Growth temperature control of the epitaxy, magnetism, and transport in \( \text{SrTiO}_3(001)/\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) thin films

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The authors report a detailed study of the influence of deposition temperature on the microstructure, phase purity, nanoscale chemical homogeneity, stoichiometry, and magnetic and electronic properties of epitaxial \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) thin films grown on \( \text{SrTiO}_3(001) \) substrates via reactive dc magnetron sputtering. The results are interpreted in terms of the temperature-dependent interplay between crystallization, strain relaxation, and cation mobility (which improve with increasing deposition temperature), and oxygenation (which deteriorates at the highest deposition temperatures). In addition to the established approach to epitaxial sputter deposition based on high temperature deposition combined with subsequent \( \text{ex situ} \) annealing in \( \text{O}_2 \), our results also identify a narrow deposition temperature window \( \sim \)600–625 \( ^\circ \)C, where single phase, highly crystalline, low surface roughness epitaxial films can be obtained with close to ideal stoichiometry without postdeposition annealing. Electronic and magnetic properties similar to bulk single crystals can be obtained in this region. © 2011 American Vacuum Society. [DOI: 10.1116/1.3622621]

I. INTRODUCTION

Doped perovskite cobaltites such as \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) (LSCO) are the subject of considerable current research activity due to potential applications in catalysis,\(^1,2\) gas sensing,\(^2,3\) as electrodes in solid oxide fuel cells\(^2,3\) and ferroelectric random access memory,\(^2,3\) and in oxide spintronics.\(^4,5\) They also exhibit fascinating magnetic and electronic phenomena such as spin-state transitions and magnetic phase separation, generating considerable interest from the basic science viewpoint.\(^6-12\) This situation has resulted in a large body of research in bulk single- and polycrystalline perovskite cobaltites, with LSCO emerging, for a variety of reasons, as the most extensively studied system.

The study of perovskite cobaltites such as LSCO in thin film form, or as components in oxide heterostructures, is essential for development of potential applications and also opens up exciting possibilities for the discovery and elucidation of new physical phenomena. Recent work clearly highlights this latter point, having lead to the discovery of unanticipated magnetic and electronic behaviors, such as interfacial magnetic phase separation\(^5\) and a spin-state superstructure accompanying the \( \text{O} \) vacancy ordering\(^13\) in \( \text{SrTiO}_3(001)/\text{LSCO} \), in addition to the surprising observation of strain-stabilized insulating ferromagnetism in \( x = 0 \) \( \text{LCO} \) films.\(^14-16\) The latter effect is likely related to non-equilibrium spin states for the Co ions, which appears to be preserved even at high \( x \).\(^17\) From the materials science perspective these epitaxial films have also yielded significant surprises, including the seemingly ubiquitous presence of \( \text{O} \) vacancy ordering,\(^4,5,13,18-20\) the elucidation of its role in accommodating lattice mismatch with the underlying substrate,\(^5,13,19\) and the resulting depth-wise variations in stoichiometry in \( \text{SrTiO}_3(001)/\text{LSCO} \), which dominate the near-interface magnetic and electronic properties.\(^5\)

Despite this recent interest in thin film perovskite cobaltites, they remain relatively poorly understood in comparison to related materials such as manganites, certainly from the perspective of a fundamental understanding of growth mechanisms and structure–property relationships. As is typical for such materials, most of the work performed to date has employed pulsed laser deposition (e.g., Refs.\(^3, 14–16, \) and \( 21–25)\) and reactive sputtering (e.g., Refs.\(^2, 4, 5, 13, 17, 19, \) and \( 20)\). The majority of this research has focused on optimization of parameters such as \( \text{O} \) partial pressure during growth, total gas pressure, or postdeposition \( \text{O}_2 \) annealing, i.e., parameters that control the \( \text{O} \) stoichiometry, which subsequently strongly influences the properties. Reported deposition temperatures lie in the relatively wide range between 500 and 850 \( ^\circ \)C\(^2,5,13-17,19-25\) the influence of deposition temperature being remarkably poorly understood. In fact, we are aware of no detailed study of the deposition temperature dependence of the microstructure and electronic/magnetic properties of LSCO. This is particularly surprising given that the deposition temperature will undoubtedly play a key role in the oxidation and growth kinetics. One would expect that these kinetics must be understood in order to attain even a
qualitative understanding of the O vacancy ordering, or the tendency to form a second phase composed of epitaxially oriented CoO inclusions, an effect which has emerged as a serious issue in recent work.

