Thickness-Dependent Double-Epitaxial Growth in Strained SrTi$_{0.7}$Co$_{0.3}$O$_{3−δ}$ Films

Aster A. Tang,† Mehmet C. Onbasli,‡ Xueyun Sun,‡ and Caroline A. Ross*†‡

†Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
‡School of Materials Science and Engineering, Harbin Institute of Technology, P.O. Box 433, Harbin 150001, China
§Koç University, Department of Electrical and Electronics Engineering, Sarıyer, 34450 Istanbul, Turkey

Supporting Information

ABSTRACT: Perovskite-structured SrTi$_{1−x}$Co$_x$O$_3$ (STCo) films of varying thicknesses were grown on SrTiO$_3$(001) substrates using pulsed laser deposition. Thin films grow with a cube-on-cube epitaxy, but for films exceeding a critical thickness of about 120 nm, a double-epitaxial microstructure was observed, in which (110)-oriented crystals nucleated within the (001)-oriented STCo matrix, both orientations being epitaxial with the substrate. The crystal structure, strain state, and magnetic properties are described as a function of film thickness. Both the magnetic moment and the coercivity show maxima at the critical thickness. The formation of a double-epitaxial microstructure provides a mechanism for strain relief in epitaxially mismatched films.

KEYWORDS: perovskite, thin film, epitaxy, magnetism, pulsed laser deposition, Co substitution

INTRODUCTION

Perovskite oxides of generic formula ABO$_3$ exhibit a range of compositions and functionalities due to their ability to accommodate a variety of metal cations and valence states in the A and B sites through distortions or rotations of the oxygen octahedra. Consequentially, they have many technological applications, including cathodes in solid oxide fuel cells, oxygen and hydrocarbon sensors, and nonvolatile memory devices. Control over material properties can be further expanded in perovskite thin films by introducing epitaxial strain as a variable, resulting in the enhancement or emergence of useful properties. SrTiO$_3$ (STO) is a prototypical perovskite, thin films grow with a cube-on-cube epitaxy, but for films exceeding a critical thickness of about 120 nm, a double-epitaxial microstructure was observed, in which (110)-oriented crystals nucleated within the (001)-oriented STCo matrix, both orientations being epitaxial with the substrate. The crystal structure, strain state, and magnetic properties are described as a function of film thickness. Both the magnetic moment and the coercivity show maxima at the critical thickness. The formation of a double-epitaxial microstructure provides a mechanism for strain relief in epitaxially mismatched films.
was observed in SrTi$_{1-x}$Fe$_x$O$_{3-\delta}$ (STF) grown on (001) Si buffered by ceria/yttria-stabilized zirconia, in which wedge-shaped STF crystals with (110) orientation and well-defined interfaces formed within a (001) STF film. A double-epitaxial microstructure was also reported for LaFeO$_3$ on STO and for CeO$_2$ (co-deposited with LaSrMnO$_3$) on STO. Despite these observations, double epitaxy is not well studied in perovskite thin films compared to other strain-reducing mechanisms. In this article, we describe the thickness dependence of the microstructure and the magnetic properties of a substituted perovskite, SrTi$_{1-x}$Co$_x$O$_{3-\delta}$ (STCo) with $x = 0.3$, grown on STO(001), showing that the second crystal orientation forms for films above a critical thickness corresponding to maxima in the magnetic anisotropy and coercivity.

■ EXPERIMENTAL METHODS

STCo films were fabricated on (001) STO substrates using a Neocera pulsed laser deposition (PLD) system (KrF, 248 nm, 1.4 J cm$^{-2}$ fluence) with a substrate temperature of 650 °C and a base pressure during deposition of 1 μTorr. The target had a nominal composition of SrTi$_0.7$Co$_{0.3}$O$_{3-\delta}$. All films were grown under nominally the same conditions, but measured growth rates were $0.705 - 2.19$ nm min$^{-1}$ due to variations in the deposition system conditions over time, with growth rates higher for thicker films.

