Unusual Strain Accommodation and Conductivity Enhancement by Structure Modulation Variations in Sr$_4$Fe$_6$O$_{12+\delta}$ Epitaxial Films**

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Mixed ionic and electronic conducting (MIEC) films can be applied in solid state electrochemical devices such as oxygen separation membranes for producing pure oxygen, gas sensors or as cathode in solid oxide fuel cells. The current interest in layered perovskite-related phases, like Sr$_4$Fe$_6$O$_{13}$ (SFO), arises from their significant oxygen permeability as predicted from theoretical studies. Nevertheless, before any practical application further fundamental study on this fairly unknown oxide is needed mainly to assess the mechanisms affecting the transport properties. Epitaxial Sr$_4$Fe$_6$O$_{12+\delta}$ (SFO) films of b-axis orientation with different thicknesses have been prepared by the pulsed laser deposition technique onto different perovskite substrates: SrTiO$_3$, NdGaO$_3$ and LaAlO$_3$. The strain accommodation has been found to vary as a function of film thickness as well as the substrate material causing different type of defects in the film microstructure, as well as variations in the oxygen anion content and ordering. Correspondingly, the total electrical conductivity of the films has been also found to vary significantly as a function of thickness and substrate type showing an unexpected enhancement for strained thin films. The variations in the transport properties are discussed in terms of the different strain accommodation mechanisms and the variation of the modulated structure observed for this compound.

1. Introduction

It is already known that the physical properties, such as resistivity, magnetoresistance and ferroelectricity, of strongly correlated electron systems like transition metal oxide materials, can be significantly modified by changes in the epitaxial strain.[1–3] However, no systematic studies of such influence are reported in semiconducting materials which present localized electronic states where transport takes place mainly by a thermally activated process, such as a polaron hopping mechanism. This is the case of most of the typical perovskite and perovskite-related oxide materials used as cathodes in solid oxide fuel cells (SOFCs) in their range of operation temperature (600–900 °C). In the last years large effort has been made to study this kind of materials for its application as thin film electrodes in diverse devices. The motivation to fabricate thin film ceramics derives from the benefits associated with the lowering of ohmic losses as the membrane thickness is reduced, giving rise to electrochemical devices able to operate at lower temperatures still retaining high efficiencies and using cost effective materials.

The current interest in layered perovskite-like phases based on the Sr$_4$Fe$_6$O$_{13}$ crystal structure arises from their mixed oxygen and electron conductivity with considerable oxygen permeability as predicted by some theoretical calculations.[4]

The Sr$_4$Fe$_6$O$_{12+\delta}$ (SFO) structure is built up of SrO and FeO$_2$ perovskite-type layers alternating along the b-direction with Fe$_2$O$_2$ layers (δ = 1) of five-coordinated iron polyhedra. Due to the high structural anisotropy of the Sr$_4$Fe$_6$O$_{12+\delta}$ compounds (oxide-ion conduction is strictly two-dimensional, confined to the layers formed by the double Fe$_2$O$_2$ layers)[5] the application of this material in integrated devices essentially depends on the ability to prepare highly textured or epitaxial layers.

However, before approaching its practical applications in solid state electrochemical devices it is important to ascertain the role that the strain, induced by the epitaxial growth, might have in the high-temperature electronic transport properties, especially for such highly anisotropic layered perovskite-type oxides.

In fact, the existence of an oxygen occupancy modulation on Sr$_4$Fe$_6$O$_{12+\delta}$ compounds has been reported recently in thin films[6,7] as well as in bulk form.[8,9] The anion-deficient Sr$_4$Fe$_6$O$_{12+\delta}$ (δ < 1) derivatives present, in comparison with the stoichiometric Sr$_4$Fe$_6$O$_{13}$ phase, a very similar layered structure but with lower oxygen content in
the Fe$_2$O$_3$-$d_{2}$ layers. Thus, rows of oxygen atoms and vacancies running along the $c$ axis in the layers formed by trigonal bipyramids and square pyramids alternate in an ordered manner along the $a$ axis resulting in the appearance of satellite reflections corresponding to a modulation vector $q = a 0 d$ [superspace group $Xmm2(000)00$ with centring vectors $(0, \frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}, 0), (\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$. It was demonstrated that the $a$ component provides an accurate measurement of the average oxygen content of the Sr$_4$Fe$_6$O$_{12+d}$ phases, being $b = 2a$. Other modifications of this complicated superstructure are extensively discussed elsewhere.\cite{9}