The current paper provides a detailed study of deposition temperature effects in SrTiO$_3$(001)/LSCO, combining structural and chemical studies via high resolution x-ray diffraction, scanning probe microscopy, and electron microscopy/spectroscopy, with basic electronic and magnetic characterization. We find that deposition temperatures as low as 500 °C produce crystalline, epitaxial films, but with significant cation nonstoichiometry and chemical inhomogeneity. At higher temperatures the chemical homogeneity and cation stoichiometry improve and strain relaxation becomes increasingly apparent, resulting in increased roughness and mosaicity, but distinctly improved magnetic and electronic properties. At temperatures in excess of 625–650 °C, however, we begin to detect a secondary phase in the form of nanoscopic, epitaxially oriented CoO precipitates, which can be eradicated by postdeposition annealing in O$_2$. The results thus establish two reliable routes to single phase epitaxial LSCO films on SrTiO$_3$(001); high temperature deposition followed by O$_2$ annealing, or deposition in the temperature window 600–625 °C without the need for postdeposition treatment. We argue that these results can be understood in terms of the temperature dependent interplay between crystallization, strain relaxation, cation mobility, and oxidation kinetics.

II. EXPERIMENTAL DETAILS

Films were deposited via reactive dc magnetron sputtering from a 2 in. ceramic La$_{0.5}$Sr$_{0.5}$CoO$_3$ target, under conditions optimized in prior work. Details on target fabrication and the SrTiO$_3$(001) substrate preparation are provided in Ref. 4. Deposition was carried out at a total gas pressure ($P_{\text{total}} = P_{\text{Ar}} + P_{\text{O}_2}$) of 70 mTorr and an oxygen/argon partial pressure ratio of $P_{\text{O}_2}/P_{\text{Ar}} = 0.4$, in a system with a base pressure of $1 \times 10^{-8}$ Torr. The deposition power was fixed at 100 W and the deposition temperature was varied from 450 to 700 °C. Postdeposition, the films were transferred to a load-lock chamber and cooled to room temperature over a time period of approximately 2 h in 500 Torr of O$_2$. A subset of the samples were also subjected to a postdeposition annealing procedure. These samples were ex situ annealed in a tube furnace in flowing O$_2$ at 500 °C for 2 h, then cooled to room temperature at approximately 1.3 °C/min. Note that the film thickness (as determined by grazing-incidence x-ray reflectivity) was held constant at 250 Å for all films in this study, with the exception of the samples for electron microscopy which were 400 Å thick.

High-resolution x-ray diffraction was done using Cu $K\alpha$ radiation in a Panalytical X’Pert system in the following modes: wide angle x-ray diffraction (WAXRD) i.e., 0–20 coupled scans), rocking curves (i.e., $\omega$ scans), grazing incidence x-ray reflectivity (GIXR), and grazing incidence in-plane diffraction (GID) i.e. $\phi$ scans. Ex situ atomic force microscopy (AFM) was performed in tapping mode at ~1 Hz. Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) data were acquired using a VG Microscopes HB501UX and a Nion Ultra STEM operated at 100 kV and equipped with a Nion aberration corrector and a Gatan Enfina EEL spectrometer. Specimens for STEM were prepared by conventional methods, by grinding, dimpling, and Ar ion milling. Magnetometry measurements were performed in a commercial superconducting quantum interference device magnetometer from 10 to 300 K in magnetic fields to 70 kOe. Transport measurements were done from 4.2 to 300 K in a custom immersion probe using an ac excitation at 16 Hz. A four-wire van der Pauw geometry was employed, using In as a contact material.

