystallography and MX Rolling BioSAXS proposals.
This document should consist of a **maximum** of **two A4 pages** (including references) with a minimal font size of **12 pt**.

Proposal Summary (should state the aims and scientific basis of the proposal) :

We propose the study by XRD and XPS/HAXPES of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) epitaxial thin films deposited on $SrTiO_3$ (STO) by pulsed laser deposition with and without a segregated non ferromagnetic layer (NFL) induced by epitaxial strain during deposition. The presence of this flat and uniform NFL is highly dependent on the growth conditions and the magnitude of the biaxial strain induced by epitaxy. This NFL, referred in the literature as dead layer, seems to be of antiferromagnetic (AFM) nature and it appears at the top surface of a ferromagnetic (FM) layer.

The aim of this work is to prove whether the loss of ferromagnetism (FM) is due to tiny perturbations caused by biaxial strain, therefore breaking the degeneracy of Mn 3d e_g and t_{2g} orbitals due to the tetragonal distortion. The NFL can be induced due to such small crystal structure deformations as 0.1Å, deformations that we cannot detect with our X-ray diffraction or TEM techniques. Thus, we propose to study 4 different samples, one without NFL and 3 with different thicknesses of the NFL, by XRD and XPS/HAXPES, to explore the microscopic origin of the NFL in comparison with standard FM films by searching for small deviations of the crystal lattice which could be responsible for the segregation of the new phase, which might be coupled to the presence of oxygen deficiency or cationic defects.

Scientific background :

One of the parameters governing the physics of manganites is the geometry of the MnO_6 octahedra in the perovskite structure. The strain-induced elongation, compression, or rotation of the MnO_6 units lead to crystal field splitting of the $x^2 - y^2$ and $3z^2 - r^2$ levels, thus modifying their electron occupancy and leading to complex orbital reconstruction [1,2]. Thus, manganites are good candidates among the complex oxides for the tuning of physical properties by controlling the electron occupancy of the Mn 3d orbitals via strain.

Previous works have demonstrated that the substrate induced strain effect plays an important role in the formation of an NFL, commonly referred in the literature as dead layer, either close to the substrate−film interface or the free surface of the film. The loss of ferromagnetism can have different origins, some of them of chemical nature such as oxygen vacancies that expand the lattice unit cell volume, Mn valence instabilities at the surface of LCMO grown on LAO due to the formation of Mn^{2+} by air exposure , cation segregation or interface chemical diffusion .

In our samples, a chemical origin for the NFL has been in principle discarded by a careful spectroscopic analysis carried out by STEM-EELS on LCMO layers with NFL. From these studies the chemical composition and the nominal valence of Mn seems to be homogeneous throughout the whole layer thickness at room temperature within the experimental accuracy of these techniques, so cation segregation and the presence of oxygen vacancies were discarded as the cause of the formation of the observed NFL. As explained before, the ferromagnetic ordering could also be suppressed by structural modifications related to the film growth modifying the magnetic ordering. Tiny perturbations caused by biaxial strain may break the degeneracy of Mn 3d e_g and t_{2g} orbitals due to the tetragonal distortion [2]. This orbital reconstruction causes a selective orbital occupancy that suppresses the FM order.

For different substrates and growth conditions the tetragonality of LCMO at room temperature, defined as $\tau = |c - a|/a$, is the driving force for a phase coexistence above an approximate critical value of $\tau \approx 0.024$. Theoretical calculations prove that the increased tetragonality changes the energy balance of the FM and AFM ground states in strained LCMO, enabling the formation of magnetically inhomogeneous states [3].

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc) :

As discussed with the beamline staff, we plan to perform X-Ray Diffraction (XRD) simultaneously to XPS/HAXPES, in order to obtain an accurate structural, electronic and chemical characterization. A photon energy of 15 KeV will be used in order to access a large portion of the reciprocal space and to ensure a large penetration depth for the photoemission characterization. The crystallographic space group and lattice atomic structure will be obtained by measuring different non-specular scans along the substrate CTRs and layer RODs. Simultaneously hard X-Ray La3d and Ca 2p signals will be collected in order to determine the presence or absence of cationic disorder. Based on the obtained stoichiometry, analysis of the Mn3s with electron kinetic energies close to 15KeV will enable the determination of the Mn valence and therefore the presence or absence of oxygen vacancies. The use of high kinetic energy electrons is mandatory in order to explore the complete sample depth (tens of nanometers). A comparison with Soft X-ray Photoemission data will be performed to discriminate between surface and bulk effects.

We intend to analyze 4 samples (with dimensions 5x5 mm^2) formed by LCMO deposited on STO (001) as substrate. One of the samples not showing dead layer (NFL) and the other 3 with different NFL thicknesses respect to the total thickness. The total thickness of the samples will be about 10, 20 and 30nm. The measurements will be collected below the FM order temperature of LCMO (T<160K).

Beamline(s) and beam time requested with justification :

BM25B allocates a multi-purpose 2+3 diffractometer in horizontal geometry which incorporates a high kinetic energy analyzer and a L-He cryostat fulfilling perfectly the requirements imposed by the proposed experiment. We request a total of 18 shifts (6 days). We estimate that a complete XRD and XPS/HAXPES analysis for each sample will take 4 shifts. Therefore, the total required beam time will be 4 samples x 4 shifts + 2 shifts of alignment, sample transfer under vacuum conditions, and cooling down the sample = 18 shifts.

Results expected and their significance in the respective field of research :

We foresee that the results of the proposed experiment will be very relevant for the study of the properties of perovskite films with a high scientific interest such as manganites. The result of this study could give the key evidence that could open a new route to synthesize strain-induced exchanged-biased FM−AFM bilayers in single thin films, which could serve as building blocks of future spintronic devices. The possibility of a single material showing at the same time FM and AFM behaviour in different regions of the film is highly interesting when thinking in simplifying fabrication of potential spin valves and exchange biased transistors, thus reducing costs and improving the final result.

References

(1) Abad, L.; Laukhin, V.; Valencia, S.; Gaup, A.; Gudat, W.; Balcells, L.; Martínez, B. Adv. Funct. Mater. 2007, 17, 3918.
(2) Tokura, Y.; Nagaosa, N. Science 2000, 288, 462.
(3) Marín L.; Rodríguez, L.A.; Magen, C.; Snoeck, E.; Arras, R.; Lucas, I.; Morellon, L.; Algarabel, P.A.; de Teresa, J.M.; Ibarra, R. Nano lett., 15 (2015) 492-497.