Combinatorial Substrate Epitaxy Investigation of Polytypic Growth of $AEMnO_3$ ($AE = Ca, Sr$)

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Abstract

Combinatorial substrate epitaxy (CSE) was used to study the orientation relationships (ORs) and polytypic stability for $AEMnO_3$ ($AE = Ca, Sr$) thin films grown on polycrystalline $SrMnO_3$ and $SrTiO_3$ substrates. $SrMnO_3$ films with the stable four-layered hexagonal (4H) and metastable three-layered cubic (3C) structures were also grown on (111) and (100) $SrTiO_3$ single crystal substrates, respectively. Electron backscatter diffraction data was used to determine the following ORs, which hold true regardless of the substrate surface orientation: $(001)[100]_{4H\ SrMnO_3} || (001)[100]_{4H\ SrMnO_3}$, $(111)[\bar{1}00]_{3C\ CaMnO_3} || (001)[100]_{4H\ SrMnO_3}$, and $(001)[100]_{4H\ SrMnO_3} || (111)[\bar{1}00]_{3C\ SrTiO_3}$. These are all simply the eutactic OR, which aligns the eutactic planes and directions; its ubiquity indicates the interface energy is generally lower for the eutactic OR than for all other possible ORs. $3C\ SrMnO_3$ was found to grow only on very near (100) $3C\ SrTiO_3$ grains. This narrow range of epitaxial stabilization suggests that the penalties of higher interfacial and/or strain energies between polytypic perovskites adopting the eutactic OR are not significant enough to overcome the volumetric formation energy of the stable phase, in these growth conditions, except for very special orientations.
1. Introduction

Epitaxial stabilization is a method known to direct growth of a specific compound in a particular crystal structure as a film, using a supporting substrate as the template. Importantly, it has been used to grow metastable phases where other synthesis methods have failed. When optimized for epitaxial stabilization, nucleation of a bulk metastable phase is thermodynamically preferred due to a lower free energy of formation for its epitaxial nuclei, with important contributions from the film-substrate interface and strain energies modifying stability. Most epitaxy studies use commercially available single crystal substrates with polished, low Miller index surfaces and high planar symmetries. These experiments are therefore limited to a small number of structural, strain, orientation, and symmetry states of surfaces, usually those representing special interfaces of a limited number of structural types. Therefore, our understanding of epitaxy and our ability to stabilize polymorphs across wide ranges of structures is hindered by the lack of available commercial isostructural substrates across wide-ranging orientations.

Combinatorial substrate epitaxy (CSE) is a high-throughput method to investigate epitaxial growth that overcomes those limitations of traditional epitaxy investigations. In CSE, polished polycrystalline substrates are used, which can be prepared in-house for a wide range of structural families, and each grain of the substrate can be viewed as a single crystal with a unique orientation. Electron backscatter diffraction (EBSD) is used in CSE as a high-throughput local structural probe to create phase and orientation maps across large areas of the substrate surface, as well as the deposited film. A single deposition of a film onto a polycrystalline substrate yields thousands of observations from which a broad understanding of phase stability and film-substrate orientation relationships (ORs) can be
developed. For example, only a few ORs were found for epitaxial films on polycrystalline substrates across all of orientation space of the substrate. One common preferred epitaxial orientation (PEO) is called the eutactic OR, which aligns the eutactic (or nearly close-packed) planes and directions between the film and substrate. Furthermore, CSE has been used many times now to investigate polymorph stability, including anatase vs rutile TiO$_2$, and rutile vs scrutinyite SnO$_2$. Following on these prior observations, we use CSE herein to epitaxially grow SrMnO$_3$ and CaMnO$_3$ perovskite polytype thin films on both cubic and hexagonal polycrystalline perovskite substrates, investigating epitaxial stabilization and preferred orientation relationships.

Alkaline earth (AE) manganese oxide perovskites, AEMnO$_3$ (AE = Ca, Sr, and Ba), are of special interest because they can form over the full range of perovksite polytypes and exhibit varying physical properties. These polytypes differ in the relative number or order of cubic and hexagonal stacking of the eutactic AEO$_3$ planes, which leads to variations in the number of corner-shared or face-shared MnO$_6$ octahedra. Because many of the physical properties of manganese oxide perovskites are associated with details of the Mn-O bonding, controlling the polytype formation is critical to engineering properties as a function of composition. The primary approach used to control polytype formation is to control the Goldschmidt tolerance factor, $t$, which describes the relative similarity between the AE-O and Mn-O bond lengths (more information about $t$ can be found in §S1). Under normal processing conditions, BaMnO$_3$ ($t \approx 1.06$) forms in the 2$H$ structure, with all face-sharing octahedra and a stacking sequence $ABAB$; SrMnO$_3$ ($t \approx 0.99$) forms in the four-layered hexagonal (4$H$) structure, with half face-sharing and half corner-sharing octahedra and a stacking sequence $ABCB$; and CaMnO$_3$ ($t \approx 0.94$) forms in an orthorhombic variant of the 3$C$ polytype, with all corner-sharing octahedra and a stacking sequence $ABC$.

Importantly, the polytype formed for a given cation composition depends on temperature,
pressure, and oxygen activity.\textsuperscript{7} At temperatures above 1400°C, for example, SrMnO$_3$ evolves sufficient oxygen that the 4\textit{H} structure transforms to 3\textit{C}.\textsuperscript{7} Interestingly, Song et al.\textsuperscript{7} determined the influences of oxygen pressure and temperature on the phase stability of SrMnO$_3$ thin films, using (111) 3\textit{C} SrTiO$_3$ substrates, which were similar to those for bulk material. While CaMnO$_3$ and BaMnO$_3$ form in different variants or polytypes of their respective structures at elevated temperatures,\textsuperscript{7} neither have been formed with complete hexagonal or cubic stacking, respectively.

It is of interest to develop synthetic methods that would allow access to distinct polytypes independent of composition and tolerance factor, which would thus open up observation of new materials, such as ferroelectric and ferromagnetic 3\textit{C} BaMnO$_3$.\textsuperscript{7} Epitaxial stabilization has been used to grow 3\textit{C} SrMnO$_3$ films on single crystal \{100\} 3\textit{C} perovskite substrates,\textsuperscript{7} \textsuperscript{7} \textsuperscript{7} \textsuperscript{7} \textsuperscript{7} \textsuperscript{7} in conditions that the 4\textit{H} polytype is known to be stable as a thin film on (111) 3\textit{C} SrTiO$_3$. These observations support the ideas that epitaxial stabilization offers an independent parameter to influence polytype stability and that the observed epitaxial polytype will be a strong function of substrate orientation. However, very little is known for perovskite polytype epitaxy across orientation space on hetero-polytypic substrates, especially on 4\textit{H} substrates, as they are not available in single crystal forms. While one can envision specific substrates will serve as strong drivers for stabilizing metastable polymorphs, there is no clear understanding the competitive nucleation events occurring during perovskite polymorph formation as epitaxial films.