III. RESULTS AND DISCUSSION

High resolution specular WAXRD data are shown in Fig. 1 at deposition temperatures ($T_{\text{Dep}}$) from 450 to 700 °C. For the 700 °C case, the data are also shown after postdeposition annealing in flowing O$_2$ at 500 °C, as described in Sec. II. The WAXRD data were taken from 20° to 60°, but we show here only the representative region in the vicinity of the [002] film and substrate reflections (40°–50°). The data at $T_{\text{Dep}} < 500$ °C [Fig. 1(a)] provide no indication of any discernible diffraction peaks from the film, only the [001] family of SrTiO$_3$ (STO) peaks being observed. Considering additional data presented below, it is likely that films grown at $T_{\text{Dep}} < 500$ °C are in fact amorphous, consistent with experimentally determined crystallization temperatures for LaCoO$_3$, which are observed to lie in the range 450–500 °C. Significantly different results are obtained in the range 500 °C ≤ $T_{\text{Dep}}$ ≤ 600 °C [Figs. 1(b) and 1(c)], where strong LSCO film diffraction peaks are observed. Only the [001] family of LSCO peaks is found, with no evidence of other LSCO planes, or secondary phases. The films are thus epitaxial, at least in the direction normal to the substrate. Finite size fringes are observed around the LSCO [002] reflection.
(they are consistent with the film thickness), indicating smooth film surfaces on short lateral length scales. The extracted c-axis lattice parameters in this $T_{\text{Dep}}$ range lie in the 3.79–3.81 Å region. Although this is below the bulk value of 3.83 Å, as expected from the tensile strain imposed by the SrTiO$_3$(001) substrate (lattice parameter of 3.905 Å, i.e., a 1.9% mismatch), these out-of-plane film lattice parameters are in fact anomalously large. This is returned to below and explained in terms of cation nonstoichiometry. Most importantly, a reciprocal space map around the (013) reflection for a film grown at 600 °C, revealed an in-plane lattice parameter of 3.91 Å, essentially identical to that of the substrate, demonstrating fully strained pseudomorphic growth at these lower deposition temperatures. The films are thus tetragonally distorted.

At $T_{\text{Dep}} \geq 650$ °C [Figs. 1(d) and 1(e)] the LSCO [001] film peaks persist, but with suppressed finite size fringe intensity indicating higher roughness. The extracted c-axis lattice parameters at these higher deposition temperatures lie around 3.775 Å, relatively independent of $T_{\text{Dep}}$. This value is slightly relaxed toward the bulk value (3.83 Å) in comparison to that obtained for fully strained pseudomorphic films [verified by reciprocal space maps around the (013) reflection], which have c-axis lattice parameters of 3.768 Å at $T_{\text{Dep}} = 700$ °C. These higher $T_{\text{Dep}}$ films thus exhibit slight strain relaxation. This is consistent with our earlier work, which explored the full thickness dependence at a fixed $T_{\text{Dep}}$ of 700 °C, enabling determination of the critical thickness for strain relaxation ($t_{\text{crit}}$), which was found to be 200 Å. The film thickness in this study (250 Å) thus exceeds the critical thickness at $T_{\text{Dep}} = 700$ °C. This $t_{\text{crit}}$ apparently increases with decreasing $T_{\text{Dep}}$, however, exceeding the 250 Å film thickness below ~600–625 °C, where we observe fully strained pseudomorphic films. This increasing tendency toward strain relaxation at higher $T_{\text{Dep}}$, which is quite typical, will be discussed in the context of several other results provided below.

In the $T_{\text{Dep}} \geq 650$ °C temperature range a small but detectable CoO[002] peak also emerges, growing in intensity with increasing $T_{\text{Dep}}$, indicating the formation of a secondary impurity phase. This impurity phase, which was also detected in prior work at $T_{\text{Dep}} = 700$ °C, takes the form of epitaxially oriented CoO inclusions, ~20 nm in size. Consistent with our earlier work, Fig. 1(f) demonstrates that this CoO impurity phase is eliminated by postdeposition ex situ annealing in flowing O$_2$ at 500 °C. Within the resolution of our measurements the LSCO [002] diffraction peak is apparently unaltered by this annealing process. The fact that the binary oxide impurity phase forms only at the highest $T_{\text{Dep}}$, and that it is eradicated by postdeposition annealing in O$_2$, suggests that the CoO (which has Co ions in the 2−valence state) forms due to insufficient oxygenation. This is perhaps unsurprising given the known difficulty of obtaining bulk stoichiometric LSCO at $x$ greater than ~0.5 (i.e., Co$_{2-x}^{3+}$)$_6$ and the fact that bulk SrCoO$_3$ (Co$^{4+}$) can be obtained only via methods based on the use of high pressure oxygen. As discussed below in more detail, STEM/EELS data provide more information on the evolution of the oxygen content, and its nanoscale homogeneity, with $T_{\text{Dep}}$, elucidating the mechanism by which these CoO inclusions form.