TEM revealed that different variants of anion ordering can be present in one bulk sample.\cite{9} In comparison with the bulk material, epitaxial Sr$_4$Fe$_6$O$_{12+d}$ films have rather homogeneous $a$ values, indicating that oxygen enters homogenously in the thin films.\cite{6,7} Previous works also showed that the oxygen content in SFO films deposited on STO decreases with increasing strain, indicating that the anion ordering provides an additional mechanism for strain relaxation.\cite{7} and that the transport properties of epitaxial SFO films deposited on NdGaO$_3$ (NGO) revealed a dependence on film thickness, although no clear correlation with the oxygen modulation was observed for films grown on NGO, although for the thicker films the out-of-plane parameter is slightly shorter than for STO.

We have to notice that films grown on LAO substrates which are expected to present the larger compressive strain, showed an out-of-plane cell parameters more similar to the SFO single crystal values, indicating that for a similar thickness, these films grow in a more relaxed way than the films deposited on STO and NGO. The in-plane parameters values of the films on LAO, although showing a large scattering, are almost independent of thickness. Nevertheless this fact cannot be interpreted as a direct consequence of the relaxed state due to the inaccuracy in the determination of the diffraction peaks position caused by the large orientation spread induced by the twin domains in the LAO substrates.

From those measured in-plane and out-of-plane film parameters we have calculated the cell volume variations with thickness for films grown on different substrates as shown in Figure 2. An apparent increase of the volume with thickness ($\sim$0.5%), which tends to the bulk volume (1.176 nm$^3$\cite{12}), is observed. For films deposited on LAO it was not possible to calculate the volume because of the above mentioned inaccuracy in the in-plane parameter determination.

Although the cell volume changes in non strained samples are generally attributed to a variation in the composition, i.e.,
more likely in the oxygen composition δ, it is not possible to rule out that the observed variations are merely the result of the elastic response of the structure to the in-plane compressive strain. The residual strain of the films in the transverse (⊥) and longitudinal (∥) directions were calculated using the expressions:

\[ \varepsilon_{\perp}(\%) = \frac{b_{\perp} - b_0}{b_0} \times 100; \quad \varepsilon_{\parallel}(\%) = \frac{a_{\parallel} - a_0}{a_0} \times 100 \]  

where \( b \) and \( a \) (\( \approx d_{200} \)) are the out-of-plane and the in-plane parameters, respectively. The sub index “s” indicates the strained films values and “0” the values for the equilibrium structure, depending on the used substrate. The equilibrium values for the out-of-plane \( b \) parameter were taken from the thicker films in Figure 1 as 1.9009 nm on STO, 1.8982 nm on NGO, and 1.895 nm on LAO. The results are depicted in Figure 3, which shows the \( \varepsilon_{\perp} \) and \( \varepsilon_{\parallel} \) strain values of the films versus the thickness (note that \( \varepsilon_{\parallel} \) has opposite sign than \( \varepsilon_{\perp} \)).

As expected from the lattice parameters evolution, the films are completely strained below a thickness of around 25 nm, as shown by the “plateau” region in \( \varepsilon_{\perp} \), corresponding to about +1.0% and −0.9%, for the out-of-plane and in-plane directions, respectively. Above this thickness the films relax continuously and the absolute value of the strains (both \( \varepsilon_{\perp} \) and \( \varepsilon_{\parallel} \)) follow a power law decay with exponent close to −1. Films grown on LAO substrates follow the same dependence, although the strain values are slightly lower than on NGO and STO for the same thicknesses. The thinnest films on LAO substrates show out-of-plane strain values smaller than 0.5%, confirming that the theoretical larger strain, as expected for their larger mismatch, has been already released. Unfortunately, the uncertainty in the measurement of the in-plane parameters for SFO/LAO films did not allow us to extract any value of \( \varepsilon_{\parallel} \). The observed dependence, with exponent −1, above a critical thickness is a very typical observation of strain release in thin films, and is generally attributed to the generation of misfit dislocations, although other mechanisms might show also a similar dependence.\[13\]