Herein, we have carried out CSE experiments in which $AE$MnO$_3$ ($AE = \text{Ca, Sr}$) films were deposited on 4\textit{H} SrMnO$_3$ and 3\textit{C} SrTiO$_3$ polycrystalline substrates, as well as (100) and (111) 3\textit{C} SrTiO$_3$ single crystals. We test whether the eutactic OR is the PEO for SrMnO$_3$ films deposited on 3\textit{C} SrTiO$_3$ and 4\textit{H} SrMnO$_3$ polycrystalline substrates, as well as CaMnO$_3$ films on 4\textit{H} SrMnO$_3$ substrates. We find that the eutactic OR is the PEO for all film-substrate combinations, indicating the eutactic OR results in low energy interface relative
to all other possible ORs. We also investigate phase stability of SrMnO$_3$ on SrTiO$_3$ over the entire range of substrate orientations, finding a surprisingly narrow range of orientations that stabilize 3C films in growth conditions for which 4H SrMnO$_3$ are stable.$^7$ We discuss these observations in the context of the interface energies for the eutaxial films and how they may influence perovskite polytype stability.

2. Experimental details

Polycrystalline 3C SrTiO$_3$ (preparation described elsewhere$^7$), 3C CaMnO$_3$, and 4H SrMnO$_3$ ceramics were prepared using standard ceramic methods as targets and/or substrates. For 3C CaMnO$_3$ and 4H SrMnO$_3$ substrates, stoichiometric amounts of CaCO$_3$ or SrCO$_3$ and MnO$_2$ were mixed in ethanol, then ball milled wet for 12 h, and subsequently pressed uniaxially in a stainless-steel die at pressures >10,000 psi. Samples were fired in air at 700, 1000, and 1350°C for 2, 24, and 24 h, respectively. Prior to the second and third heating steps, samples were reground dry, a portion used to monitor phase progression (using x-ray diffraction), and the rest pressed again for firing. Substrate (target) pellets were $\approx$ 0.5 (5) mm thick and 12 (25) mm in diameter. Sintered substrates were polished to a mirror finish using SiC paper and Al$_2$O$_3$ suspensions. Additionally, 5 $\times$ 5 $\times$ 0.5 mm$^3$, one-side polished single crystals of (111) and (100) SrTiO$_3$ were purchased from MTI Corporation.

All films were grown using a pulsed laser deposition (PLD) system$^7$ and a KrF ($\lambda$=248 nm) laser. Prior to deposition, substrates were ultrasonically cleaned in methanol and ethanol for ten minutes each, dried with compressed air, and attached to the substrate heater with silver paint. The chamber was pumped to base pressures around $10^{-5}$ torr. Substrates were heated to 850°C at 10°C/min. The laser energy density was maintained at $\approx$ 1.5 J/cm$^2$ and the target-to-substrate distance at $\approx$ 6 cm. Target surfaces were laser conditioned first at the base pressure for 10,000 and 2,000 pulses, at 4 and 3 Hz, respectively.
Then the O$_2$ pressure was brought up to the deposition pressure of 2 mTorr and target surfaces were laser conditioned for 2,000 pulses at 3 Hz and at 850°C. Films were deposited for 6,000 pulses to obtain a thickness of $\approx$ 60 nm, based on a deposition rate of $\approx$ 0.1 Å/pulse. The deposition rate was determined using x-ray reflectivity of $\text{AEMnO}_3$ films grown on (111) MgO, using 6,000 pulses at 850°C and 2 mTorr. Films were cooled at a rate of 10°C/min in 200 Torr O$_2$.

Phase and orientation for substrates and films were determined using EBSD in a Quanta 200 scanning electron microscope (SEM), as described elsewhere.$^7$ Identical areas were mapped on the substrate and the films, respectively before and after deposition. EBSD patterns from the substrates were sharp and readily indexed using default settings in the Orientation Imaging Microscopy (OIM) Analysis software by EDAX. Film patterns were more diffuse, as reported elsewhere.$^7$ from internal strain, and automated indexing was optimized by manual selection of reflectors used by OIM. An alternative indexing method, called dictionary indexing, is implemented in §S5. EBSD patterns were indexed using cubic symmetry 3C structures (the small orthorhombic distortions in CaMnO$_3$ were ignored, which improved the confidence index (CI) in OIM) and hexagonal symmetry 4H structures. All raw orientation maps were processed using a minimum grain size of 5 $\mu$m and a grain tolerance angle of 5°. ORs were extracted from the EBSD data as described elsewhere.$^7$ SrMnO$_3$ films were also deposited on single crystals of (111) and (100) SrTiO$_3$, and their structures were characterized using XRD and EBSD.

3. Results

Deposition on 3C SrTiO$_3$ single crystals was used to establish growth conditions for epitaxy and phase competition that are similar to literature observations. The XRD patterns from 60 nm SrMnO$_3$ films deposited (at 850°C and 2 mTorr O$_2$) on (111) and (100) 3C SrTiO$_3$
single crystal substrates are shown in Figure ??a) and b), respectively. Film peaks on both crystal substrates appear as reported in the literature for epitaxial growth of SrMnO₃, indicating the growth conditions should be appropriate for CSE.

In Fig. ??a), the highest intensity peaks belong to the (111) and (222) reflections of the (111) 3C SrTiO₃ substrate \((2\theta = 39.9° \text{ and } 86.2°)\), while the two smaller peaks are attributed to the (002) and (006) reflections \((2\theta = 19.6° \text{ and } 61.4°)\) of 4H SrMnO₃. This indicates that the stable polymorph forms on this orientation of SrTiO₃ in these deposition conditions, as expected. The \(c\)-axis lattice parameter computed from these values is \(\approx 9.04 \text{ Å}\), which differs by \(0.2\%\) from the bulk 4H SrMnO₃ \(c\)-axis measured by Chamberland et al. In Fig. ??b), the (100), (200), and (300) reflections from the (100) 3C SrTiO₃ substrate correspond to the high intensity peaks at \(2\theta = 22.7°, 46.4°, \text{ and } 72.5°\), respectively. The lower intensity peaks at \(2\theta = 23.4° \text{ and } 48.0°\) correspond respectively to the (100) and (200) reflections of 3C SrMnO₃, though the peaks are shifted to larger \(2\theta\) values by \(\approx 0.6° \text{ to } 1.3°\) compared those expected for relaxed, stoichiometric 3C SrMnO₃. The out-of-plane lattice parameter computed for the 3C film is 3.80 Å, which is smaller (by \(-0.3 \%\))
than the bulk value of 3.81 Å. This is consistent with either in-plane tensile and out-of-plane compressive strains from epitaxial mismatch with the cubic substrate (3.905 Å) or compositional deviations that lead to a change in lattice parameter along one or two directions of the pseudo-cubic cell, with a short (long) axis out-of-plane (in-plane) for a preferred epitaxial match. We did not further differentiate these possibilities. This pattern indicates that the metastable polymorph forms on this orientation of 3C SrTiO$_3$ in these deposition conditions, as expected. Since the films in Fig. were deposited simultaneously, the polytype of SrMnO$_3$ films is a function of substrate orientation.