In-plane epitaxy of the LSCO [001] films was established via GID (i.e., $\phi$ scans), as shown for the representative case of $T_{\text{Dep}} = 700$ °C in Fig. 2(a). Four peaks are observed in a 360° $\phi$ scan, spaced by 90°, and comparison to the equivalent substrate data (not shown) confirms the expected cube-on-cube epitaxial relationship. All films with $T_{\text{Dep}} \geq 500$ °C exhibited similar GID data, indicating that films grown at a high enough $T_{\text{Dep}}$ to induce crystallinity are in fact epitaxial.

Further information on the film microstructure was obtained from transverse scans (i.e., rocking curves) through the [002] LSCO reflection at deposition temperatures from 500 to 700 °C [Fig. 2(b)]. Although these rocking curves can be “force-fit” to a single Gaussian to extract a full-width at half-maximum (FWHM), as in prior work, careful fitting reveals that the peak shape can be properly described by neither a Gaussian nor a Lorentzian. As exemplified by the 600 °C data, the rocking curves are in fact composed of two superimposed Gaussian peaks, one having a significantly

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**FIG. 2.** (Color online) (a) Grazing incidence in-plane diffraction ($\phi$ scan) for a STO(001)/LSCO film deposited at 700 °C. (b) Rocking curves ($\omega$ scans) through the (002) LSCO diffraction peak for films deposited at 500, 600, 650, and 700 °C (with and without annealing). (c) Rocking curve ($\omega$ scan) for the 700 °C film illustrating the two Gaussian fitting procedure.
larger peak width than the other. In the $T_{\text{Dep}} = 600 \, ^\circ\text{C}$ case these two widths are 0.38° and 0.05°. This decomposition was quantified by a two Gaussian fitting procedure, as illustrated in Fig. 2(c) for the representative example of $T_{\text{Dep}} = 700 \, ^\circ\text{C}$. As in all other cases the two superimposed Gaussians provide a good fit to the data. At 700 °C the fitting yields $I_B/I_N$ (the ratio of “broad” to “narrow” intensities) of approximately 0.5, with broad and narrow peak widths of 0.26° and 0.07°, respectively. A full discussion of the $T_{\text{Dep}}$ dependence of these parameters is described in the following, but we mention at this stage that there are essentially two main trends; an abrupt increase in the overall peak width with $T_{\text{Dep}}$ above 600 °C, and a similarly abrupt increase in $I_B/I_N$, also occurring above 600 °C. Our prior work on the film thickness dependence of the structural and microstructural parameters at a fixed $T_{\text{Dep}}$ of 700 °C (Ref. 4) provides a framework to understand these trends. Specifically, we observed an increase in rocking curve FWHM, surface roughness, and microstrain contribution to the WAXRD, consistent with the behavior of the in-plane lattice parameter ($c$), the rms surface roughness from 2 × 2 μm AFM images ($\sigma$), the total FWHM of the LSCO [002] rocking curve ($\Delta\omega$), the previously defined $I_B/I_N$, and the ratio of intensity from the CoO[002] and LSCO[002] diffraction peaks ($I_{\text{CoO}}/I_{\text{LSCO}}$). Starting with Figs. 4(c)–4(e) we observe the abrupt increase in $\sigma$, $\Delta\omega$, and $I_B/I_N$ near 625 °C, previously discussed in connection with Figs. 1–3. These trends all indicate an increasing tendency toward strain relaxation at these higher temperatures. Given this conclusion, which, as discussed earlier, is directly