Six films with thicknesses of around 50, 60, 80, 120, 180, and 220 nm were characterized. All thicknesses were measured by profilometry. Thicknesses of the first four thinnest films were also determined by cross-sectional transmission electron microscopy (TEM), which agreed with the profilometry data.

X-ray diffraction (XRD) $\omega-2\theta$ scans and in-plane pole figure scans were performed using a Rigaku SmartLab multipurpose diffractometer with an incident beam Ge(022) double-bounce monochromator and the SmartLab Guidance data collection program. The XRD data profile fits were performed with PANalytical HighScore Plus. Atomic force microscopy (AFM) was conducted on a Veeco Metrology NanoScope V scanned probe microscope controller using a Bruker RTESP-300 probe. TEM cross-sectional images of samples prepared using a focused ion beam (FEI-600) were collected with an FEI G2 F30 transmission electron microscope at 300 kV and a JEOL 2010 transmission electron microscope at 200 kV. Magnetic hysteresis loops were measured using a Digital Measurement System 7035B vibrating sample magnetometer (VSM).

■ RESULTS AND DISCUSSION

The STCo films showed only perovskite diffraction peaks without detectable elemental Co, CoO, or other phases. The XRD $\omega-2\theta$ results in Figure 1a indicate that all of the STCo films had out-of-plane lattice parameter $c$ vs thickness $t$ with error bars corresponding to the full width at half-maximum (FWHM). (c) Pole figure scans for STCo(101) from the 50, 120, and 180 nm films taken up to $55^\circ$. The 50 nm film shows strong peaks (A) from the (001)-oriented film. The 120 nm film shows a peak (B) from the (110)-oriented regions of the film. The 180 nm film shows a third set of peaks (C) indicating a third epitaxial relationship.

Figure 1. (a) $\omega-2\theta$ scans of 50, 60, 80, 120, 180, and 220 nm STCo films on STO(001) single-crystalline substrates. (b) Out-of-plane lattice parameter $c$ vs thickness $t$ with error bars corresponding to the full width at half-maximum (FWHM). (c) Pole figure scans for STCo(101) from the 50, 120, and 180 nm films taken up to $55^\circ$. The 50 nm film shows strong peaks (A) from the (001)-oriented film. The 120 nm film shows a peak (B) from the (110)-oriented regions of the film. The 180 nm film shows a third set of peaks (C) indicating a third epitaxial relationship.
This is consistent with an oxygen deficiency ($\delta > 0$), which leads to an increase in lattice parameter as a result of chemical expansion.\(^{40}\)

Clear splitting of the (002) film peaks was observed for films 120 nm and thicker, suggesting strain relaxation in part of the film, as seen in other epitaxial systems, such as Sr(Ti,Ga,Fe)-O$_{3-\delta}$ films grown on (La,Sr)(Al,Ta)O$_3$,\(^{41}\) where the strain in the upper layer of the film was released. Two out-of-plane lattice parameters, near 3.95 and 4.00 Å, were determined by XRD for films with split peaks, and are shown in Figure 1b. The error bar in the figure was determined from the full width at half-maximum (FWHM). The RSM of the 220 nm film (Figure S1) showed two film peaks, in agreement with the XRD, and further that both peaks corresponded to the same in-plane lattice parameter as the substrate. In contrast, the thinner films had a broader peak, which was not clearly resolved as two separate peaks by $\omega-2\theta$ XRD. Fitting to a single peak yielded out-of-plane lattice parameters of $\sim 3.96$ Å.