Orientation maps were constructed using EBSD data to further confirm the phase and epitaxial orientation of SrMnO$_3$ films on SrTiO$_3$ single crystal substrates (results shown in §S2). Using XRD data in conjunction with EBSD data, the epitaxial relationships for the 4H and 3C SrMnO$_3$ films deposited on (111) and (100) 3C SrTiO$_3$ substrates, respectively, were determined. The 4H film on the 3C substrate ($f - s$) has the epitaxial relationship: (001)$_{4H-f} || (111)$_{3C-s}$, which is the eutaxial OR. The 3C film on the 3C substrate has a unit-cell over unit-cell epitaxial OR: (100)$_{3C-f} || (100)$_{3C-s}$, which is also consistent with the eutaxial OR.

Orientation maps of a 4H SrMnO$_3$ substrate and 4H SrMnO$_3$ film deposited on the same region are shown in Figure ?. The entire film was indexed as 4H SrMnO$_3$ (the phase map is shown in §S3), even when the OIM software considered the 3C phase as a possibility. A minimum image quality (IQ) was set to remove erroneous orientations related to physical holes on the surface of the substrate or film, which are colored black. The average CIs for phase and orientation assignment given in Fig. a) and b) were 0.50 and 0.39, respectively. Note that between substrate and film maps (as with others shown later), there is a slight rotation due to remounting of the sample inside of the chamber. However, the film grew in a grain-over-grain fashion, as the number, shapes, and colors of grains are similar in both images, as seen in grains labeled $a - d$. It should also be noted that a smaller step size was
used during EBSD pattern acquisition in Fig. ??b) compared to that of Fig. ??a).

Figure 2: Orientation maps of a) a 4H SrMnO$_3$ substrate with b) a 4H SrMnO$_3$ film deposited on the same region.

Figure ?? shows the orientation maps for the deposition of 3C CaMnO$_3$ on a 4H SrMnO$_3$ substrate. The phase map shown in §S3 indicates that the CaMnO$_3$ film was almost entirely 3C. Thus, only the 3C CaMnO$_3$ partition is shown in the orientation map of Fig. ??b). The average CI for the substrate and film in Fig. ??a) and b) was 0.40 and 0.19, respectively. Despite the polytype difference between film and substrate, the growth again appears as grain-over-grain growth, as the number and shapes of grains are similar in both images. The colors in each image represent different orientations, and similarity/differences in color require further interpretation using the OR analysis discussed later.

Figure ?? shows the orientation maps of the SrMnO$_3$ film on a 3C SrTiO$_3$ substrate. The phase map is shown in §S3. The CI of the 3C SrTiO$_3$ substrate in Fig. ??a) was 0.41, which is similar to those from the single crystal substrates discussed in §S2. Furthermore, these CIs are similar to the 4H SrMnO$_3$ substrates, indicating that OIM is relatively confident in determining grain orientations using a single 3C or 4H phase. The average CI for the 4H SrMnO$_3$ film partition (Fig. ??b)) was 0.34, which is slightly lower than those described
Figure 3: Orientation maps of a) a 4$H$ SrMnO$_3$ substrate with b) a 3$C$ CaMnO$_3$ film deposited on the same region.

above for 4$H$ films and substrates, but still reasonable for a thin film. The average CI for the 3$C$ SrMnO$_3$ partition (Fig. ??c)) was 0.21, which is higher than that of the film on a (100) 3$C$ SrTiO$_3$ and similar to the previous 3$C$ CaMnO$_3$ film. As for both previous CSE cases, the SrMnO$_3$ film grew largely in a grain-over-grain fashion. While the majority of the film indexed as the stable 4$H$ polytype in Fig. ??b), several distinct regions indexed as the metastable 3$C$ SrMnO$_3$ polytype, shown in Fig. ??c). The 4$H$ film grains in Fig. ??b) are mostly red/orange to mauve/yellow in color, in contrast to the full color range observed for the films on the 3$C$ substrate. This indicates that the 4$H$ structure tends to grow in a limited region near the (001) orientation of hexagonal orientation space, despite the substrate exhibiting all orientations across the cubic orientation space. This observation is similar to the CSE growth of hexagonal Fe$_2$O$_3$ on SrTiO$_3$, owing to the eutaxial OR governing the CSE growth.

The 3$C$ SrMnO$_3$ partition shown in Fig. ??c) shows that areas of 3$C$ growth were (100) oriented and correlated to substrate grains that are near (100), similar to results from single crystal experiments above. Examples include grains marked 1, 2, and 3. Grain 1 is
an example of grain-over-grain growth of metastable 3C SrMnO$_3$ on 3C SrTiO$_3$. Grains 2 and 3 were indexed as near (100) 3C SrMnO$_3$ and near (0334) 4H SrMnO$_3$, while the substrate grains were also near (100) 3C SrTiO$_3$. The Kikuchi patterns that indexed as having different polytypes throughout Grains 2 and 3 looked mostly identical within each grain, although some patterns had missing bands. As a result, OIM had difficulty assigning the local phase and orientation in these grains. Compared to other CSE investigations for metastable film growth, the angular region of 3C epitaxial stabilization is narrower than reported for other metastable phases, but the preference for an individual orientation stabilizing metastable polymorphs is similar.

ORs between substrate and film grains were analyzed for all three CSE experiments using OIM data and our in-house program that determines the angle between specific crystallographic vectors in the film and substrate. The distribution of orientations for all substrates and films are shown in their respective stereographic triangles in §S4. An assessment of the eutaxial OR is plotted in Fig. ??, as the angles between the normals to the eutactic planes and the angle between eutactic directions lying in the eutactic planes. In Fig. ??, the grains have been ordered by increasing angular differences between planar normals.

