Epitaxial Oxygen Getter for a Brownmillerite Phase Transformation in Manganite Films

J. D. Ferguson, Y. Kim, L. Fitting Kourkoutis, A. Vodnick, A. R. Woll, D. A. Muller, and J. D. Brock

Complex oxide systems are promising candidates for materials in solid oxide fuel cells, oxygen sensors, and other applications requiring oxygen anion diffusion. In particular, mixed mode conductors such as the manganite oxides are of interest as cathode materials for solid oxide fuel cells. One interesting property of some complex oxides is their ability to form distinct, oxygen-deficient ordered phases with high ionic conductivity. Here, we report the discovery, using in situ synchrotron-based X-ray techniques, of a new method for creating oxygen vacancy ordered phases in epitaxial manganite thin films. The method involves depositing an oxygen deficient complex oxide film on top of a stoichiometric manganite film to act as an oxygen getter. Once the getter layer exceeds a critical thickness, a phase transition to an oxygen vacancy ordered superlattice occurs in the manganite film. We demonstrate the use of oxygen deficient SrTiO$_{3-\delta}$ (STO) and LaAlO$_{3-\delta}$ (LAO) as getter layers and superlattice formation in four manganite systems: La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO), Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ (PCMO), La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO), and LaMnO$_3$ (LMO). The superlattices may be maintained at ambient conditions after cooling to room temperature. This growth technique constitutes a new procedure for preparing such structures, and may lead to the discovery of new, technologically diverse phases of complex oxide materials that cannot be grown by traditional deposition techniques.

Reflection high energy electron diffraction (RHEED) and X-ray scattering are commonly employed to monitor thin film thickness, roughness, morphology, and structure during deposition. The penetrating power of X-rays makes them uniquely suited for structural studies of the buried layers in heterostructures. To monitor film thickness during deposition, the intensity at “anti-Bragg” positions may be monitored in real time. During homoepitaxial layer-by-layer growth, this intensity oscillates with the period corresponding to the deposition of 1 unit cell, hereafter referred to as a monolayer (ML). For heteroepitaxial growth, the anti-Bragg intensity oscillates with a period of either 1 or 2 MLs, depending on the details of the system. Here, we use this method by measuring the intensity of specularly reflected X-rays at the (001) position on the crystal truncation rod of the substrate ([010] is the surface normal).

The Anti-Bragg intensity measured during pulsed laser deposition (PLD) of a LSMO/STO/LAO heterostructure on SrTiO$_3$ is shown in Figure 1a. The oscillations during the LSMO deposition are shown in green, and the time between deposition.

Figure 1. a) Anti-Bragg intensity oscillations for the deposition of a LSMO/STO/LAO heterostructure. The large intensity increase during the LAO deposition is the result of a Bragg peak forming due to oxygen vacancy ordering in the buried LSMO film. b) The post deposition X-ray reflectivity.
local maxima corresponds to deposition of 1 ML. The [21.2 ML] LSMO film was grown in 10⁻¹ Torr of O₂ so that the film is (nearly) fully oxygenated. Next, approximately 6 MLs of oxygen deficient STO were deposited on top of the LSMO. The intensity oscillations corresponding to the STO deposition are shown in red. The oxygen deficient STO was deposited in 10⁻³ Torr of O₂. Low angle annular dark field scanning transmission electron microscopy (STEM) of films grown under these conditions [in our PLD system] show that the resulting strain fields are similar to those reported previously, confirming that the films are oxygen deficient. The film was then capped with LAO (blue line), again in 10⁻³ Torr of O₂. After ~6 MLs of LAO are deposited, the intensity increases abruptly. As shown below, the sharp rise in intensity is due to the formation of a superlattice, resulting in a Bragg reflection near the (010) of LSMO. Subsequent diffraction and microscopy measurements (described below) demonstrate that the superlattice forms in the buried LSMO film, rather than in the capping layer or the bulk STO substrate.

As illustrated in Figure 1a, the formation of the superlattice is dependent upon the continuous deposition of LAO. When the deposition of the LAO is halted, the superlattice formation ceases and the intensity remains constant. If the sample is then heated, the intensity begins to decrease. When the LAO deposition is resumed, the intensity begins to rise again, until approximately 3600 s. At this point, the intensity saturates. As discussed below, we interpret this saturation as corresponding to near-complete conversion of the LSMO layer from its as-deposited form to the new phase. We have never observed the signal to increase except during deposition. Following the deposition, the sample was cooled to room temperature in ~1.5 h in the same O₂ pressure used for the deposition of the getter layer. After the sample reaches room temperature, the structure is (meta)stable in atmospheric conditions.

