ESRF EXPERIMENTAL REPORT
Proposal number: 25-02 629 at CRG BM25

Title: Strain-induced chemical changes in oxide heteroepitaxies

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Beamline: BM25B
Used shifts: 18

The aim of this experiment was to investigate the possible gradual relaxation of epitaxial strain with thickness in LCMO thin films. The eventual presence of gradual epitaxial relaxation could explain the unexpected but generally observed decrease in the magnetic and transport properties in the films [1].

Reflectivity curves were first collected to determine the total thickness of the films. This information was previously inaccessible as the analysis of the diffracted intensity along truncation rods did not report any Q_z oscillations. Fig. 1 shows one illustrative example of the recorded reflectivity curves. Reciprocal space maps of several reflections in films grown on different substrates and displaying different textures were performed. Measurements were performed at two different incident angles, 0.1º and 1º , thus probing the X-ray diffraction at a depth of 23 nm and over 1 micron, respectively, according to the beam energy of 18 keV. Results are summarized in table I.

(001)				
thickness (nm)	STO $\mu = 1$			
8	a = 3.909	α = 89.96		
	b = 3.9053	β = 89.93		
	c = 3.8978	γ = 90.03		
	V = 59.50			
	LCMO $\mu = 1$		LCMO $\mu = 0.1$	
	a = 3.927	α = 89.86	a = 3.946	α = 89.03
	b = 3.912	β = 90.01	b = 3.915	β = 91.14
	c = 3.797	γ = 90.19	c = 3.808	γ = 90.52
	V = 58.33		**V = 58.81**	
thickness (nm)	STO $\mu = 1$			
60	a = 3.9065	α = 89.97		
	b = 3.9052	β = 89.91		
	c = 3.8982	γ = 90.05		
	V = 59.46			
	LCMO $\mu = 1$		LCMO $\mu = 0.1$	
	a = 3.918	α = 89.92	a = 3.916	α = 89.39
	b = 3.909	β = 90.05	b = 3.910	β = 90.64
	c = 3.799	γ = 90.18	c = 3.800	γ = 90.10
	V = 58.18		**V = 58.18**	

Table I: Summary of the lattice parameters for the LCMO(001)/STO(001) thin films.

Data show in all cases that the in-plane parameters are expanded, the out-of-plane parameter is contracted in agreement with the simplest epitaxial lattice strain picture. However, the unit cell volume is increased respect to the bulk V_{LCMO} = 57.5 Å^3 revealing a non-Poisson like scenario that could be related with our recent observation by EELS of cations redistribution driven to reduce the elastic energy [2]. Thicker films present an average unit cell volume closer to the bulk value, likely indicating the recovery of an elastic behaviour with the increased thickness. The differences after the analysis at different incident angles is negligible or, surprisingly, suggesting that the bulk-like parameters are predominantly present at the interface leaving more distorted unit cells on the top-most surface. The scenario could be understood as a progressive incorporation of segregates in the matrix, potentially distorting the strain fields. An illustrative comparison between the measurements performed at different angles is shown in Fig. 1

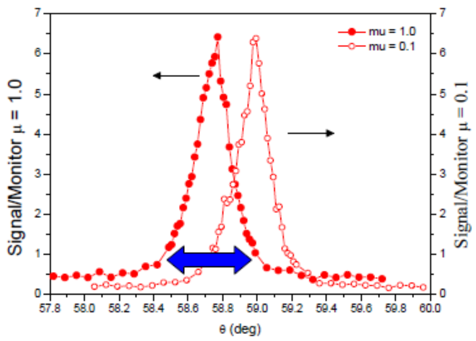

Fig. 1: Scans around the (103)LCMO peak at different incident angles

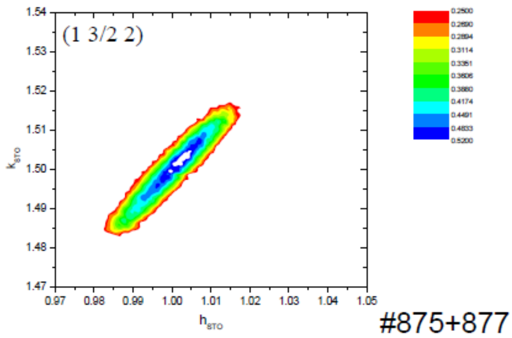

Fig. 2: Reciprocal space map around (1 1.5 2)LCMO reflection.

In contrast, films presenting a (110) out-of-plane texture provided data which could be explained by a simple gradual relaxation of the films via dislocations. On one hand, thicker films a less distorted unit cell volume and, on the other hand, the analysis with grazing incidence angle, revealed an even reduced unit cell volume. It is interesting to note that the distribution of diffracted intensity in the maps is located along a reciprocal space radial trajectory thus indicating the presence of a gradually relaxed material (Fig. 2).

Our attempts to obtain further information on the stoichiometry of the samples were founded on the collection of intensities along different truncation rods of the perovskite and assuming that the form factors are only varied due to chemical changes (occupancy) and, in turn, preserve the space group and relative positions of atoms. It came out that none of the basic models running on small deviations in the stoichiometry described properly the data, most probably indicating another possible origin or an incorrect collection of the background. In any case, the peaks collected at different angles did not show significant intensity differences in spite of the expected chemical composition inhomogeneity in depth.

References

[1] J.H. Park, E. Vescovo, H.J. Kim, C. Kwon, R. Ramesh, T. Venkatesan, Phys. Rev. Lett. 81, 1953 (1998)
[2] S. Estradé, J.M. Rebled,, J. Arbiol, F. Peiró, I.C. Infante, G. Herranz, F. Sánchez, J. Fontcuberta, R. Córdoba, B.G. Mendis, A.L. Bleloch, Applied Physics Letters 95, 072507 (2009)