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Lattice mismatch accommodation via oxygen vacancy ordering in epitaxial La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ thin films

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The properties of complex oxide films depend sensitively on epitaxial strain. This strain affects bond lengths and angles, and defect types and densities, thus impacting physical properties. In this work we perform detailed characterization of depth-dependent strain in epitaxial La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (LSCO) films on SrTiO$_3$(001), SrTiO$_3$(110), and LaAlO$_3$(001) substrates, combining high resolution x-ray diffraction and scanning transmission electron microscopy, in addition to geometric phase analysis. We elucidate a fundamental link between strain state and O vacancy ordering in LSCO films, where lattice mismatch and crystallographic orientation can be used to manipulate the modulation vector of the long-range vacancy order, thus providing a new approach to tailor the properties of such films. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4809547]

Physical phenomena such as magnetic phase separation, spin-state crossovers, and mixed ionic conduction make perovskite cobaltite films of great interest both for basic science and for applications in solid oxide fuel cells, gas separation membranes, etc. High quality epilayers on single crystal substrates are favored for fundamental studies and for proof-of-principle device work (e.g., with oxygen/hole transport in fuel cell cathodes). In such structures, the epitaxial strain due to the lattice mismatch with the substrate provides a means to controllably modify structure, thus manipulating properties. LaCoO$_3$ provides a good example as it adopts a low-spin “non-magnetic” ground state in bulk, but exhibits strain-stabilized ferromagnetism in films. In the doped case, e.g., in bulk La$_{1-x}$Sr$_x$CoO$_3$ (LSCO), substitution of Sr$^{2+}$ for La$^{3+}$ changes the Co valence, inducing metallic ferromagnetism, but also O vacancies. Without the use of high pressures, these vacancies form in high concentrations for $x > 0.5–0.6$, eventually forming ordered superstructures, as exemplified by Brownmillerite SrCoO$_{2.5}$ (SCO). In tensile-strained thin film LSCO on (001) SrTiO$_3$ (STO), recent work has highlighted the complex interplay between strain and these O vacancies. For example, interfacial magnetic phase separation occurs in STO(001)/LSCO, driven by accumulation of O vacancies near the substrate. These O vacancies undergo long-range ordering somehow related to epitaxial strain. Recently observed consequences of this vacancy ordering/interfacial accumulation include spin-state superlattice formation, induced cation order, and a giant coercivity enhancement. Comparisons can be drawn with similar systems such as rare-earth cuprates, where interfacial oxygen disorder effects impact critical current density. The goal of the current work is to more fully elucidate the interplay between strain state and O vacancy formation/ordering in LSCO films.

We studied the effects of epitaxial strain on $x = 0.50$ LSCO films grown on (001)- and (110)-oriented STO, and on (001)-oriented LaAlO$_3$ (LAO), i.e., STO(001)/LSCO, STO(110)/LSCO, and LAO(001)/LSCO, respectively. The nominal lattice mismatch between film and substrate is $\pm 1.8\%$

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for STO and +1.3% for LAO (Table I). Films were grown by reactive sputtering at 700 °C, with 100 W of DC power, in O₂ and Ar pressures of 20 and 50 mTorr, and with post-deposition cooling in 500 Torr of O₂. High resolution Cu Ka x-ray diffraction (XRD) was performed in wide-angle XRD (WAXRD), rocking curve (RC), and reciprocal space mapping (RSM) modes. RSMs were acquired with a 4-bounce Ge monochromator on the primary beam, but no secondary beam monochromation, resulting in slightly reduced resolution and increased fluorescence background, but improved signal to noise ratio. Scanning transmission electron microscopy (STEM) employed a Nion UltraSTEM operated at 100 kV with a Nion aberration corrector. High resolution Z-contrast images were processed using the software geometrical phase analysis (GPA) in the Digital Micrograph (Gatan) environment. Specimens for STEM were prepared by conventional methods: grinding, dimpling, and Ar ion milling. Samples were tilted to a [100] pseudocubic zone axis for STEM.