The thicker films (120 nm and above) additionally showed ($hh0$) peaks. Pole figure scans for the (200), (101), and (111) peaks were measured, and Figure 1c shows pole figures of the (101) peak, where $0^\circ$ represents the (110) direction of the film and $45^\circ$ represents the (100) directions of the film and substrate. The discrete spots indicate that both the (001)- and (110)-oriented regions in the film had an epitaxial relationship with the substrate. This is characteristic of double epitaxy observed in STF on ceria-buffered Si.\(^{36}\) The (001)-oriented part of the film showed cube-on-cube epitaxy with the (001) substrate (i.e., STCo[001]||STO[001]), whereas in the (110)-oriented part of the film, the [001] and [110] in-plane directions align with in-plane [110] and [1T0] of the substrate, respectively. Furthermore, in films with thickness 180 nm and higher, an additional set of discrete peaks was observed, which could correspond to perovskite Miller indices (631) or (221) on the basis of their position in the pole figure. The XRD peaks associated with these Miller indices fall outside the scan range of the diffractometer and are absent in the reference powder file and consequently are not visible in the $\omega-2\theta$ scans.

Figure 2a illustrates the typical surface topography observed during tapping-mode AFM exemplified by the 60 and 120 nm thick films. Figure S2 gives an AFM image of the 220 nm thick film, which is similar to that of the 120 nm film. There is a qualitative change in the film surface for thicknesses of 120 nm and above. The 50, 60, and 80 nm thick films showed $\sim 20$ nm diameter rounded features a few nanometers tall, but films 120 nm and thicker showed taller elongated and faceted features primarily oriented along orthogonal in-plane directions. We attribute the faceted features to the (110) regions of the film by analogy to the microstructure observed in double-epitaxial STF.\(^{36}\) These features are also similar in appearance to the protruding crystals observed in the SEM images of (110) STF on (110) STO.\(^{22}\) As shown in Figure 2b, both the average roughness of the films and percent area covered by surface features increase as thickness increases, with the exception of the thickest film. Average roughness was determined from the topographical scan using NanoScope Analysis 1.5 software, whereas percent area of the surface features was calculated using ImageJ software to determine the area of features protruding higher than 25% of the full-scale peak-valley distance. The density of the features was similar for all films.
 TEM cross sections of a 220 nm thick film along the substrate [010] zone axis, as seen in Figure 3a,b, demonstrate that tapered features initiated after ~100 nm film growth. The dark-field image in Figure 3b shows two tapered crystals with a common orientation. The corresponding diffraction pattern is shown in Figure 3c. The spot from which the dark-field image was taken is located at the center of the red circle.

Another sample from the same film was cut at 45° to the first sample such that the beam is parallel to a [110] zone axis in the film plane. An image of the film–substrate interface is shown in Figure 3d. Planar defects perpendicular to the interface are clearly visible as well as local contrast in the planes parallel to the substrate. The fringe contrast indicates that the planar defects are not parallel to the zone axis but pass through the thin sample at an angle to the beam direction. Figure S3 shows a map representing lattice strain parallel to the interface. The contours are not straight, indicating inhomogeneity in the lattice spacing of the STCo film and local strain variations.

Figure 3e,f shows a bright-field and dark-field image pair from a region of the film around one of the tapered features, which is delineated by moiré fringes. The diffraction pattern in Figure 3g corresponds to Figure 3e,f and shows symmetry corresponding to the [110] axis. Elemental analysis (Figure S4) indicated a uniform Co content along a linescan parallel to the top surface of the film within the noise limit of the measurement, without enrichment or deficiency of Co in the tapered regions.

The film initially grows with a strained cube-on-cube (100) orientation. The electron diffraction pattern in Figure 3c as well as the XRD data confirms cube-on-cube growth of the film. Small scale variations in contrast among planes parallel to the interface may be a result of an inhomogeneous distribution of oxygen vacancies, which can form ordered layers as seen in brownmillerite and other anion-deficient perovskites.32 These films are highly oxygen-deficient due to the growth environment; consequently, ordering of point defects is expected, which can account for the inhomogeneous strain in the out-of-plane direction indicated in Figure S3. In addition, the film exhibits planar defects perpendicular to the interface, which propagate through the film thickness, leading to a columnar appearance. The film therefore has a mosaic-type structure, with the planar defects assumed to define regions of different octahedral tilt or rotation, anion ordering, or other structural distortions, even though the film overall has an epitaxial relation to the substrate.