Figure 4 provides a concise summary of the $T_{\text{Dep}}$ dependence of the most critical structural and microstructural parameters, specifically the deposition rate ($R$), the out-of-plane ($c$-axis) lattice parameter ($c$), the rms surface roughness from 2 × 2 μm AFM images ($\sigma$), and the ratio of intensity from the CoO[002] and LSCO[002] diffraction peaks ($I_{\text{CoO}}/I_{\text{LSCO}}$). Starting with Figs. 4(c)–4(e) we observe the abrupt increase in $\sigma$, $\Delta\omega$, and $I_B/I_N$ near 625 °C, previously discussed in connection with Figs. 1–3. These trends all indicate an increasing tendency toward strain relaxation at these higher temperatures. Given this conclusion, which, as discussed earlier, is directly
verified by the measurement of in-plane lattice parameters, one might naively expect an increase in \( c \)-axis lattice parameter with increasing \( T_{\text{Dep}} \), i.e., a gradual approach toward the bulk lattice parameter of 3.83 Å. Figure 4(b) shows that this is not the case; \( c \) in fact decreases with increasing \( T_{\text{Dep}} \), leveling off at 625 °C and above. We ascribe these anomalously large \( c \) values to cation nonstoichiometry at low \( T_{\text{Dep}} \), an interpretation that is based on three main arguments. First, it has recently been demonstrated in related (and more extensively investigated) perovskites, such as SrTiO\(_3\), that cation nonstoichiometry (be it Ti or Sr excess) invariably leads to an increase in lattice parameter. This effect is sufficiently strong that attainment of the minimum possible lattice parameter has even been used as a guide to deposition of stoichiometric perovskites. Second, we will show later that in this \( T_{\text{Dep}} \) regime the saturation magnetization, Curie temperature, and resistivity all exhibit significant departures from the values obtained on stoichiometric bulk material. Given that at higher \( T_{\text{Dep}} \) we are able to obtain bulk-like physical properties, and that we will argue that anion stoichiometry is a serious issue only at higher \( T_{\text{Dep}} \) for these deposition conditions, it is natural to ascribe this to cation stoichiometry issues. Third, and most directly, we provide STEM/EELS data that directly indicate substantial variations in the La/Co ratio on a 10 nm lateral length scale for films deposited in this lower temperature range. This obviously implies cation nonstoichiometry. It is interesting to note that the deposition rate [Fig. 4(a)] also exhibits a change in \( T_{\text{Dep}} \) dependence near 625 °C. The noticeable decrease in rate beyond this \( T_{\text{Dep}} \) is likely also connected to the improved cation stoichiometry. In general terms an improvement in cation stoichiometry with increasing \( T_{\text{Dep}} \) is not unexpected and can be ascribed to increased cation mobility, which is returned to below.

The final parameter plotted in Fig. 4 is the \( I_{\text{CoO}}/I_{\text{LSCO}} \) ratio [Fig. 4(f)], which reveals that the onset of CoO impurity phase formation is remarkably abrupt. Any CoO impurity phase exists at volumes beneath the detection limit of our x-ray diffraction measurements below 650 °C. At this temperature and above the CoO intensity rises dramatically, a point that will be important for discussions later in the paper. Note that even in the worst case the CoO diffraction intensity is only about 2% of the LSCO intensity. As we already mentioned, the formation of nanoscopic CoO clusters is driven by the inability to achieve proper oxygenation at the O fugacity occurring during the growth and cooling processes employed here, a conclusion that is supported by the fact that postdeposition annealing in flowing \( O_2 \) at 500 °C completely eradicates the CoO impurity phase. The results of this postdeposition annealing process are shown as open symbols in Fig. 4. In addition to the elimination of the CoO impurity phase, we also observe a decrease in rocking curve width, likely associated with some annealing of defects. There is apparently no change in the strain state of the films however, consistent with the annealing temperature being well below the deposition temperature at which strain relaxation occurs.

