Thickness-dependent transport properties of Sr$_4$Fe$_6$O$_{13}$ epitaxial thin films

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Abstract

High-quality epitaxial thin films of Sr$_4$Fe$_6$O$_{13}$ have been deposited on NdGaO$_3$(001) substrates by pulsed laser deposition. The transport properties have been characterized by impedance spectroscopy. The temperature dependence of conductivity suggests a mechanism of adiabatic hopping by small polarons, in agreement with previous results in bulk samples. The transport properties show a clear dependence on the film thickness with the thinner films (10 nm) presenting conductivity values in oxygen one order of magnitude higher than the thicker ones (313 nm). We correlate this behaviour with the thickness dependence of the epitaxial strain.

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1. Introduction

Mixed oxygen-ion and electron conducting (MIEC) oxides have attracted great attention in the last years because of their potential use in oxygen separation membranes, cathodes for solid oxide fuel cells, and gas sensors [1]. Some complex oxides with perovskite-related intergrowth structure, such as the Sr$_4$Fe$_{6-x}$Co$_x$O$_{13+\delta}$ ($x \leq 2$) family, have shown high mixed conductivity and high stability over a wide range of temperature and oxygen pressure [2]. By increasing the cobalt content $x$ in the Sr$_4$Fe$_{6-x}$Co$_x$O$_{13+\delta}$ series, higher conductivity values are obtained [3] but the stability range becomes narrower, and secondary phases tend to appear for $x > 1.5$ [4]. The parent member Sr$_4$Fe$_6$O$_{13+\delta}$ is a more stable, single-phase material with appreciable mixed conductivity [5]. The room-temperature structural of stoichiometric bulk Sr$_4$Fe$_6$O$_{13}$ consists of an alternating stack along the $b$-axis of Sr–Fe–O perovskite-type layers, and Fe–O double layers formed by FeO$_5$ polyhedra sharing corners and edges (orthorhombic lattice parameters $a=1.1103$ nm, $b=1.8924$ nm, and $c=0.5572$ nm) [6]. The properties of this layered compound are expected to be anisotropic, and in particular it has been suggested that the oxygen-ion conductivity should be dominant along the $a$–$c$ planes [3]. In fact the formation of oxygen vacancies and incorporation of interstitial oxygen atoms in bulk Sr$_4$Fe$_6$O$_{13+\delta}$ occur only in the non-perovskite layers, whilst maintaining the same structure over a wide range of oxygen nonstoichiometry $13+\delta$ [7].

The structure, microstructure and physical properties of epitaxial thin films can differ substantially from those of ceramic materials and bulk single crystals with the same composition. The absence of high-angle grain boundaries (or in some cases the presence of a small amount of grain boundaries of a very specific type related to the parallel domain orientation), epitaxial strain, presence of particular growth-induced defects (stacking faults, anti-phase domains, etc.), limited-size effects and the high surface-to-volume ratio can be responsible for these differences. Examples are found in high-$T_c$ superconducting [8], magnetostrictive [9] or ferroelectric films [10]. Indeed, a new structure —different from the one reported for the bulk material— was identified recently using electron diffraction and high-resolution transmission electron microscopy in high-quality $b$-axis oriented epitaxial thin films.
of Sr$_4$Fe$_6$O$_{13-\delta}$ grown by pulsed laser deposition on SrTiO$_3$(001) substrates [11]. These oxygen-deficient films present an incommensurate modulation of the oxygen superstructure in the Fe–O double layer along the $a$ axis. The experimentally determined $\alpha$ component of the modulation vector $q=\alpha a_{\text{m}}^\star$ is related to the local oxygen content, so that $13-\delta=12+2x$. X-ray diffraction experiments in Sr$_4$Fe$_6$O$_{13-\delta}$ films of various thickness deposited on SrTiO$_3$ under the same conditions revealed a close correlation between the thickness, the $\alpha$ component (and so the oxygen content $13-\delta$), and the in-plane $a$ parameter [12]. The modification of the modulation of the superstructure therefore provides a mechanism for the release of compressive epitaxial strain. The variation of both oxygen content and epitaxial strain with the thickness could have an influence on the transport properties. The objective of this work is to study the electrical conductivity of epitaxial thin films of Sr$_4$Fe$_6$O$_{13-\delta}$ and its dependence on the film thickness, temperature and atmosphere.

2. Experimental

Dense ceramic pellets of Sr$_4$Fe$_6$O$_{13-\delta}$ for the ablation target and for electrical measurements in bulk samples were sintered by solid state reaction at 1150 °C in air. The pulsed laser deposition of thin films was carried out at $1.0 \times 10^{-4}$ mbar O$_2$ pressure and 750 °C substrate temperature, with variable number of laser pulses in order to prepare samples with different thickness. Previous works [11,13] provide further details on the growth, structure and microstructure of epitaxial Sr$_4$Fe$_6$O$_{13-\delta}$ films on SrTiO$_3$ substrates.