For the homoepitaxial deposition of 4H SrMnO$_3$ on the 4H SrMnO$_3$ substrate, 69

Figure 4: Orientation map of a) a polycrystalline 3C SrTiO$_3$ substrate with b) the 4H SrMnO$_3$ film grains partition and c) the 3C SrMnO$_3$ film grains partition.
Figure 5: Angle between a) 4H SrMnO$_3$ film on 4H SrMnO$_3$ polycrystalline substrate from Fig. ??, b) 3C CaMnO$_3$ film on 4H SrMnO$_3$ polycrystalline substrate from Fig. ??, and c) 4H SrMnO$_3$ film on 3C SrTiO$_3$ polycrystalline substrate from Fig. ??.

Black dots represent the angles between the normals of the eutactic planes of film and substrate. Red dots represent the angles between directions in the eutactic planes. $f$ stands for film and $s$ stands for substrate.

90 substrate-film pairs were recorded. All grain orientations in the 4H SrMnO$_3$ film correspond to a similar orientation of the 4H substrate (see grains $a$ – $d$ in Fig. ??), with the exception of a few points, leading to a similar distribution of points in orientation space (see §S4). The average angle between the normals of the eutactic (001) planes is 3.3° with a standard deviation of 1.0°, while the average angle between the in-plane direction, [100], is 2.7° with a standard deviation of 1.0°. The average difference between these angles, ≈ 3°, arises primarily from an uncertainty in remounting the sample in the SEM chamber. The standard deviation arises from uncertainty in the absolute assignment of orientations, grain averaging during processing, and local variations from relaxation during film growth.

These values support that these homoepitaxial films adopt the eutaxial OR, which here corresponds to the alignment of hexagonal unit-cells, as expected. This OR can be written as (001)[100]$_{4H-f}$(001)[100]$_{4H-s}$.

For the deposition of 3C CaMnO$_3$ on the 4H SrMnO$_3$ substrate, 90 substrate-film pairs were recorded. Substrate and film grain orientations were evenly distributed across orientation space (see §S4), though the corresponding indices are different owing to the different crystal systems. From the data shown in Fig. ??b), the average angle between the normal to
the eutactic planes, (001) for 4H and (111) for 3C, is 2.6° with a standard deviation of 0.4°, while the average angle between the eutactic directions within the planes, [100] for 4H and [110] for 3C, is 1.8° with a standard deviation of 0.7°, ignoring two outliers. The two outliers had an in-plane rotation of 28° and were not examined any further. These values support the assertion that the epitaxial OR is the eutaxial OR, regardless of substrate orientation, for 3C CaMnO₃ film on a 4H SrMnO₃ substrate (observed for 98% of grains). This OR can be written as: (111)[1\bar{1}0]₃Cₘ₃||[(001)[100]₄Hₘ₄].

For the deposition of SrMnO₃ on the 3C SrTiO₃, 54 substrate-film pairs were identified for 4H SrMnO₃ grains, and 3 substrate-film pairs for those corresponding to 3C SrMnO₃ grains (grains partially indexed as 4H and 3C were included in both distributions, e.g., grains 2 and 3 in Fig. ??). The substrate grains are distributed across orientation space, while the 4H and 3C grains (see §S4) are clustered around the (001) for both phases. From the data shown in Fig. ??c), the average angle between eutactic plane normals for the 4H film and 3C substrate is 3.7°, with a standard deviation of 1.6° (ignoring the outliers) while the average angle between the in-plane eutactic directions is 7.6°, with a standard deviation of 1.1° (again ignoring outliers). The latter value is relatively large, and is likely related to relaxations occurring for this heteroepitaxial system. These values support that the epitaxial OR is the eutaxial OR for a 4H SrMnO₃ film on 3C SrTiO₃. This can be written as: (001)[100]₄Hₘ₄||[(111)[1\bar{1}0]₃Cₘ₃]. For the three 3C grains, the unit-cell over unit-cell, eutaxial OR is observed.

4. Discussion

Using CSE, we have analyzed the polytypic epitaxial growth of 3C and 4H perovskites on 3C and 4H substrates. As observed for other CSE experiments,?? ?? ?? ?? ?? ?? our films exhibited grain-over-grain epitaxy, allowing each individual grain to be treated as a single
crystal, even for orientations with high Miller indices. All of the data shown above supports
the hypothesis that the eutactic OR is the PEO for \( AEMnO_3 \) films on \( 4H \) SrMnO\(_3\) and \( 3C \)
SrTiO\(_3\) polycrystalline substrates, over all of orientation space (ignoring the few outliers).
We then observed that the range of orientations of \( 3C \) SrTiO\(_3\) that stabilized the metastable
\( 3C \) SrMnO\(_3\) phase was very narrow and close to (100) in these growth conditions, which were
similar to those investigated previously using single crystals. There were no significant ob-
servations of metastable \( 4H \) CaMnO\(_3\) film grains on \( 4H \) SrMnO\(_3\) polycrystalline substrates.
Overall, these observations shed light onto polytype epitaxy and epitaxial stabilization in
the perovskite system, described below.

The observations reported here support the utility of CSE as a high-throughput ap-
proach to establishing general PEOs for different film-substrate structural pairs under spe-
cific epitaxial growth conditions. The existence of a single OR (the eutactic OR) over all
of orientation space for all film-substrate pairs also supports the assertion that growth, or
computational modeling of growth energetics,\(^7\) on select low-index orientations may be
sufficient to predict growth over most of orientation space. In the standard models of epitax-
ial energetics,\(^7\) the observation that the eutactic OR is found for all substrate orientations
(and subsequent substrate-film interface and film surface planes) implies that either: (1) the
interfacial energies of the eutactic OR are lower than interfacial energies of all other potential
ORs, for all substrate orientations, or (2) the kinetic barriers to formation of critical nuclei
are lower for the eutactic OR than for ORs with lower overall interface energies.

In homopolytypic growth, e.g. \( 3C \) on \( 3C \) or \( 4H \) on \( 4H \), the eutaxial arrangement is
the unit-cell over unit-cell arrangement, which is well known in epitaxial growth of \( 3C \)
perovskites on single crystals. In prior CSE work, it was shown that \( 3C \) BiFeO\(_3\) grew in this
fashion on \( 3C \) La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\)-buffered \( 3C \) LaAlO\(_3\) substrates,\(^7\) as did \( 3C \) Sr\(_2\)FeMoO\(_6\) on
\( 3C \) Sr\(_2\)MgWO\(_6\).\(^7\) For the metastable \( 3C \) SrMnO\(_3\) investigated herein, this was also observed
on (100) oriented SrTiO\(_3\) single crystals, similar to earlier reports,\(^7\)\(^7\) and on (100) oriented
grains in SrTiO$_3$ polycrystals. By using 4$H$ SrMnO$_3$ polycrystalline substrates, we have shown that homoepitaxial growth occurs over all of orientation space and is consistent with the eutaxial OR, or unit-cell over unit-cell OR. For homopolytypic growth, one expects the unit-cell over unit-cell OR to lead to the lowest energy interface, as all bonds can be nominally satisfied across the interface.