A global picture of the thickness (t)-dependent strain relaxation from WAXRD is shown in Fig. 1(a), which plots the strain relaxation percentage [SRP = ϵ/ε(pcm) - ϵ/ε(abm) × 100%, where ϵ is the out-of-plane lattice parameter, and a relaxed and a strained are its fully relaxed (bulk) value and fully-strained (pseudomorphic) value, respectively]. Note that the a relaxed used here is that of stoichiometric, undistorted cubic LSCO (Table I). The films are strained (SRP < 100%) at all t, but exhibit a very different t dependence on the three substrates. In STO(001)/LSCO, we find a critical thickness for strain relaxation (tcrit) around 200 Å. Above this value the SRP increases only slowly, reaching approximately 20% at t ≈ 400 Å. On LAO(001) substrates, tcrit is lower (∼75 Å), the SRP reaching larger values of 60%–70% at 400 Å. Remarkably, and despite the identical mismatch to STO(001), in STO(110)/LSCO the SRP increases almost immediately from t = 0, suggesting tcrit lies below 30 Å, if in fact it exists at all. As discussed previously, strain relaxation in LSCO is also reflected in RCs, through broad and narrow peak components (high and low mosaicity), associated with relaxed and fully strained regions. The t dependence is shown in Fig. 1(b), which plots I broad(I broad + I narrow), where I broad and I narrow are the intensities of the broad and narrow Gaussian components. The trends are similar to Fig. 1(a), the most noteworthy conclusion again being the efficient strain relaxation on STO(110) compared to STO(001). To probe the strain state in more detail, RSMs (Figs. 2(a)–2(c)) were acquired around asymmetric reflections at t = 200 Å. For STO(001)/LSCO and LAO(001)/LSCO, the (013) reflection was chosen. For STO(110)/LSCO, the fourfold in-plane symmetry is broken, and we chose the (310) and (222) reflections to probe two orthogonal high symmetry in-plane directions ([1-10] and [001]). In all cases, white crosses mark the positions of the fully strained (pseudomorphic) and fully relaxed (bulk) LSCO reflections. For STO(001)/LSCO (Fig. 2(a)), consistent with Fig. 1, we find negligible strain relaxation. The situation is similar for LAO(001)/LSCO (Fig. 2(c)), but with minor relaxation. This is in stark contrast to STO(110), however (Fig. 2(b)), where we find substantial strain relaxation in both in-plane directions. Simple estimates give relaxations ≈40% at this t (200 Å), consistent with Fig. 1(a).

The origin of the unusually efficient strain relaxation on STO(110), and indeed the entire strain state/O vacancy interplay, is elucidated by STEM. Figures 2(d)–2(f) show annular dark field Z-contrast STEM images from the interface regions. These images confirm cube-on-cube epitaxy, with the expected epitaxial relationships, in addition to a coherent interface. They also reveal an obvious

<table>
<thead>
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<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>ε (apc/abm)</th>
<th>ε (apc/bbm)</th>
<th>ε (cbm/abm)</th>
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<td>La₀.₅Sr₀.₅CoO₃ (pc)</td>
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<td>...</td>
<td>...</td>
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<tr>
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<td>5.556</td>
<td>15.690</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>SrTiO₃</td>
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<td>...</td>
<td>...</td>
<td>−1.8%</td>
<td>−0.7%</td>
<td>0.5%</td>
</tr>
<tr>
<td>LaAlO₃</td>
<td>3.789</td>
<td>...</td>
<td>...</td>
<td>1.3%</td>
<td>2.3%</td>
<td>3.5%</td>
</tr>
</tbody>
</table>
FIG. 1. (a) Thickness \( t \) dependence of the strain relaxation percentage (SRP), as determined from the out-of-plane lattice parameter, for \( x = 0.5 \) LSCO films on STO(001), STO(110), and LAO(001). The thickness (as determined by x-ray reflectivity) was varied from 30–400 Å in 20 separately grown samples. In the thinnest samples, with broad WAXRD peaks, the out-of-plane lattice parameter was determined by subtracting out a symmetric substrate reflection and fitting the isolated film peak with a Gaussian. (b) Percentage contribution of the broad intensity component from two-Gaussian fitting of rocking curves for the same films. \( I_{\text{broad}} \) and \( I_{\text{narrow}} \) are the intensities of the two contributions.

FIG. 2. (a), (b), and (c) are asymmetric reciprocal space maps for 200 Å thick \( x = 0.50 \) LSCO films on STO(001), STO(110), and LAO(001), respectively. In (a) and (c), the data were collected around the (013) reflection; in (b) around the (310) and (222) reflections. The expected positions of the fully strained and fully relaxed LSCO reflections are marked. (d), (e), and (f) are high resolution Z-contrast STEM images of the interface regions in films grown on STO(001), STO(110), and LAO(001), respectively. Yellow lines mark the O deficient Co–O planes. The modulation vector, \( q \), is marked.

superstructure, contrast modulation occurring on every other Co–O plane (see yellow lines). This contrast is well known to be due to the structural relaxations that result from the ordering of O vacancies in this system.\(^{11}\) O vacancy ordering occurs in the related bulk SCO and high \( x \) LSCO compounds\(^ {6,7}\) and similar superstructures have been found in epitaxial LSCO.\(^ {8–11,18–21}\) These superstructures are indicators of O vacancy ordering. In the present set of STO(001)/LSCO samples, we have previously reported direct observation of O content modulation by atomic-resolution electron energy loss spectroscopic imaging.\(^ {11}\) Note that in Z-contrast images, the dark/bright pattern of Co–O planes arises due to a modulation in cation spacing resulting from the O content modulation\(^ {6,7,11}\) or to displaced Co ions.\(^ {21}\) It does not arise from the variation in O content directly.