Therefore, no reliable information about the strain release mechanisms can be extracted from the observed strain variations. It is obvious from the above mentioned results that epitaxial films on NGO and LAO did not follow the expected coherent growth with the substrate, even for the thinnest films, probably due to the existence of a critical thickness, \( t_c \), above which SFO films cannot store the energy associated to the cell deformation, giving rise to a strain release in the films. As the 25 nm films deposited on STO still show a coherent growth onto the substrate, we can estimate the maximum energy that can be stored in the SFO film which is expected to be an intrinsic parameter of the material. This critical energy \( E_c \), is proportional to the strain and the volume and can be defined as

\[ E_c \propto \varepsilon_{\text{Max}}^{\parallel} \cdot t_c \]  

where \( \varepsilon_{\text{Max}}^{\parallel} \) is the maximum in-plane strain and \( t_c \) the critical thickness. By using the expression

\[ t_c^{\text{NGO, LAO}} = \left| \frac{\varepsilon_{\text{Max}}^{\parallel}}{\varepsilon_{\text{Max}}^{\parallel, \text{STO}}} \right| \cdot t_c^{\text{STO}} \]  

Figure 2. Thickness variation of the volume of the films grown on STO and NGO substrates.

Figure 3. In-plane and out-of-plane residual strain variation with thickness.
along with the $E_c$ determined from Equation 2 for the STO films, we were able to estimate critical thickness values of $t_{c}^{NGO} \approx 9$ nm and $t_{c}^{LAO} \approx 5$ nm for NGO and LAO, respectively. These values correspond to thicknesses below the explored region in this experiment. This explains the fact that, unlike the films deposited on STO, no fully strained films were obtained on NGO and LAO even for films as thin as 20 nm.

From the strain values it was also possible to calculate the Poisson’s ratio, $\nu$, taking into account that thin films are under biaxial strain. Therefore the distortion is almost pure tetragonal and can be described as

$$\varepsilon = \frac{2\nu}{1-\nu} \varepsilon ||$$

(4)

where $\varepsilon_{\perp}$ and $\varepsilon ||$ are the out-of-plane and in-plane residual strains of the films, respectively. All the films have shown a similar Poisson’s ratio with an average value of 0.35(1), independently of the substrate. This indicates that the cell volume variations observed in Figure 3 were mainly related to an elastic deformation rather than to significant composition variations, otherwise they would have shown variations in their elastic response, and thus in their Poisson’s ratio.

### 2.2. Microstructural Characterization

As already mentioned, the complex structural behavior of the $\text{Sr}_4\text{Fe}_6\text{O}_{12+\delta}$ phases is related to changes occurring in the $\text{Fe}_2\text{O}_{2+\delta/2}$ layers upon varying $\delta$, being $\delta = 2\alpha$. The compound composition can therefore be formulated as $\text{Sr}_4\text{Fe}_6\text{O}_{12+2\alpha}$. Films with similar thickness, 60 nm, were prepared onto STO, NGO and LAO and studied by ED and HREM in order to determine any possible relation between the film strain and the oxygen modulations. ED was used to estimate the oxygen modulation of the SFO thin films while HREM of the film cross-section allowed us to study the film/substrate interface as well as the microstructure and defects present in the SFO films.

