doi: 10.1017/S1431927609094380
Microsc Microanal 15(Suppl 2), 2009

Structural and Chemical Details of $La_{05}Sr_{0.5}CoO_{3-\delta}$ Thin Films

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Cobaltite thin films provide a unique opportunity to study magnetoelectronic phase separation, which is intense in cobaltite materials [1], in a reduced dimensionality environment. Interfacial magneto-electronic phase separation has recently been observed in epitaxial thin films of the doped perovskite cobaltite $La_{1-x}Sr_xCoO_3$ at doping values where no such phase separation exists in bulk [2]. In order to understand this phenomenon, atomic resolution characterization of the films in real space is essential, including a comprehensive study of structure, chemistry and electronic properties. For this aim, the combination of aberration corrected scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) and theoretical calculations is a very useful tool which allows simultaneous probing of these properties with atomic resolution [3-5].

Here, we will present a detailed investigation of the structure and the chemistry in epitaxial $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) thin films on $SrTiO_3$ (001) substrates, and compare these results with those obtained from parent compounds with different Sr concentration values. Films are epitaxial, and the interface with the substrate is coherent, as shown in Fig. 1a. A closer examination reveals the presence of a superstructure, Fig. 1b, usually attributed to oxygen vacancy ordering [6,7], which is not seen in the parent compounds, Fig. 1c. EELS spectrum imaging was applied to check the compositional homogeneity of these films. Fig. 2 shows that the as-grown films have relatively large regions (a few tens of nm in size) where the Co concentration is enhanced and the La and Sr signals are reduced, pointing towards precipitation of a Co-O phase. High temperature annealing eliminates these Co-O phases, resulting in films which are more chemically homogeneous. The analysis of the fine structure of the O K edge and the Co L edge in these films shows that a region a few nanometers thick near the interface is electronically different from the rest of the film, showing a reduced hole density which does not correlate with any chemical inhomogeneity. These results will be discussed in the scenario of interface driven electronic phase separation.

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[9] The authors are grateful to J.T. Luck for help with STEM specimen preparation. Research at ORNL sponsored by the Division of Materials Sciences and Engineering of the US

Department of Energy and by the LDRD Program of ORNL. Work at UMN was supported by NSF DMR and DoE BES.

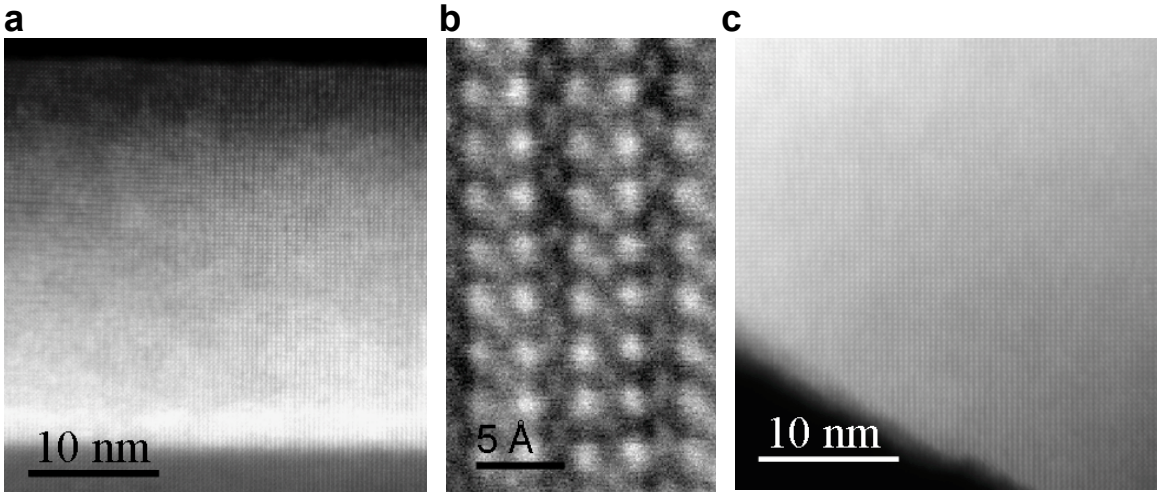

FIG. 1. (a) Annular dark filed (ADF) image of the LSCO taken in the [100] zone axis orientation. (b) ADF high-resolution image of the superstructure. The effect attributed to oxygen vacancy ordering is the change of brightness in every second lattice column in the [010] orientation [6,7]. (c) ADF image of the LSCO parent compound.

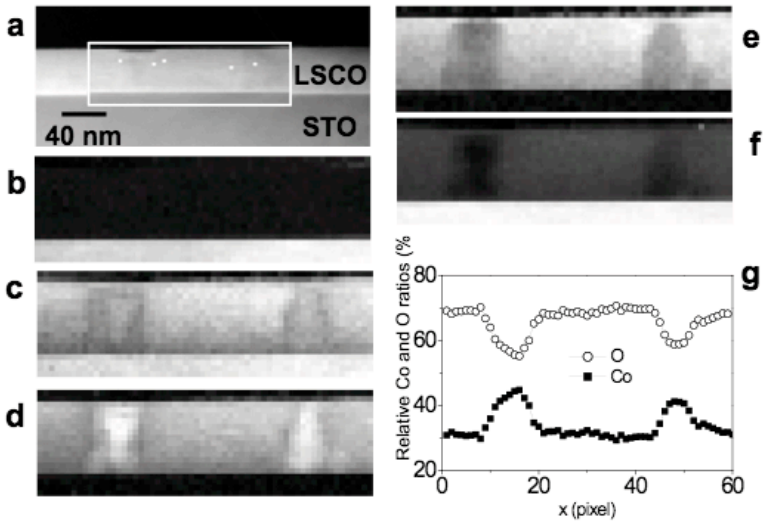

FIG. 2. (a) Low magnification image of a LSCO (x=0.5) thin film. A white rectangle marks the approximate region where an EELS spectrum image was collected. The simultaneously acquired ADF signal is shown within the rectangle. The rest of the figure shows the elemental maps for Ti $L_{2,3}$ around 455 eV (b), O K near 530 eV (c), Co $L_{2,3}$ around 779 eV (d), La $M_{4,5}$ near 832 eV (e) and Sr $L_{2,3}$ around 1940 eV (f). All maps have been produced from the same spectrum image, applying Principal Component Analysis to remove random noise, removing the background using a power law fit and integrating a 30 eV wide window below the edge (except for the Sr map, where a 200 eV wide window was used). (g) Relative Co (black squares) and O (open circles) ratios along the direction parallel to the interface, averaged in the growth direction (calculated from the raw EEL spectra). Results are from the aberration corrected VG Microscopes HB501UX [Adapted from Ref. 8].

https://doi.org/10.1017/S1431927609094380 Published online by Cambridge University Press