For the heteropolytypic epitaxial growth, which includes 3$C$ CaMnO$_3$ on 4$H$ SrMnO$_3$ and 4$H$ SrMnO$_3$ on 3$C$ SrTiO$_3$, the eutaxial arrangement is also observed as the PEO across orientation space. Most importantly, this further supports the eutaxial OR as being a general description of epitaxy when the structures of the film and substrate can be described by eutactic packing, regardless of the substrate orientation, consistent with prior CSE observations for films with different structures than the substrates. The preference for the eutactic OR likely arises because it leads to the lowest energy interface amongst the myriad of potential ORs. One expects a relatively low energy interface when the eutactic plane is also the interfacial plane, because these can usually be described as coherent interfaces whose energies can be computed. The interface energies across the rest of orientation space for the eutactic OR are less obviously considered as low energy, as such interfaces can be (at best) described as semi-coherent (discussed below for a 4$H$-3$C$ interface and elsewhere for rutile and anatase on 3$C$ perovskites). Nevertheless, the semi-coherent interfaces for the eutactic OR need only have energies that are lower than those for any other potential OR (also likely generating a semi-coherent to incoherent interface) to be consistently observed as the PEO for all orientations, even though their specific interface energies may be significantly higher than that of the coherent eutaxial interface. Further experimental and computational work is needed to support this as a general rule of interfacial energies.

Surprisingly, heteropolytypic growth of perovskites is not discussed much in the literature, in contrast to the wealth of information available for 3$C$ growth on 3$C$ substrates. Epitaxial 4$H$ BaRuO$_3$ was stabilized on (111) and (100) SrTiO$_3$ single crystals. The eutaxial OR
was reported on the (111) SrTiO$_3$ single crystal, in agreement with 4$H$ SrMnO$_3$ deposited on single crystals and polycrystals via CSE herein. The epitaxy of 4$H$ BaRuO$_3$ on (100) SrTiO$_3$ was described as $\{0223\}\langle2\overline{1}10\rangle_{4H-\beta}\parallel\{001\}\langle110\rangle_{3C-\beta}$. The in-plane relationship is identical to the eutaxial arrangement, while the out-of-plane relationship leads to a small angular difference (of 2.6 °) from the perfect eutaxial angle for SrMnO$_3$. There is another high index plane, the $\{0334\}$, which is observed herein as the orientation of 4$H$ SrMnO$_3$ in grains 2 and 3 from Fig. ?? This orientation is only 0.6° away from the exact eutaxial angle for SrMnO$_3$. The two cases have an angular separation of 3.2° and in general agree with the eutaxial OR as the epitaxy driver, while the exact local plane that satisfies the eutaxial arrangement is the one that best satisfies overall energy minimization. A similar set of arguments can be used to predict the OR on the 3$C$ $\{110\}$ planes, which would be the 4$H$ $\{01\overline{1}3\}$ plane with the eutactic directions aligned. This also has only partial epitaxial matching between the planes (has a semi-coherent interface), and the exact plane observed may vary by a few degrees. The variation across orientation space of the exact angle between the eutactic planes and directions is consistent with some local variation of this sort.

Lee et al.?? pointed to a similarity of local structural motifs between the 4$H$ $\{02\overline{2}3\}$ and the 3$C$ $\{100\}$ planes, specifically the AEO elements, along with a reasonable coherency along the (eutactic) in-plane directions, to rationalize the specific epitaxial OR observed. However, it is difficult to extrapolate that rationalization of an individual result to a larger predictive trend, as the overall structural match is generally quite poor between these two planes. They both consist of stripes less than 1 nm wide of similar bonding along the eutactic directions, but these stripes do not have any short range coherency (e.g. < 7 nm) in the orthogonal direction. Importantly, the same arguments can be made for the similarity of the 4$H$ $\{03\overline{3}4\}$ with the 3$C$ $\{100\}$ plane. Thus, qualitatively considering the planar arrangements, either interface appears reasonable, and both are semi-coherent to incoherent. Using CSE observations that the PEO is the eutactic OR, one can broadly
predict the expected epitaxy across all of orientation space, regardless of the specifics of the local interface. This is further supported by CSE observations that the eutactic OR is observed across all of orientation space for the growth of 3C CaMnO₃ films on 4H SrMnO₃ substrates, which essentially the inverse growth to that described above.

It is always important in CSE, or any high-throughput characterization method, to ensure that automated phase identification is accurate for all phases and orientations. Based on the positive identification of all substrate grains as the expected phase, we are confident that the phase identification process is accurate for bulk materials. However, in film patterns with lower CIs, the accuracy of phase identification becomes questionable using OIM as the patterns become more diffuse. This issue is primarily relevant for the case of 3C films grains 2 and 3 from Fig. 2. Slight rotations away from the 3C (100) substrate appear to cause some Kikuchi bands from the film to disappear, making it difficult for the OIM software to distinguish between possible phases and orientation. An alternative indexing approach, called dictionary indexing (DI), was used to generate orientation and phase maps from the film in Fig. 2 (shown in 55) using a pattern similarity metric (see 55). In the DI approach, only grain 1 indexed as the 3C polytype, while grains 2 and 3 were 4H. It is conceivable that both 4H and 3C polytypes were grown on the latter grains, but further analysis using transmission electron microscopy may be needed to resolve this issue. The impact on the conclusions herein is minimal, as these grain orientations are near the phase boundary, and one expects possible two phase nucleation events near boundaries.

The limited range of epitaxial stabilization of metastable compounds in the AEMnO₃ family indicates that the penalties of higher interfacial and/or strain energies for heteropolypotypic growth of the stable phase are not significant enough to overcome the inherent preference in volumetric formation energy for the stable phase, across most of film-substrate synthesis space. That 3C CaMnO₃ epitaxially deposited on a 4H SrMnO₃ polycrystalline substrate showed no significant evidence of a new hexagonal phase reinforces this difficulty
in stabilizing metastable perovskite polytypes by epitaxy, in these growth conditions. In the conditions used here, the $4H$ polytype of SrMnO$_3$ is stable. Only the (100) surface of 3C SrTiO$_3$ substrate inverts the polytype stability during growth of SrMnO$_3$. At lower oxygen pressures, one expects growth of oxygen deficient SrMnO$_{3-\delta}$ with less hexagonal and more cubic stacking, leading to a transition from $4H$ to $3C$ polytype for SrMnO$_{3-\delta}$ as $\delta$ increases. Unfortunately, the exact composition of the films are not known in these conditions, nor are the differences in formation energies of the two polytypes of SrMnO$_{3-\delta}$ and of CaMnO$_{3-\delta}$, nor are the interfacial and strain energies for any of the film-substrate pairs investigated. Therefore, high-throughput empirical methods, such as CSE, are needed to drive materials design using epitaxy, particularly by establishing PEOs and epitaxial stability windows.