The superlattice structure was determined by ex situ X-ray specular reflectivity. The specular intensity is plotted as a function of STO reciprocal lattice units (r.l.u.) in Figure 1b. In addition to sharp (010) and (020) Bragg peaks from the STO substrate, thin-film peaks and Kiessig thickness fringes are clearly visible. Fitting the (010) region to a simple finite-size line-shape, we obtain a periodicity of 8.2 Å and a film thickness of 77.5 Å. This thickness is about three LSMO unit cells less than the thickness obtained by counting the number of LSMO growth oscillations, suggesting that most, but not all of the LSMO is transformed. The observed thickness is not consistent with either the STO or the LAO layers. Thus, we conclude that the ½-order peak corresponds to a superlattice in the LSMO layer.

We note that, because the superlattice forms in a buried layer rather than the surface, the transition beginning at t = 1400 s would not have been observed using conventional RHEED, which probes only the near surface region. Thus, X-ray scattering was critical for identifying this transition.

The superlattice shown in Figure 1 was formed with both oxygen deficient LAO and STO as capping layers; however the transformation may also be induced using only one film of either LAO or STO. To further investigate the conditions required to form the superlattice, a series of identical LSMO films were grown (615 °C, 10⁻³ Torr O₂) and capped with STO, grown under varying conditions. The results are shown in Figure 2. In this phase diagram, the green region represents the pressure/temperature regime where a getter layer induces the superlattice phase transition. The boundaries in the phase diagram represent approximate midpoints between data points. The superlattice forms at temperatures as low as 415 °C in 10⁻² Torr of O₂ and as high as 615 °C in 10⁻¹ Torr of O₂.

In addition to the growth conditions for the capping layer indicated in Figure 2, two additional conditions are necessary to form and stabilize this type of buried superlattice structure in the LSMO film:

1. The LSMO film must be grown under oxygen rich conditions, presumably to form a (nearly) stoichiometric layer. LSMO films deposited in 10⁻³ Torr O₂, followed by the deposition of the getter layer, do not exhibit superlattice peaks.
2. After growth, increasing the partial pressure of oxygen while still at growth temperature destroys the superlattice within seconds. Thus, the post-deposition anneal in oxygen frequently applied to oxide films eliminates the structure.

To examine the nature of the superlattice, Figure 3a shows a STEM image of the film grown in Figure 1. The high-angle annular dark field STEM image clearly shows a superlattice of dark planes in the LSMO layer, confirming the X-ray measurements. These dark planes coincide with the position of MnO₂ layers in a stoichiometric LSMO film, suggesting that the film is either manganese or oxygen deficient. These low density planes appear in the LSMO layer with a period of 2 angstroms. Since the superlattice structure is highly dependent upon the oxygen partial pressure (see Figure 2), and annealing in a high oxygen environment destroys the superlattice, we conclude that the dark planes result from missing oxygen rather than missing manganese cations. Electron Energy Loss Spec-
tetroscopy (EELS) measurements confirm the presence of Mn, further supporting this conclusion (see Supporting Information). Evidently, since the phase transition occurs during deposition of an oxygen-deficient overlayer, the formation of the structure is driven by oxygen diffusion from the LSMO film into the capping layer. Therefore the capping layer is acting as an oxygen getter. This picture is consistent with the results of Takahashi et al. in which LaAlO$_3$ and LaTiO$_3$ overlayers were shown to remove oxygen from a buried anatase TiO$_2$ layer on STO. They found that oxygen gettering decreased the ordering in their system. In contrast, in this case, oxygen gettering results in increased ordering in the manganite layers.

Figure 3a strongly resembles other high resolution STEM images of brownmillerite systems. The brownmillerite family of crystal structures is associated with oxygen vacancy ordering in a perovskite lattice. The idealized brownmillerite crystal structure is orthorhombic, has space group Pcmn, and is shown in Figure 3b with the corresponding perovskite unit cell outlined in green. The two unit cells are rotated $45^\circ$ from each other, and the cell parameters are related by: $a_{BM} = c_{BM} = \sqrt{2}a_{PV}$ and $b_{BM} = 2a_{PV}$. In this notation, the surface normal is in the [010] direction, the BM subscript refers to the brownmillerite crystal system, and the PV subscript refers to the perovskite crystal system.