Three additional findings suggest that this O vacancy superstructure provides the primary mechanism of lattice mismatch accommodation and strain relief. First, while in bulk such vacancy
ordering is well-known in high $\times$ LSCO and SCO, it has not been reported in $\times = 0.50$ bulk compounds to the best of our knowledge, and does not occur in our own bulk samples. There is thus some mechanism promoting O vacancy order in epitaxial films, strain being a likely candidate. Second, we find a remarkable scarcity of misfit dislocations, strongly suggestive of an alternative strain relaxation mechanism involving O vacancy order. A superstructure-related strain relief mechanism has in fact recently been advanced for undoped epitaxial LaCoO$_3$, although the origin of the superstructure is still under debate in that case. Finally, as can be seen from Figs. 2(d)–2(f), the modulation vector of the O vacancy superstructure responds to both strain types (tensile vs. compressive), and crystallographic orientation [(001) vs. (110)], pointing to a fundamental link between strain state and O vacancy order.

A likely candidate for the superstructure in Figs. 2(d)–2(f) is the orthorhombic Brownmillerite structure of bulk SCO. This phase has stoichiometry SrCoO$_{2.5}$, with lines of oxygen vacancies along the [110] direction in alternate (001) Co–O planes, quadrupling the unit cell along the c-axis (see Table I). In STO(001)/LSCO (Fig. 2(d)), we propose that the tensile strain is relieved by the formation of a Brownmillerite-like superstructure with O vacancy planes perpendicular to the interface, i.e., superlattice modulation vector ($q$) parallel to the interface. The measured (La,Sr)–O interplanar spacings alternate between 3.60 $\pm$ 0.20 Å and 4.25 $\pm$ 0.30 Å (errors are half-widths of spacing distributions), giving an in-plane lattice parameter of 7.84 Å, very close to twice the SrTiO$_3$ lattice parameter (7.81 Å, see Table I). In essence, the mismatch with the substrate is accommodated by formation (at low energy cost) and ordering of O vacancies, thus generating a fundamental link between strain, O vacancy density, and order. In the case of compressive strain on LAO(001) (Fig. 2(f)), the O vacancy planes stack parallel to the interface, with $q$ out-of-plane, to enable out-of-plane expansion, and thus in-plane compression. A simple analytical model supports this strain-relief scenario. The $q$ vector can also be controlled by crystallographic orientation. As expected in a Brownmillerite-type structure, in the (110) orientation the O vacancy planes make an angle close to 45$^\circ$ with the interface (yellow lines in Fig. 2(e)). Lower magnification images of 400 Å thick films are shown in Figs. 3(a)–3(c), illustrating a domain structure. In Fig. 3(a), for example, variants with O vacancy planes running both perpendicular and parallel to the interface are seen. Close to the interface the perpendicular variant dominates, a transition to a multi-domain state occurring $\approx$200 Å from the interface, consistent with $t_{\text{crit}}$.

Fourier analysis of these images was performed with GPA to obtain spatially resolved information on the local lattice relaxation. In this technique, strain, or deformation, is measured with respect to some reference area, in our case the substrates. The extracted strain values are thus referred to the substrate, as opposed to bulk LSCO, such that fully pseudomorphic growth leads to zero strain. Circular masks with radii producing a lateral resolution $\approx$1 nm in the GPA images were defined around the (001) reflections for STO(001)/LSCO and LAO(001)/LSCO, and the (110) reflections for STO(110)/LSCO. The extracted in-plane ($\varepsilon_{xx}$) and out-of-plane ($\varepsilon_{yy}$) strains (again, with respect to the substrate) are shown in Figs. 3(d)–3(f) and in Figs. 3(g)–3(i), respectively. Positive and negative values refer to compressive and tensile strains, respectively. In Fig. 4, lateral averages of these strains are plotted vs. distance from the interface, overlaid on sections of the maps from Fig. 3 (to scale).