It has been postulated by Mehta et al. that, given the ideal differences in the interfacial and strain energy terms, metastable phases could be stabilized epitaxially if the volumetric difference $\lesssim 20$ kJ/mol. Xu et al. showed that computational methods can guide understanding of polymorph competition during growth of anatase and rutile on low index surfaces, especially when the PEO is well established. The relative order of stability computed using density functional theory (DFT) for the two polymorphs across orientation space agreed with both single crystal and CSE experiments. The empirical results here imply that the magnitude of volumetric energy difference that can be overcome is possibly more narrow for these polytypic structures when growth is driven on the eutactic planes, where the penalty along the eutactic packing direction to form a different polytype is essentially identical to stacking faults, which are known to form in all of the hexagonal polytypes. Thus, computational estimates of the stacking fault and strain energy penalties for eutactic epitaxy between polytypes could provide important guidance to the level of metastability that can be surmounted in the $AEMnO_{3-\delta}$ ($AE = Ca, Sr, and Ba$) system, especially when linked to composition. On the other hand, the planar lattice matching of the eutaxial ORs along the non-eutactic low-index 3C substrate orientations (such as the $\{100\}$ and $\{110\}$)
are similar to the semi- or in-coherent interfaces discussed in Mehta et al.,\textsuperscript{7} and should be relatively high in energy compared to isostructural interfaces on the same surfaces. In this view, the origin of the limited orientation range of stable 3C SrMnO$_3$ is still in question. To unravel this, both computational and physical experiments are needed to understand the role of synthesis conditions, especially temperature, oxygen pressure, and deposition rate, on phase stability and growth, especially in the 2H / 4H / 3C competition in the AEMnO$_3$ systems. It is clear that epitaxial stabilization of distinct polytypes, such as 3C BaMnO$_3$ on 3C perovskite substrates, will require strict control over the chemical, strain, and interfacial energies by appropriate choices of deposition conditions and perhaps novel substrates.

5. Conclusions

The PEOs were determined using orientation data from EBSD for 4H and 3C perovskite polytypes of CaMnO$_3$ and SrMnO$_3$ films, grown on several polycrystalline 4H and 3C substrates via pulsed laser deposition. A single epitaxial OR was found to describe the PEO for all polytypic film-substrate pairs, which we call the eutaxial OR, or the OR that aligns the eutactic planes and direction between their respective crystal structures. This can be written as follows for the specific films explored here: (001)[100]$_{4H-f}$||(001)[100]$_{4H-s}$; (111)[110]$_{3C-f}$||(001)[100]$_{4H-s}$; (001)[100]$_{4H-f}$||(111)[110]$_{3C-s}$. These were clearly observed over almost all of substrate orientation space for 4H SrMnO$_3$ on polycrystalline 4H SrMnO$_3$ and 3C SrTiO$_3$, as well as 3C CaMnO$_3$ on polycrystalline 4H SrMnO$_3$. This prevalence of the eutaxic OR can be understood if its interface energies represent the lower bound of interface energies regardless of orientation. Epitaxial stabilization of metastable 3C SrMnO$_3$ was observed only in a very narrow range of orientation space on 3C SrTiO$_3$ substrates: on (100) single crystals and on nearly (100)-oriented surfaces of polycrystals. This narrow range stands in contrast to many other CSE observations, indicating that, in these growth condi-
tions, the energetic penalty of the interface between different polytypes is relatively low, and unable to drive extensive epitaxial stabilization. The absence of substrate driven metastable 4H CaMnO$_3$ further supports this conclusion. The combined results, however, support the idea that CSE can quickly unravel the nature of epitaxial growth and competitive polymorph nucleation, and should allow for computational predictions of epitaxial growth.

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References


• **Figure 1**: XRD patterns for a) a $4H$ SrMnO$_3$ thin film grown on (111) SrTiO$_3$ and b) a $3C$ SrMnO$_3$ film grown on (100) SrTiO$_3$. $f^i$ ($s$) indicates film (substrate) peaks of phase $i = h$ (hexagonal) or $c$ (cubic). The subscripts give the Miller indices of each peak.

• **Figure 2**: Orientation maps of a) a $4H$ SrMnO$_3$ substrate with b) a $4H$ SrMnO$_3$ film deposited on the same region.

• **Figure 3**: Orientation maps of a) a $4H$ SrMnO$_3$ substrate with b) a $3C$ CaMnO$_3$ film deposited on the same region.

• **Figure 4**: Orientation map of a) a polycrystalline $3C$ SrTiO$_3$ substrate with b) the $4H$ SrMnO$_3$ film grains partition and c) the $3C$ SrMnO$_3$ film grains partition.

• **Figure 5**: Angle between a) $4H$ SrMnO$_3$ film on $4H$ SrMnO$_3$ polycrystalline substrate from Fig. ??, b) $3C$ CaMnO$_3$ film on $4H$ SrMnO$_3$ polycrystalline substrate from Fig. ??, and c) $4H$ SrMnO$_3$ film on $3C$ SrTiO$_3$ polycrystalline substrate from Fig. ???. Black dots represent the angles between the normals of the eutactic planes of film and substrate. Red dots represent the angles between directions in the eutactic planes. $f$ stands for film and $s$ stands for substrate.
CSE Supplementary Materials
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This section contains more information on the structure of $AEMnO_3$ ($AE = Ca, Sr, Ba$), EBSD as a method for determining epitaxy, phase maps, orientation space of the CSE experiments, and dictionary indexing.