The brownmillerite structure has BO$_6$ octahedra at the unit cell corners, with the oxygen vacancies ordering into missing rows oriented in the [100]$_{BM}$ direction, causing the unit cell to alternate between oxygen octahedra and oxygen tetrahedra centered on the B cation sites. The missing rows of oxygen are shifted by a half unit cell in the $c_{BM}$ direction for each half unit cell translation in the $b_{BM}$ direction. Small rotations of the oxygen tetrahedra and octahedra can further distort the unit cell. Many of the resulting variants of the brownmillerite structure have been reported in bulk La$_{1-x}$Sr$_x$MnO$_3$ samples. The (110)$_{BM}$ Bragg peak corresponds approximately to $(\frac{1}{2} \pm \frac{1}{2})_{PV}$—the difference is due to the lattice mismatch between the STO substrate and LSMO. Ex situ X-ray diffraction measurements (not shown) exhibit a weak Bragg peak near $(\frac{1}{2} \pm \frac{1}{2})_{PV}$ with fourfold rotation symmetry about the surface normal, strongly supporting the brownmillerite structure. The measured out-of-plane lattice parameter is $b_{BM} = 16.47 \pm 0.01$ Å. Since the in-plane lattice parameters are locked to the STO substrate, the measured lattice constant should not be identified as the equilibrium value.

To investigate whether this growth technique is applicable to other material systems, heterostructures were grown with LSMO, PCMO, LCMO, and LMO. The intensity oscillations during the deposition of these heterostructures are shown in Figure 4a. The deposition of the AMnO$_3$ films is represented with a white background, while the dark background represents the deposition of a STO getter layer. The growth temperatures of the AMnO$_3$ films were 615 °C, 850 °C, 615 °C, and 830 °C for the LSMO, PCMO, LCMO, and LMO, respectively. All four AMnO$_3$ films where grown to a thickness of about 20 MLs, with a background oxygen pressure of 10$^{-1}$ Torr for the LSMO, PCMO, and the LCMO. The LMO film was grown at 3 × 10$^{-5}$ Torr O$_2$. For each heterostructure, the STO getter layer was deposited at 615 °C in 10$^{-5}$ Torr of O$_2$. All the manganite materials investigated exhibited the dramatic increase of the anti-Bragg intensity. After cooling to room temperature, ex situ X-ray reflectivity measurements on all four samples (Figure 4b) exhibit the (0 1 0) superlattice peak. The LMO film shows an additional peak near (0 2 0), indicating a further reduction in symmetry.

An interesting feature seen in Figure 4a is that the phase transition occurs at approximately the same getter layer thickness (~12 MLs) for all AMnO$_3$ films. A possible explanation for this critical thickness is that the number of oxygen vacancies must reach a critical density to induce the transition. Specifically, if the oxygen affinity of the capping film is larger than that of the manganite layer, one would expect oxygen to diffuse into the getter throughout the deposition, which is consistent with Takahashi et al. Although no vacancy ordering was found in their system, it was shown that oxygen was removed for getter layers grown as thin as 1 unit cell. Since STO did not act as a getter, the difference in oxygen affinity was determined to be the diffusion driving force, rather than an energetic effect due to PLD. Our data alone
the superlattice formation occurs exemplifies the difficulty of growing stoichiometric phases in oxide heterostructures. While we demonstrated this technique for manganite films, the method may be applicable to other materials systems and lead to the discovery of new, useful phases of complex oxide materials. Finally, this work clearly demonstrates the utility of real-time X-ray structural studies during thin film deposition.

**Experimental Section**

All thin films were grown by PLD using a KrF excimer laser (248 nm) at a repetition rate of 1 Hz. The target was 6 cm from the substrate. The substrate temperature was measured using an optical pyrometer (∆θ = 4.8–5.3μm, ε = 0.8). To regulate the O₂ pressure, oxygen was inserted into the chamber atmosphere. The laser spot size on the target was 7.4 mm² for all films, with a fluence of 1.2 J cm⁻² for the LSMO, PCMO and LCMO films. The laser fluence was 1.6 J cm⁻² for LMO. The STO and LAGO getter layers were deposited with a fluence of 0.8 J cm⁻² and 1.6 J cm⁻², respectively. All films were grown on SrTiO₃(010) substrates, prepared to have TiO₂ terminated surfaces[26] and AFM ensured the substrates had unit cell high steps separated by large terraces. The in situ X-ray measurements were performed in the pulsed laser deposition/ X-ray diffraction system in the G3 experimental hutch at CHESS. The X-ray reflectivity shown in Figure 1b was performed at the G2 hutch (ΔE/E = 0.2%), while the data shown in Figure 4b was collected at G3(ΔE/E = 1.5%).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

We thank R. Chopdekar, D.S. Dale, M. Liberati, R. Misra, B. Nelson-Cheeseman, P. Schiffer, D.G. Schlom and Y. Suzuki for their help with this work. This work was supported in part by the Cornell Center for Materials Research (CCMR) with funding from the Materials Research Science and Engineering Center program of the National Science Foundation (NSF) (DMR-0520404) and by the NSF (DMR-0705361). Additionally, this work is based upon research conducted at the Cornell High Energy Synchrotron Source (CHESS) which is supported by the NSF and the National Institutes of Health/National Institute of General Medical Sciences (DMR-0225180).

Received: September 30, 2010
Revised: November 9, 2010
Published online: January 27, 2011

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