The tapered features are believed to correspond to the protrusions seen in the AFM scans and to represent (110)-oriented crystals within the (100) STCo matrix. In the [010] zone axis, there are few diffraction spots from the (110)-oriented crystals because the electron beam is not parallel to a low-index zone axis, due to the in-plane 45° rotation of the rectangular net of the (110)-oriented crystals with respect to the substrate. Tapered crystals are also seen in the [110] zone axis sample, with moiré fringes assumed to correspond to the overlap of the tapered region with the matrix. Additional HRTEM images are shown in Figure S5.

The development of tapered crystals having a (110) orientation is consistent with the appearance and increase of (110) peak intensity with increasing film thickness in the X-ray pole figure and XRD ω−2θ scans. Crystals with a tapered shape were similarly found in BaTiO3 grown on a SrRuO3 buffer layer36 and STF on buffered Si.37 The results suggest that both defect nucleation and double epitaxy provide mechanisms for strain relief in the films.

The epitaxial STCo thin films are believed to follow a Stranski–Krastanov growth mode.32 Initially, the film is expected to grow via a two-dimensional layer-by-layer process until it reaches a critical thickness, at which three-dimensional...
island growth becomes dominant, as exemplified by PLD-grown BaTiO$_3$/SrRuO$_3$/STO. From the TEM images and XRD data, lattice mismatch appears to be accommodated by lattice strain, point defects, planar defects, and surface perturbations. As the film continues to grow, strain energy in the film may continue to increase faster than it can be relaxed by these defects. We infer that the double-epitaxial structure forms when nucleation of a second crystal orientation occurs more readily than other strain release mechanisms, such as twinning. Favorable growth of the (110) nuclei leads to tapered features, and their facets on the top surface produce the crystallographically oriented elongated topography, as seen in Figure 2b. In LaFeO$_3$ on STO, islands of the second orientation were said to be more likely to grow if deposition conditions favored low flux or low adatom diffusion length (e.g., from high lattice mismatch).  

We now discuss the effects of the film thickness on the room-temperature magnetic properties. Magnetic hysteresis curves for selected samples and the saturation ($M_s$), coercivity ($H_c$), remanence ($M_r$), and anisotropy ($K_u$) vs thickness are shown in Figure 4. In all samples, the out-of-plane direction was the easy axis and the maximum field (10 kOe) available from the VSM was not able to saturate most of the films in-plane, limiting the accuracy of background subtraction for the in-plane loops.

For the out-of-plane loops, $H_c$, $M_s$, and $M_r$ varied with thickness, with maxima for the 120 nm thick sample, as shown in Figure 4b. The films had $M_s = 34 - 43$ emu cm$^{-3}$ for thicknesses of 50 – 120 nm, although the $M_s$ of the thickest films was only 8 – 9 emu cm$^{-3}$. Figure 4c shows estimates of the net uniaxial anisotropy constant $K_u$ determined from the area difference between the anhysteretic easy-axis loop and the hard-axis loop. The anhysteretic loop is the average of the ascending and descending branches of the easy-axis loop. For the 60, 80, 120, and 180 nm films, the hard-axis loop was normalized to the saturation magnetization of the easy-axis loop, and the calculation gives a lower limit on anisotropy. The anisotropy is maximum for the 120 nm film, and is approximately 50 – 80% of the anisotropy measured for STF.

The saturation magnetization values are comparable to prior works, in which (100)-oriented STCo with 23% Co has $M_s = 0.5$ – 1 μemu/Co-ion (23 – 46 emu cm$^{-3}$) and an out-of-plane easy axis when grown at pressures of 1 – 3 μTorr. The magnetic moment was attributed to Co within the perovskite rather than to phases such as metallic Co, according to results from elemental analysis, as well as prior X-ray photoelectron spectroscopy and X-ray absorption near-edge spectroscopy results, which indicated primarily Co$^{2+}$ and Co$^{3+}$ occupying octahedral sites but no significant metallic Co. Temperature-dependent magnetization measurements have shown a linear (except at the lowest temperatures) decrease in magnetization and a Curie temperature of above 1000 °C and suggest a spin-glass-like behavior. A density functional theory study predicted 1.6 μemu/Co (73 emu cm$^{-3}$) for STCo with 25% Co and δ = 0.125. The out-of-plane easy-axis magnetic anisotropy of STCo is attributed primarily to magnetoelastic anisotropy with minor contributions from shape and magnetocrystalline anisotropy, similar to the case of STF. Changes to the strain state of the film are expected to have an impact on the magnetic properties largely through their impact on the magnetoelastic anisotropy.