The STEM/EELS data presented in Figs. 5 and 6 provide much additional information on the structural quality, interface structure, and chemical homogeneity. Figures 5(a) and 5(c) show \( Z \)-contrast images of the interface region (over a lateral length scale of \( \sim 50 \) nm) in samples deposited at 600 and 700 °C, respectively. Figures 5(b) and 5(d) show higher resolution images at the same locations. Consistent with prior work the interface is coherent and abrupt, with no evidence of significant interdiffusion. The images are in fact very similar to those we obtained in recent work on the SrTiO\(_3\)(001)/Nd\(_{1-x}\)Sr\(_x\)CoO\(_3\) system, where depth profiling of the EELS signature of Ti and Co demonstrated that the interdiffusion was limited to length scales on the order of a single unit cell. The most interesting feature is the obvious superstructure formed by the dark stripes running mostly perpendicular to the interface. This superstructure is simply verified via fast Fourier transforms of the images, and has been observed before in STO(001)/LSCO films by several groups. The superstructure is due to an O vacancy ordering effect, which results in every other CoO2 plane presenting weaker contrast in the STEM images. It appears to play an important role in STO(001)/LSCO thin films, having been implicated as the mechanism by which lattice mismatch is accommodated, and as a means to stabilize an unusual spin-state superstructure for the Co ions. Obviously, the observation of O vacancy ordering also implies the existence of some level of O deficiency in these films. Although direct quantification is difficult, the noteworthy point that emerges from comparison of samples deposited at 600 and 700 °C is the stronger superlattice contrast in the \( T_{\text{Dep}} = 700 °C \) sample, suggesting an increased density of ordered O vacancies at...
higher $T_{\text{Dep}}$, as might be expected from simple thermodynamic arguments.

The chemical homogeneity of the films was analyzed via EEL spectral imaging. The top panel of Fig. 6 [i.e., Figs. 6(a), 6(e), and 6(i)] present lower magnification (150 nm lateral length scale) Z-contrast images for samples with $T_{\text{Dep}} = 600$, 700, and 700 °C plus postdeposition annealing in O$_2$. The lower panels [(b,c,d), (f,g,h), and (j,k,l)] show elemental maps (acquired in the region marked on the Z-contrast images) from the O, Co, and La edges, for the three samples. It is perhaps simplest to begin the discussion with the $T_{\text{Dep}} = 700$ °C (as deposited) data, i.e., Figs. 6(e)–6(h). Although the Z-contrast image [Fig. 6(e)] appears quite uniform (higher resolution images do reveal CoO inclusions, identifiable by their characteristic interplanar spacings$^{27}$), the O, Co, and La elemental maps [Figs. 6(f)–6(h)] clearly reveal the CoO clusters. These inclusions extend through the entire thickness of the film (roughly consistent with the analysis of the WAXRD CoO [002] peak widths), and have lateral sizes of ≈20 nm. They appear as regions that are deficient in La and O, and rich in Co. As discussed in our prior work, the nominal CoO regions have measured average Co:O ratios of 1:1.2, cf. 1:2.5 in the remainder of the film. Comparison to the images from postdeposition annealed films [Figs. 6(i)–6(l)] reveal that the ex situ annealing leads to radical homogenization of the chemical composition. In fact, we observe no evidence whatsoever of lateral inhomogeneity in cation or oxygen stoichiometry. We must emphasize that this provides no contradiction to our prior work$^{5}$; subtle depth-wise variations in Sr, and particularly O content, certainly exist (these depth-wise variations become obvious when lateral averaging is performed, as in Ref. 5), and have important implications for the interface magnetism.