S1 Structures of $AEMnO_3$

The stable polytype of an $AEMnO_3$ perovskite can be reasonably predicted by the Goldschmidt tolerance factor, $t$:

$$t = \frac{r_{AE} + r_O}{\sqrt{2}(r_{Mn} + r_O)}$$  (1)

where $r_{AE}$, $r_{Mn}$, and $r_O$ are ionic radii of the $AE$, $Mn$, and $O$ ions, respectively. Perfectly matched bond lengths ($t \approx 1$) would differ by $\sqrt{2}$ in the prototypical cubic perovskite. Compounds adopting this structure stack the eutactic planes ($ABCABC$) along the $h111$ and all MnO$_6$ octahedra share corners. This structure is known as the $3C$ polytype. When $t < 1$, compounds retain the $3C$ stacking and corner sharing octahedra, but have reduced symmetry owing to octahedral rotations that help alleviate the bond mismatch. When $t > 1$ and the $AE$-site cations are too large to fit in the cubic framework, compounds adopt structures in which the stacking of the eutactic planes leads to hexagonal symmetry. Pure hexagonal stacking of $AEO_3$ planes ($ABAB$), occurs along the $\langle 001 \rangle$ with chains of face sharing octahedra. This structure is known as the $2H$ polytype, and occurs for large values of $t$. Between the extremes of $3C$ and $2H$, other polytypes exist with different fractions of cubic and hexagonal stacking sequences, and concomitant fractions of octahedra connected by corner-sharing and face-sharing.
For epitaxial growth in CSE, the PEO dictates the specifics of the polymorph competition, which ultimately determines whether metastable phases can be stabilized. A common PEO found in CSE experiments is the eutactic OR. For 3\textit{C} perovskites, the eutactic plane is \{111\} and the eutactic direction within the plane is \langle 1\overline{1}0 \rangle. For 4\textit{H} perovskites (such as SrMnO$_3$), the eutactic plane is \{001\} (or \{0001\} in the Miller-Bravais 4-index notation) and the close packed direction within the plane is \langle 100 \rangle (or \langle 2\overline{1}10 \rangle). \textsuperscript{4,5}

**S2 EBSD on Single Crystal Experiments**

Orientation maps were constructed using EBSD data to further confirm the phase and epitaxial orientation of SrMnO$_3$ films on SrTiO$_3$ single crystal substrates, as well as to calibrate the indexing of films of different polytypes for later CSE investigations. Figure S1 shows the orientation maps, using inverse pole figure (IPF) coloring along the surface normal (z) direction for: a) the 4\textit{H} SrMnO$_3$ partition of the film on (111) 3\textit{C} SrTiO$_3$, and b) the 3\textit{C} SrMnO$_3$ partition of the film on (100) 3\textit{C} SrTiO$_3$. The average CI for the (111) and (100) substrates were 0.46 and 0.48, respectively. When indexing the film deposited on these two substrates, the OIM software chose between the 3\textit{C} and 4\textit{H} polytype, as well as all unique orientations of each polytype. In Fig. S1a), the phase indexed almost exclusively as (001) oriented (red) 4\textit{H} SrMnO$_3$ (note that the EBSD software uses Miller-Bravais 4-index notation), with a few low CI points colored black. The average CI of the film was 0.46, which is relatively high for thin film patterns. In Fig. S1b), the phase indexed primarily as near (100) oriented (magenta/red) 3\textit{C} SrMnO$_3$, though many points (≈ 11.1\%, black) are poorly indexed, primarily due to the roughness of the film surface. The average CI was only 0.11, after removing points of low confidence (≤ 0.01), which is significantly lower than that of the 4\textit{H} film, but still standard for automated indexing of a film.

Overall, these local orientations are in agreement with the average orientation determined
Figure S1: Orientation maps of a) the 4H SrMnO₃ partition of the film deposited on (111) SrTiO₃ and b) the 3C SrMnO₃ partition of the film deposited on (100) SrTiO₃. c) and d) are the in-plane orientation maps for the films from a) and b), respectively. Color keys of orientations are given as insets and are stereographic triangles for the specific crystal system.

from the XRD data in Fig. 1, but also indicate that the phases propagate to the film surfaces, maintaining high-quality epitaxy to most of the surface. The phase formation of the 3C metastable polymorph appears less perfect than that of the stable 4H near the surface region.

In-plane orientation maps are given in Fig. S1c) and d), where they are colored by their orientation in the [100] and [110] eutactic directions of the substrates, for the 4H and 3C film phases, respectively. In Fig. S1c), the orientation map indexes as the [100] direction (or [2110] in Miller-Bravais notation as displayed in the inset). This indicates that the film has the epitaxial relationship: (001)[100]₄H-d||(111)[110]₃C-s, which is the eutaxial OR. The
in-plane orientation map in Fig. S1d) shows that the direction is [1\bar{1}0], which is the eutactic direction for the 3C phase. The 3C polytype therefore has a unit-cell over unit-cell epitaxial OR (100)[1\bar{1}0]_{3C-f}|| (100)[1\bar{1}0]_{3C-s}, which is also consistent with the eutaxial OR.

**S3 Phase Maps**

Phase maps of the films grown on 4H SrMnO₃ and 3C SrTiO₃ polycrystalline substrates are shown in Figure S2. In the SrMnO₃ film phase map in Fig. S2a), the nearly complete red color indicates that film grew as the 4H polytype over all 4H SrMnO₃ substrate grains in this region, as expected for this homo-epitaxial growth of the stable polytype. The few small regions of green points, indexed as 3C SrMnO₃, were not further considered, largely being associated with poorly crystalline regions (low CI and IQ).

In the CaMnO₃ film phase map of Fig. S2b), three polytypes (3C, 2H, and 4H) were allowed to be selected by OIM, using theoretical lattice parameters reported by Sondena et al.². The film indexes as nearly 3C CaMnO₃ deposited over the entire 4H SrMO₃ substrate region, with small regions of yellow areas indexed as 4H. These regions were not considered to be significant areas of 4H growth, occurring near pores or in other regions of poor CI and IQ.

Fig. S2c) shows the phase map for the polytypic SrMnO₃ film deposited on 3C SrTiO₃. While most of the film indexed as the 4H polytype, a few grains (labeled 1, 2, and 3) indexed as the 3C polytype.

**S4 Orientation Space Sampling**

The sampling of orientation space for all materials involved are shown in Figure S3. Figs. S3a), c), and e) show the distribution of orientation space for all substrates (4H SrMnO₃
Figure S2: Phase maps of a) the 4H SrMnO₃ film on a 4H SrMnO₃ substrate from Fig. 2, b) the 3C CaMnO₃ film on a 4H SrMnO₃ substrate from Fig. 3, and c) the SrMnO₃ film on a 3C SrTiO₃ substrate from Fig. 4.

The distribution is relatively uniform across their respective orientation ranges, indicating that the space of possible substrate orientations was sampled uniformly. Figs. S3b), d), f), and g) show the distribution of the deposited films. The homoepitaxial deposition of 4H SrMnO₃ have grain orientations nearly identical to that of the substrate. Examples include grains marked a – d from Fig. 2 in the paper. For Fig. S3d), the distribution of film orientations is uniform across all of orientation space, even though the substrate is of a different polytype. Figs. S3f) and g) show the orientation distribution of the 4H and 3C SrMnO₃ film, respectively, grown on 3C SrTiO₃. Film orientation of both polytypes grew near the (001), similar to observations from⁶.