The ED patterns of the SFO/STO and SFO/NGO specimens are showed in Figure 4a and b, respectively. The ED patterns are formed by the superposition of the diffraction patterns produced by film and substrate; the most intense reflections are due to the substrates, whereas the weaker ones are due to the SFO film. From the [001]SFO ED pattern of the film grown on STO (Fig. 4a), an $\alpha = 0.36$ was deduced and thus the compound composition can be formulated as $\text{Sr}_4\text{Fe}_6\text{O}_{12.72}$, which corresponds to an incommensurate modulation. For the SFO film grown on NGO an $\alpha = 1/3$ value was experimentally deduced from the [001]SFO ED pattern of Figure 4b. In this case the SFO film presents a commensurate modulation with a composition $\text{Sr}_4\text{Fe}_6\text{O}_{12.67}$ already reported in bulk SFO samples.

Slight differences were observed in films deposited on LAO. An ED pattern along the [001]SFO zone axis is shown in Figure 4c; it is also formed by the superposition of the diffraction patterns from the film and the substrate. The most intense reflections are due to the LAO substrate, whereas the weaker ones are due to the SFO film. The indexation of the
LAO reflections has been performed using the $R\overline{3}c$ rhombohedral unit cell. The experimentally calculated $\alpha = 0.43$ value corresponds to a $Sr_4Fe_6O_{12.86}$ composition.

All three SFO films grown on STO, NGO and LAO also show $90^\circ$ rotation twins, which may overlap in the ED patterns in Figure 4.

Films grown on STO and NGO substrates exhibit similar microstructures as can be seen from the cross-section HREM images in Figure 5. At the film-substrate interface of both the SFO/STO and SFO/NGO specimens (Fig. 5a and b, respectively) a buffer layer with perovskite structure is formed. The buffer layer is more pronounced in the SFO/NGO specimen, reaching thickness of 10 nm, whereas for the SFO/STO specimen is only 4 nm thick. The corresponding FT patterns of the NGO substrate and the buffer layer are depicted in Figure 5, bottom; they present clear differences. The spots corresponding to the positions $h0l; h, l \neq 2n$ in the [$1\overline{1}1$] NGO FT pattern are not present in the FT pattern of the buffer layer (BL). The former is identical to the NGO ED pattern of Figure 4b, whilst the latter can be assigned to a perovskite structure. High-angle annular dark field (HAADF) imaging was used to obtain a qualitative composition of the buffer layer (not shown here). This technique can be interpreted as so-called $z$-contrast, in the sense that the intensity is a monotonously function of the effective projected atomic number. In the SFO/NGO sample, the buffer layer was clearly less intense than the NGO substrate due to the presence of elements with lower atomic number, namely Fe ($z = 26$) and Sr ($z = 38$), in comparison to Nd ($z = 60$) and Ga ($z = 31$). Therefore, it can be assumed that there is a Sr and Fe diffusion into the substrate and a $(Nd,Sr)(Fe,Ga)O_3\times$ solid solution is formed as an intermediate layer between the NdGaO$_3$ substrate and the $Sr_4Fe_6O_{12.86}$ film. For the SFO film deposited on the STO substrate, the differences in intensity of the HAADF images are not stressed enough to reach any conclusion due to the small differences in the atomic number of the constituent elements [Sr ($z = 38$), Fe ($z = 26$), and Ti ($z = 22$)], and the small thickness of the buffer layer (from 4 to 5 unit cells). However, it is safe to conceive that similarly as in the SFO/NGO sample, the intermediate layer in the SFO/STO sample is formed as a modified upper layer of the STO substrate due to Sr and Fe diffusion into the substrate. Therefore, the buffer layer may consist of Sr(Ti,Fe)O$_3\times$. The presence of a buffer layer with variable thickness gives rise to the formation of a high density of defects. In Figure 5b, a misfit dislocation is present at SFO/BL interface.
(outlined by white arrowheads) and is associated with the presence of a two unit cell step in the buffer layer.

Figure 6 is a HREM image of the SFO/LAO interface along [100]. The difference with the [100] HREM images of the other samples (Fig. 5a and b) is straightforward as no perovskite buffer layer is observed for the SFO film grown on LAO. Instead, the SFO/LAO interface is dominated by a substrate miscut angle less than 0.2°, implying that the minimum width of a substrate terrace is 109 nm. The presence of terraces in the LAO substrate together with the compressive misfit strain of the film gives rise to the formation a high density of dislocations in the substrate-film interface (indicated with the “T” signs in the image). Usually, the first layer deposited is a perovskite-type layer that starts to grow at the steps of the LAO substrate and extends throughout the terraces but at a certain moment it is laterally transformed into a double layer. This lateral transformation is associated with a dislocation. Moreover, misfit dislocations due to the large lattice mismatch between the film and the LAO substrate are located very close to the lateral transformations.