The 600 °C case [Figs. 6(a)–6(d)] is perhaps the most interesting, in that it sheds considerable light on the mechanism of formation of the CoO clusters and the related cation nonstoichiometry deduced from the earlier diffraction data. Although no CoO clusters form, consistent with WAXRD, there are clearly regions (≈10 nm in lateral dimension) that are noticeably depleted in La and enriched in Co. In essence, we observe an anticorrelation between the spectral images shown in Figs. 6(c) and 6(d). Our interpretation of these images is simple; at these intermediate deposition temperatures the low O fugacity, which provides the driving force for CoO formation, is beginning to influence the stoichiometry, but the temperature is sufficiently low (at this deposition rate) that the cation mobility is inadequate to enable the full
segregation of La and Co ions that is required to form CoO clusters. The result is some level of nanoscale lateral inhomogeneity in cation stoichiometry, but no complete formation of CoO inclusions. The local cation variations being observed over lateral length scales of order 10 nm, i.e., significantly smaller than the 20 nm CoO regions found at 700 °C, is consistent with this idea. Using this temperature-dependent length scale as a very crude measure of the diffusion length, \( l_d(T) = [D(T) t]^{1/2} \), where \( D \) is a diffusion constant (with an assumed simple activated form) and \( t \) is time, results in activation energies of order 0.1 eV, i.e., 1 order of magnitude lower than typical values.

The temperature \( T \) dependence of the magnetization \( (M) \) and resistivity \( (\rho) \) are shown in Fig. 7 as a function of \( T_{Dep} \). The first point to note in discussing these data is that the films deposited at 450 °C display dramatically different electronic and magnetic properties in comparison to all others. The \( M(T) \) curves provide no evidence for any form of spontaneous magnetization, while the resistivity is very large and \( \rho(T) \) is strongly insulating. In short, there is no resemblance to the ferromagnetic metallic behavior observed in bulk crystalline specimens, which exhibit \( M_s \approx 2 \mu_B/Co, T_C \approx 245 \) K, and \( \rho(T \rightarrow 0) \approx 100 \mu\Omega \text{ cm} \). Given the structural characterization data presented previously, it is clear that this behavior is due to the amorphous nature of the films deposited at \( T_{Dep} < 500 \) °C. As \( T_{Dep} \) is increased from 500 to 600 °C, a clear evolution of the magnetic and electronic properties occurs. First, significant spontaneous magnetization emerges, the \( M(T) \) curves showing behavior consistent with ferromagnetism, with a Curie temperature \( (T_C) \) that increases from \( \sim 150 \) to \( 200 \) K. At the same time the residual resistivity decreases by almost an order of magnitude, eventually reaching a state with a metallic-like temperature dependence (i.e., \( d\rho/dT > 0 \)) over the whole \( T \) range, and a clear inflection point near \( T_C \). This behavior is quite consistent with the structural characterization data presented earlier, specifically the improvement in cation stoichiometry with increasing \( T_{Dep} \) [consider Fig. 4(b)] and the onset of strain relaxation [see Fig. 4(e) for instance], at \( T_{Dep} \geq 625 \) °C, just as for the structural characterization data presented in Fig. 4, a new regime is entered. The \( M(T) \) and \( \rho(T) \) become practically \( T_{Dep} \) independent, the only obvious deviation from bulk behavior being the slightly depressed \( T_C \), as expected for a film of thickness 250 Å. We believe that the significant relaxation of tensile strain [see, e.g., Figs. 4(c)–4(e)] leads to the improved magnetic and electronic properties in this regime, consistent with prior work. As could be expected, the formation of a low volume fraction of CoO clusters has essentially no effect on the electronic and magnetic properties, as illustrated by the negligible influence of the postdeposition anneal (see open symbols in Fig. 7).

The situation is summarized in Fig. 8, which plots the \( T_{Dep} \) dependence of \( T_C \), the saturation magnetization \( (M_s) \) and coercivity \( (H_C) \) extracted from 10 K hysteresis loops, and the low \( T \) resistivity. At \( T_{Dep} \leq 600 \) °C the \( T_C, M_S, \) and

![Fig. 7. (Color online) Temperature dependence of (a) the resistivity and (b) the magnetization (measured and field cooled in 100 Oe), for films deposited at 450–700 °C. Due to its relatively high resistivity the 450 °C sample is shown as an inset in (a).](image)