S5 Dictionary Indexing

All EBSD patterns in the main paper were indexed using a standard, widely-available commercial OIM software that applies a Hough transform to experimental patterns and ranks matches in Hough space using proprietary algorithms. We also used open-source, in-house codes to: (1) improve the performance of the commercial algorithm, through optimization of the bands chosen for comparison, and (2) index phases and orientations using an alternate
Figure S3: Orientations of substrate-film grain pairs used to determine epitaxial ORs plotted on stereographic triangles belonging to: the a) 4H SrMnO$_3$ substrate and b) 4H SrMnO$_3$ film from Fig. 2; the c) 4H SrMnO$_3$ substrate and d) 3C CaMnO$_3$ film from Fig. 3; and the e) 3C SrTiO$_3$ substrate and f) 4H SrMnO$_3$ film and g) 3C SrMnO$_3$ film from Fig. 4. Blue squares indicate grains associated with 4H SrMnO$_3$ film growth and red dots indicate grains associated with 3C SrMnO$_3$ film growth.
dictionary indexing (DI) approach. Compared to the Hough-based indexing algorithm used by OIM, dictionary indexing is more robust against noisy patterns, which is often a concern for EBSD indexing of thin films\textsuperscript{6–12}. Wittkamper et al. used the in-house program to simulate EBSD patterns for scrutinyite and rutile SnO\textsubscript{2} and visually compared them against experimental patterns to determine the local phase and orientation of the SnO\textsubscript{2} film grains\textsuperscript{8}. De Graef et al. used DI to demonstrate its ability to detect small deviations between lattice constants for the tetragonal structure in CuInSe\textsubscript{2} films and compared the results to that of traditional Hough-based pattern indexing, which cannot detect such deviations\textsuperscript{13}. Here we present the basics of the DI approach, which leads to essentially identical results to those presented in this paper using the commercial OIM software.

The in-house program, EMsoft, incorporates the crystal structure, SEM operating parameters, and sample orientation into a Monte Carlo simulation of electron trajectories, and those simulations, in combination with dynamical electron scattering simulations, are used to generate a so-called master pattern\textsuperscript{14}. The master pattern is then used, along with crystal symmetry and detector parameters, to generate theoretical diffraction patterns, which are saved in a dictionary, across all of orientation space.

In the first step, we used a subset of the 3\textit{C} and 4\textit{H} pattern dictionaries to optimize the performance of the OIM software. Simulated dictionary patterns were indexed in OIM by replacing the bands used by OIM with those generated by EMsoft. The number and type of bands used in the proprietary algorithm were optimized to yield high confidence indexes for the known phase and orientation of the patterns. These optimized bands were used to reindex the film from Fig. S1b) (film patterns were collected a second time; orientation map shown in Fig. S4) and resulted in an increase in the CI to 0.30. Film patterns from Fig. 4 were also reindexed but there was no significant change in the CI for either the 3\textit{C} or 4\textit{H} SrMnO\textsubscript{3} partition. This is most likely due to the poorer and varying film pattern qualities as a result of CSE.
In dictionary indexing, experimental patterns are compared, using a similarity metric (the dot product of the vectorized patterns), to all patterns in the dictionary. The orientation of the dictionary pattern with the highest similarity metric is assigned to the experimental pattern. In a second step, as a control, the 3C and 4H SrMnO₃ dictionaries were subjected to dictionary indexing against themselves and the other. In all cases, the dictionary indexing method identified the appropriate phase and orientation as the best match amongst all patterns, indicating the DI method has no known ambiguities or pseudo-symmetry issues. Normalized frequency distributions of the top dot products from dictionary indexing of either 3C or 4H dictionary patterns, indexed using 3C and 4H master patterns, are shown in Figure S5. The height of the blue bars indicate the frequency for a range of top dot products indexed using the 3C SrMnO₃ master pattern. The orange bars indicate the same but using the 4H SrMnO₃ master pattern. These figures clearly indicate that over all orientation space, the DI method has no difficulty distinguishing phase and orientation of a given 3C or 4H pattern.

In the last step, DI was used to reindex the SrMnO₃ film on 3C SrTiO₃. The same film

Figure S4: Orientation map of the 3C SrMnO₃ film on 3C SrTiO₃ indexed using EMsoft generated reflectors.
Figure S5: Normalized frequency distributions of the top dot products comparing a) simulated $4H$ SrMnO$_3$ patterns against $4H$ and $3C$ master patterns; b) simulated $3C$ SrMnO$_3$ patterns against $3C$ and $4H$ master patterns.

Patterns from Fig. 4 were analyzed using the DI approach and results are shown in Fig. S6. The raw orientation maps in Fig. S6a) and b) were generated using DREAM.3D. It should be noted that during dictionary indexing, only one phase is indexed at a time, so all patterns are indexed even if they do not actually belong to that phase (e.g. all grains are indexed in Fig. S6b)). The phase map in Fig. S6c) was generated by comparing the top dot products of the $3C$ and $4H$ phases.

Figure S6: Raw orientation maps and phase map as a result of dictionary indexing of the film from Fig. 4. a) shows the orientation map using the $4H$ SrMnO$_3$ crystal structure and b) shows the orientation map using the $3C$ SrMnO$_3$ crystal structure. c) shows the phase map.

For most grains that were indexed in this paper, only one phase and orientation was
positively identified using the OIM software. This remains true in the dictionary indexing. Further, the film grain orientations and phases are nearly identical to those produced by OIM, indicating we should have high confidence in the results already discussed. Only Grain 1 is in Fig. S6b) is indexed by DI as 3C SrMnO$_3$, with an orientation near (100). This is consistent with results on the (100) SrTiO$_3$ single crystal and the Hough indexing of the same grain, again reinforcing the positive identification of phase and orientation from EBSD patterns for these polytypic compounds.

In the case of Grains 2 and 3 from Fig. 4, OIM identifies two phases, 4H and 3C SrMnO$_3$, as belonging to the film that grew on near (100) oriented 3C SrTiO$_3$ substrate grains. As the parameters for indexing and post-processing of the orientation map varied, the phase boundaries in these grains also changed, indicating that the software had difficulty in positively assigning a phase and orientation to each pattern in these grains, even though the patterns were similar within each grain. In DI, the patterns from Grains 2 and 3 can be indexed as 3C or 4H, but the 4H has a better match with the overall pattern, which is a bit noisy as described above.

The results of dictionary indexing of the SrMnO$_3$ film on 3C SrTiO$_3$ do not change the conclusion that the preferred epitaxial orientation aligns the eutactic planes and directions (not shown here but verified). Nor does it change the essential phase map, though it suggests the space is extremely narrow and near the (100) of SrTiO$_3$. This alternative approach reinforces that EBSD patterns can be readily positively identified for the local phase and orientation of films, using either Hough or dictionary indexing.
References