The thickness of the STCo films therefore has a profound effect on their magnetic properties as well as on their structure. The room-temperature magnetic moment and anisotropy in STCo (and STF) films are related to the presence of oxygen...
vacancies and the stabilization of the magnetic moment of magnetoelastic cations in the strained lattice$^{21-25}$ and consequently are influenced by nonstoichiometry, strain state, and crystallographic orientation. This work has shown that the first ~100 nm of the film is characterized by a relatively high magnetization and anisotropy, but after the appearance of the (110) crystal orientation and strain relaxation suggested by the splitting of the perovskite XRD peak, the strain energy is partially relieved in the subsequently grown layers of the film. The magnetization and anisotropy of the overall film gradually decrease as the strain-reduced region occupies an increasing volume fraction of the film. As a final comment on the ferroelectric properties of the STCo, we found that a 120 nm thick STCo film grown on Nb-doped STO with top Au/Pt contacts did not show a ferroelectric response at temperatures down to 100 K for applied voltage up to 11 V.

### CONCLUSIONS

Pulsed laser deposition was used to grow SrTi$_{0.7}$Co$_{0.3}$O$_3$ films of thicknesses varying from around 50 to over 200 nm on (001) STO. The STCo exhibited growth of tapered crystals of a second orientation (110), at thicknesses of 100 nm and above, as confirmed by microscopy and XRD. The (110) crystals are epitaxial with the substrate and with the (001) STCo matrix and provide a strain reduction mechanism. The films also exhibit contrast from local strain that may indicate vacancy clustering, as well as vertical planar defects. Although double epitaxy was previously observed in SrTi$_{1-x}$Fe$_x$O$_3$ (STF) on buffered Si, it was not observed even in thick STF on STO, which is attributed to the better lattice match between STF/STO compared to STCo/STO. The films show room-temperature magnetic hysteresis, which is attributed to the Co-substituted perovskite phase, with a magnetization up to 43 emu cm$^{-3}$. There was no evidence of metallic Co or other magnetic phases. The critical thickness for the formation of the double-epitaxial morphology of STCo corresponds to maxima in the room-temperature magnetic moment and uniaxial magnetic anisotropy of the films, which have out-of-plane easy axis.

The formation of double-epitaxial microstructures is expected to influence other important perovskite properties, including ferroelectricity, piezoelectricity, and thermal or electronic conductivity. Moreover, it provides films containing well-defined interfaces oriented at an angle to the film plane, analogous to those present in two-phase vertical nanocomposite films$^{43}$ which may be useful in studies of transport and other properties.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b18808.

RSM, AEM, additional TEM cross-sectional images, and elemental analysis linescan data of the 220 nm STCo film (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: caross@mit.edu.*

**ORCID**

Astera S. Tang: 0000-0001-5143-9214

Caroline A. Ross: 0000-0003-2262-1249

### ACKNOWLEDGMENTS

The authors thank the MIT CMSE staff for instruction with data collection and analysis and, in particular, Charlie Settens for helpful discussions on the XRD data and Yong Zhang for guidance in collecting TEM data. The authors are grateful to Frances Ross of IBM for TEM strain mapping. This study was supported by NSF DMR-1419807 and made use of the Shared Experimental Facilities also supported in part by the MRSEC Program of the National Science Foundation under award number DMR-1419807. M.C.O. acknowledges Junior Faculty Program Award (BAGEP) 2017.

### REFERENCES