![Fig. 8. (Color online) Deposition temperature dependence of (a) the Curie temperature, (b) the saturation magnetization (from 10 K hysteresis loops), (c) the coercivity (from 10 K hysteresis loops), and (d) the low T (approximately 10 K) resistivity. The open symbols denote samples grown at 700 °C and ex situ O₂ annealed. In (d) the 450 °C data are not included as the resistivity could not be measured to sufficiently low T. The shaded region represents the \( T_{Dep} \) window discussed at the end of the paper.](image)
$H_C$ increase monotonically with increasing $T_{Dep}$, whereas $\rho$ decreases. These dependencies reflect the approach to a strongly ferromagnetic metallic state as the crystallinity improves, the cation stoichiometry improves, and, eventually, strain relaxation begins to occur. As $T_{Dep}$ is increased further, beyond 625 °C, $T_C$ and $M_S$ continue to increase slowly, while the resistivity continues to decrease, driven by the increasing strain relaxation. It is interesting to note that $H_C(T_{Dep})$ is nonmonotonic, exhibiting a decrease of about 30% beyond 600 °C. Although the origin of this effect is not entirely clear, our recent investigation of the anomalously large $H_C$ values exhibited by perovskite cobaltites grown on STO(001) substrates\(^{31}\) does provide a possible explanation. The $H_C$ enhancement was found to be intimately related to the interfacial magnetic phase separation, being due, in the thickness regime relevant to the current work, to the interfacial pinning potential provided by the magnetically phase separated layer of thickness $t^*$ at the interface with the STO.\(^{31}\) It is thus possible that the reduction in $H_C$ at the highest $T_{Dep}$ is due to a weak decrease in $t^*$ with $T_{Dep}$. The reduction in $t_{Crit}$ with increasing $T_{Dep}$ is an obvious culprit for this behavior, via the close link between strain state and O deficiency provided by the O vacancy ordering.\(^{5}\) Future work aimed at a deeper understanding of this phenomenon would obviously require measurements of the thickness dependence of the magnetic and electronic properties at multiple $T_{Dep}$, which is well beyond the scope of the current paper.

To examine the data as a whole it is instructive to compare Figs. 4 and 8, i.e., the summaries of the $T_{Dep}$ dependence of the structural, and magnetic/electronic properties. The data reveal the temperature-dependent competition between a number of key factors. Specifically, increasing $T_{Dep}$ leads to improved crystallinity, improved cation stoichiometry, and a tendency toward bulk-like properties due to increased strain relaxation. However, at sufficiently high $T_{Dep}$ the inevitable problems with full oxygenation begin, eventually leading to secondary phase formation in the form of CoO inclusions. If the goal is to deposit single-phase epitaxial films with as close to bulk-like physical properties as possible there are thus two possible routes. The first is to deposit at the highest $T_{Dep}$, leading to good crystallinity and cation stoichiometry, and the maximum extent of strain relaxation, but at the expense of CoO impurity phase formation. The CoO can then be subsequently eliminated by post-deposition annealing in O\(_2\), an approach that has been employed before (e.g., Ref. 4). The second route, which eliminates the need for postdeposition processing, is to simply grow in the relatively narrow $T_{Dep}$ window 600–625 °C. These intermediate temperatures are sufficiently high to obtain highly crystalline films with reasonable cation stoichiometry. Most importantly, in the 600–625 °C range we are afforded some degree of strain relaxation (with the concomitant benefits for the physical properties), at the same time avoiding the O stoichiometry issues and CoO impurity phase formation, which are restricted to $T_{Dep} > 625$ °C. A comparison between Figs. 4 and 8, aided by the shaded regions in the two graphs, shows that in this $T_{Dep}$ range we can obtain single phase epitaxial films with relatively low surface roughness, minimum mosaicity, and close to bulk-like Curie temperature, saturation magnetization, and resistivity.

IV. SUMMARY

In summary, we have provided a detailed study of the deposition temperature dependence of the microstructure, phase purity, nanoscale chemical homogeneity, stoichiometry, and magnetic and electronic properties of epitaxial La\(_{0.6}\)Sr\(_{0.4}\)CoO\(_3\) thin films grown on SrTiO\(_3\)(001) substrates. In addition to providing a much improved understanding of how the temperature-dependent interplay between crystallization, cation mobility, strain relaxation, and oxygenation controls the growth process in this system, our data also indicate a simple route to LSCO sputter deposition that avoids postdeposition processing. The latter should prove particularly valuable for exploration of heterostructures incorporating perovskite cobaltites.

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