Considering STO(001)/LSCO first (Figs. 3(d) and 3(g), and Fig. 4, top panel), the first observation is that the domain structure seen in Fig. 3(a) is clearly reflected in the strain maps (Figs. 3(d) and 3(g)), the strain state being remarkably inhomogeneous. As expected, $\varepsilon_{xx}$ and $\varepsilon_{yy}$ are anti-correlated (Figs. 3(d) and 3(g)). Near the interface $\varepsilon_{xx} \approx 0$ (i.e., pseudomorphic growth), and $\varepsilon_{yy} < 0$ (an out-of-plane lattice parameter smaller than the substrate), in agreement with XRD. As can be seen in the top panel of Fig. 4, $\varepsilon_{xx}$ remains small out to $\approx$150 Å from the interface, in reasonable agreement with $t_{\text{crit}}$ from XRD (200 Å). Above this thickness, $\varepsilon_{xx}$ increases in magnitude, reaching $-0.9\% \pm 0.1\%$ at the surface, where the parallel variant of the O vacancy superstructure dominates. Correspondingly, $\varepsilon_{yy}$ is relatively constant out to $\approx$150 Å from the interface, beyond which it relaxes gradually, reaching $-0.4\% \pm 0.1\%$ at the surface. This corresponds to an out-of-plane lattice parameter of 3.889 Å and a strain relaxation percentage of 23%, in good agreement with XRD (Fig. 1(a)).

In LAO(001)/LSCO (Figs. 3(f) and 3(i), and Fig. 4, bottom panel), with compressive strain and smaller mismatch, we find a more uniform strain-state, although anti-phase boundaries occur, spaced by about 50 nm. This is smaller than the coherence length in our XRD (several hundred
FIG. 3. (a), (b), and (c) are Z-contrast images of 400 Å thick STO(001)/LSCO, STO(110)/LSCO, and LAO(001)/LSCO films. The orientation of the modulation vector, \( q \), is marked. (d) and (g), (e) and (h), and (f) and (j) are in-plane (\( \varepsilon_{xx} \)) and out-of-plane (\( \varepsilon_{yy} \)) strain maps of the same three films shown in (a)–(c), from GPA analysis. Dashed lines mark the substrate/LSCO interface. The Z-contrast images do not show the regions in the substrates, as big as 10\( \times \)30 nm, that were used as reference lattices. The scale bar is 10 nm in all panels. The range of the color scale (\( \pm 10\% \)) is the same in all maps.

nm in the growth direction, several microns laterally), explaining the absence of superlattice peaks. As anticipated, \( \varepsilon_{xx} \approx 0 \) near the interface (i.e., pseudomorphic growth), increasing away from the interface. The data suggest a local \( t_{\text{crit}} \) of about 50 Å, roughly consistent with XRD (Fig. 1(a)). In the out-of-plane direction (Fig. 3(i)), we find \( \varepsilon_{yy} > 0 \) (a larger out-of-plane lattice spacing than the substrate), with a laterally averaged magnitude of 6\% \( \pm \) 0.1\% at the surface. Such large strains are consistent with the >3.5\% expected from the mismatch between LAO and Brownmillerite-like LSCO in this orientation (Table I), although they exceed XRD values. This discrepancy may result from differences between the local and average structures in this case.

Importantly, STO(110)/LSCO is significantly different from STO(001). First, the strain state is relatively uniform in comparison to STO(001) (compare Figs. 3(d) and 3(g), and Figs. 3(e) and 3(h)). We again find \( \varepsilon_{xx} \approx 0 \) near the interface, but with a remarkable depth dependence (Fig. 4,
middle panel). Consistent with spatially averaged results from XRD, we find essentially no evidence for any well-defined $t_{\text{crit}}$; strain relaxation initiates immediately at the interface, in sharp contrast to STO(001) (compare Fig. 4(a), top and middle panels). Consistent with this, the extent of strain relaxation at the film surface is substantially larger for STO(110) than STO(001). We propose that the surprisingly different strain relaxation behavior in (110)- vs. (001)-oriented films originates from the differing $q$ orientations. Specifically, in the (110) case all variants can contribute to strain relaxation, due to the $45^\circ$ angles with the growth direction, $n$ (e.g., Fig. 2(e)), which results in a finite value of $q\cdot n$. This is in contrast to the (001) case (e.g., Fig. 3(a)), where for some variants $q\cdot n = 0$. The O vacancy superstructure strain-relief mechanism thus renders crystallographic orientation very useful for controlling strain relaxation.

In summary, by combining high-resolution x-ray diffraction with geometrical phase analysis of scanning transmission electron microscopy images, we have studied the local and global strain relaxation process in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ films grown on various substrates. The lattice mismatch accommodation/strain relief mechanism is shown to be driven by formation, and ordering, of oxygen vacancies. We demonstrate that this defect ordering can be manipulated by lattice mismatch and crystallographic orientation, opening up the possibility of controlling interfacial physical properties via engineering of ordered oxygen defect structures.

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