In summary, α values for 60 nm thin SFO films were calculated in 0.36, 0.33, and 0.43, for films deposited on STO, NGO, and LAO, respectively. The oxygen content in the SFO/LAO layer (Sr$_4$Fe$_6$O$_{12.8}$) is thus higher than that of SFO/STO (Sr$_4$Fe$_6$O$_{12.72}$) and SFO/NGO (Sr$_4$Fe$_6$O$_{12.67}$). Since the ε$_\perp$ strain values measured by XRD for 60 nm thick films were about +0.3% on LAO and +0.5% on STO and NGO, this indicates that the larger strain limits the oxygen incorporation in the layers so the anion content in the layers shows a direct correlation with the film strain. A plausible cause for these differences can be the existence of a competition between the different strain accommodation mechanisms observed in the SFO films. While SFO films on STO and NGO present a similar microstructure (with the presence of a perovskite-type buffer layer and occasional misfit dislocations), the presence of a substrate miscut angle less than 0.2° and a high density of dislocations in the SFO/LAO interface may provide an effective inelastic accommodation mechanism that contributes to the relief of the misfit stress, allowing the insertion of extra oxygen atoms in the structure; the insertion of anions in the SFO structure being charge compensated by an increase in valence of the Fe ions.

2.3. Strain Accommodation Mechanisms

These previous observations indicate the existence of some intrinsic differences in the release strain mechanisms of the films depending on the substrate type. Although the presence of a buffer layer could release part of the strain in the growing film, we have not detected the presence of the high density of defects needed to fully adapt the SFO structure. The Sr$_4$Fe$_6$O$_{12.8}$ films deposited on STO and NGO should then present certain plasticity in order to adapt their cell parameters over a wide range of values without generating dislocations. On the contrary, for a larger misfit, which is the case on LAO, the strain exceeds the plastic deformation limit, and thus misfit dislocations start to form at a very early stage of the film growth. The quite large plasticity observed in the SFO films seems to rely in the ability of the SFO microstructure to vary the oxygen modulation super-structure. In order to verify this later hypothesis, the XRD technique was used to measure the α modulation not only as a function of the substrate nature but also as a function of the film thickness in a more accurate way, complementary with previous HREM observations.

Figure 7 shows the XRD α values measured for different film thickness represented as a function of the measured b-axis parameters, as well as the calculated ε$_\perp$ strain values (obviously, a similar but inverted dependence is observed as a function of in-plane cell parameters). We clearly observe that α depends linearly with the strain and thus with the cell b parameter, independently of the substrate type. On STO and NGO substrates the α values vary in a wide range from 0.40 up to 0.45 in response to the strain variations. The thinner fully strained films on STO and NGO show the lowest α parameter of about 0.40. As described in ref. [6] Sr$_4$Fe$_6$O$_{12.2}$ films with α = 0.40 correspond to a commensurate phase Sr$_4$Fe$_6$O$_{12.8}$, whereas films with lower strain showing α > 0.40 correspond to incommensurate modulations of the structure with higher oxygen content. The thicker films on STO and NGO, along with the films on LAO, regardless their thickness, show higher α parameter, close to 0.45, in accordance with their lower residual strain, and in good agreement with previous ED observation. For these films the associated oxygen content 12 + 2α reaches 12.90. The slight discrepancy in the α values obtained by ED and XRD were associated to the different
calculation method between both techniques. It is important to notice that even for the fully relaxed films, the value of $a = 0.50$, which would correspond to the generally reported $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ phase, was never reached. Therefore, the strain in the films mainly relaxes by changing the structure modulation, i.e., varying their oxygen content.

2.4. Total Conductivity

In order to correlate the structure and microstructure variations with the high temperature properties, we measured the total conductivity along the $a$–$c$ plane of films with different thickness deposited on different substrates. The non negligible substrate conductivity at high temperatures of the STO and LAO substrates limited the comparison and discussion to temperatures below 400 °C. Figure 8 shows the total conductivity dependence with temperature for films with different thickness grown on NGO, STO and LAO, and compared to the bulk material values (our work and [15]). All the films exhibit similar behavior, with an increase of the conductivity with temperature until 400 °C due to the small-polaron hopping mechanism. On NGO, where no substrate conductivity contribution is appreciated, a decrease of the conductivity above 400 °C due to a carrier density decrease related to oxygen interchange with the atmosphere can be observed. As a general trend all the films showed conductivities higher than that of the polycrystalline bulk samples, due to their highly-oriented texture, thus confirming the high anisotropy of the transport properties expected in this layered materials.

More remarkable is the fact that for films deposited on NGO the conductivity increases substantially as the thickness decreases, while for films on LAO and STO no major influence of thickness on the conductivity values was observed (only slight differences in the activation energies, which will be subject of a further study). This different behavior with thickness constitutes a direct proof that the film thickness does not affect itself the absolute value of the conductivity, on the contrary it is the strain in the film which determines the conductivity, very likely related to their $a$ modulation. The thicker films on all substrates show similar values for the conductivity, which is consistent with their lower strain, whereas the thinner films on NGO show higher conductivities given their higher strain. The films deposited on LAO substrates relax the stress by the generation of misfit dislocations, as observed by HREM, and thus their conductivity remains independent of the film thickness. This phenomenon is clearly seen in Figure 9 where the conductivity measured at 400 °C is plotted as a function of the thickness for the three substrates. Values determined for STO are rather scattered but the conductivity of films deposited on NGO clearly increases as reducing the thickness, while the conductivity of SFO/LAO remains constant in this thickness range.

As it was previously stated, the film strain release is mediated by an oxygen composition variation $12 + 2\alpha$, through the $a$ modulation parameter. Thus if the films strain controls the conductivity then the variation of the conductivity with the $a$ parameter should also be representative of this correlation. Figure 10 shows the conductivity dependence versus the $a$ modulation parameter. The conductivity increases with decreasing $a$ (increasing strain) up to about one order of magnitude for the higher strained films on NGO and STO. The conductivity values measured for films deposited on LAO, did not show any significant variation because of their almost constant $a$ parameters (small strain state). Post annealing treatment of the films at different oxygen partial pressure atmospheres did not reveal any variation of the $a$ modulation parameter, indicating a high stability of the modulated structures. We have to mention that films subjected to subsequent annealing in Ar followed by an O$_2$ treatment recovered the initial conductivity values, indicating that the oxygen content in the films might vary in a reversible way following $12 + 2\alpha \pm \varepsilon$, without affecting the stability of the modulated structure.
variation the plane of the films consisting in an oxygen composition induces important changes in the modulated structure along different degrees of compressive strain. The residual strain substrates with different thickness in order to generate thus the oxygen content (12 the higher the strain the lower the properties. As a general observation, the epitaxial strain can

3. Conclusions

We have deposited SFO epitaxial thin films on various substrates with different thickness in order to generate different degrees of compressive strain. The residual strain induces important changes in the modulated structure along the plane of the films consisting in an oxygen composition variation 12 + 2α, where α corresponds to the modulation parameter. The misfit strain between film and substrate actively participates in the stabilization of a given Sr4Fe6O12+2α structure (and oxygen content) with fixed α to better accommodate the stress.

The overall oxygen content of the films is then defined by 12 + 2α, and has been found to determine their transport properties. As a general observation, the epitaxial strain can induce a substantial enhancement of the film conductivity since the higher the strain the lower the α modulation parameter and thus the oxygen content (12 + 2 α). It is then possible to increase the conductivity of the SFO films simply by a proper choice of the substrate cell parameters and film thickness. This is true up to a certain “limit of plasticity” of the strained SFO structure, above which the material can no longer reduce the α value of the modulated structure (probably the minimum measured value α = 0.40) and releases the accumulated energy by the generation of misfit dislocations, as it is the case of the films grown on LAO, coming back to an equilibrium structure, much closer to the bulk structure, with an α higher value close to 0.45.

4. Experimental

Epitaxial b-axis oriented SFO thin films with thickness ranging from 5 to 300 nm were deposited on (100) SrTiO3 (STO), (110) NdGaO3 (NGO), and (012) LaAlO3 (LAO) substrates by pulsed laser deposition at 750 °C and 1 Pa of oxygen pressure, as was described elsewhere.16,18 These apparent different substrate orientations correspond in fact to the same close matching (001) plane of their pseudo-cubic cells and were chosen in order to promote the b-axis oriented growth of the SFO structure. In fact, the SrTiO3 (STO) substrate has a cubic perovskite structure with lattice parameter aSTO = 0.3905 nm, the NdGaO3 (NGO) structure is orthorhombic with lattice parameters aNGO = 0.5433 nm ≈ 2aSTO, bNGO = 0.5503 nm ≈ \(\sqrt{2}a_{\text{STO}}\), and cNGO = 0.7715 nm \(\approx 2a_{\text{STO}}\) and LaAlO3 (LAO) has also a perovskite-based structure. However, LAO undergoes a structural phase transition from the rhombohedral \((\alpha_{\text{LAO}} = 0.536 \text{ nm and } c_{\text{LAO}} = 1.311 \text{ nm})\) to the cubic structure as increasing the temperature above 544 °C, that induces twin domain formation in the low-temperature phase. Thus, for simplicity, the indexing will be referred to the primitive cell of perovskite structure and the LAO unit cell parameters will be expressed with reference to the pseudo-cubic lattice where \(d_{\text{LAO}} = 0.379 \text{ nm (} = \sqrt{2}/2 \cdot 0.536 \text{ nm) unless stated otherwise. Thus, the theoretical lattice mismatch, for a fixed Sr4Fe6O13 film composition, on STO, NGO, and LAO substrates along the [201] SFO direction is about +0.7%, +1.7%, and +3.7%, respectively, being all the films under compressive stress. The thickness of the films up to 100 nm was calculated using X-ray reflectometry, while for thicker samples the value was extrapolated from the growth rate determined for the thin films. The measurement of Sr and Fe cation composition was performed by wavelength dispersive X-Ray spectrometry (WDS). The Sr and Fe Kα lines from the films were monitored at 12, 15, and 20 keV, and the data were treated by STRATAGem software to extract Fe/Sr composition ratio. On STO, the coexistence of Sr in film and substrate difficulted the measurement. However, on NGO and LAO accurate composition ratios of Fe/Sr = 1.47 ± 0.5 were obtained, which correspond to the stoichiometric value of 1.5 within the experimental error of the measurement. The structural characterization was performed by means of an X-ray Philips MRD diffractometer equipped with a four-angle goniometer, and parallel beam optics. The out of plane, b parameter, was calculated from the 2\(\theta\) angular positions of different 0k0 reflections, while for the in-plane parameter an average \(d_{201}\) parameter was measured (directly comparable to the cubic perovskite substrate parameter) along the [201] direction, which was calculated from the angular positions of the 6153, 8124, and 6173 reflections, as described in previous work.\[^7\] \(^\text{[7]}\) The oxygen modulation parameter, α, was extracted from the angular positions of hhkO \((k = \text{odd})\)
in the reciprocal space maps. Cross-section samples for TEM were cut parallel to the (110) perovskite-type planes of the substrates and mechanically ground to a thickness of about 20 μm, followed by final ion-milling under grazing incidence until electron transparency. Electron diffraction (ED) and high-resolution electron microscopy (HREM) studies were performed using a JEOL 4000EX microscope. The planar conductance of the films was measured by a.c. impedance spectroscopy (HP 4192A) in the range of 5 Hz –13 MHz as the temperature decreases from 800 to 50 °C in 1 atm of pure O2.

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