To avoid any contribution from the electrical conductance of the substrate, the films were deposited on 0.5 mm thick NdGaO$_3$(001) single crystals. We measured a conductivity value as low as $3.2 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$ at 751 °C in a substrate, in perfect accordance with published results [14].

For the structural characterization of the films and the measurement of epitaxial strain we used an X-ray Philips MRD diffractometer equipped with a four-angle goniometer. X-ray reflectometry was used to determine accurately the thickness of the films up to 100 nm. For the rest of the samples the value was extrapolated from a linear fit between the number of laser pulses and the film thickness in the range 20–100 nm.

The surface morphology and the microstructure of as-deposited films were examined by scanning electron microscopy (SEM) using a JEOL JSM-6300 microscope, and by high resolution electron microscopy (HREM) using a JEOL 4000EX microscope operated at 400 kV. Samples for transmission electron microscopy (TEM) were prepared in cross-section and plan-view.

Two parallel stripe-shaped electrodes were painted on the surface of each sample with Demetron 308A platinum paste. The AC impedance measurements in the range 5 Hz–13 MHz or at 1 kHz fixed frequency were carried out with an HP 4192A impedance analyser. After heating the furnace to 800 °C filled with a slow flux of 1 bar O$_2$ or 1 bar Ar (oxygen partial pressure $\approx 10^{-5}$ bar, as measured with a YSZ probe—Rapidox 2000 from Cambridge Sensotec), the measurements were taken at 50 °C intervals on cooling down under the same atmosphere, with 15 min stabilizing period at each temperature. A type-K thermocouple measured the temperature close to the sample with $\pm 2$ °C estimated accuracy. The impedance spectra were analysed using the EQUIVCRT fitting software [15].

3. Results and discussion

As determined by X-ray diffraction $\theta$–2$\theta$ scans, all Sr$_4$Fe$_6$O$_{13-\delta}$/NdGaO$_3$(001) films are $b$-oriented, i.e. their (010) plane is parallel to the substrate plane. The NdGaO$_3$ substrate has a perovskite structure with orthorhombic lattice parameters $a=0.5433$ nm, $b=0.5503$ nm, and $c=0.77157$ nm, at 298 K [16]. Therefore its (001) cut exhibits a pseudocubic lattice with lattice parameter 0.3867 nm. The phi-scans show that the perovskite-like blocks of Sr$_4$Fe$_6$O$_{13-\delta}$ (with pseudo-cubic parameter 0.3933 nm in bulk samples [6]) are oriented parallel to the perovskite pseudocubic blocks of the NdGaO$_3$ substrate. This behaviour, widely known as “cube-on-cube” epitaxy, is common when perovskite-like films and substrates are used. These crystallographic details allow us to estimate a 1.7% average interfacial mismatch in our Sr$_4$Fe$_6$O$_{13-\delta}$/NdGaO$_3$(001) epitaxial films, somewhat higher than the 0.7% mismatch of the films deposited on cubic SrTiO$_3$(001) substrates (lattice parameter 0.3905 nm) [13].

The microstructure and crystal quality of all films are quite similar to those grown on SrTiO$_3$ substrates [13]. Rocking curves present typical full width at half-maximum values of 0.3–0.4°. Fig. 1 corresponds to an SEM image of the surface morphology of a sample deposited with 3000 laser pulses. It shows a flat surface with some needle-like precipitates oriented...
along the a and c directions of the Sr$_3$Fe$_6$O$_{13+y\alpha}$ film. Our preliminary HREM observations indicate that they consist of isolated SrFeO$_{3-x}$ perovskite precipitates that keep a cube-on-cube epitaxial relation with the Sr$_3$Fe$_6$O$_{13+y\alpha}$ film, in the same way as it was observed when SrTiO$_3$ substrates were used [11]. These SrFeO$_{3-x}$ precipitates are homogeneously distributed along the thickness of the film with only occasional connectivity between them, and their concentration does not depend on the film thickness.

The ImZ(ω)–ReZ(ω) impedance plots in the explored frequency range consist typically of a single semicircular arc, as shown in Fig. 2. The spectra can be interpreted on the basis of a parallel RC circuit, from which the resistive component $R$ can be extracted as the low-frequency intersect of a purely resistive, frequency-independent behaviour (phase $\chi=0$, modulus $|Z|=R$) below $10^3$ Hz. The AC impedance at 1 kHz fixed frequency is therefore taken as a direct measurement of the sample resistance. For some of the measured samples the resistance $R$ in the low-temperature region exceeds $10^6$ $\Omega$, which can not be directly measured with our setup. For that range the resistance values are extrapolated from the high-frequency impedance data by fitting a single arc, although the $R$ values higher than twice the upper limit of the apparatus are rejected. The contact resistance between the electrodes and the sample is considered to be negligible in all cases.

The dependence of total conductivity $\sigma$ with temperature $T$ in O$_2$ gas is presented in Fig. 3 for some of the films with different thickness. It shows a thermally activated behaviour between 100 °C and 500 °C, then reaches a maximum at $\approx 550$ °C and decreases very slowly up to 760 °C. This change of the slope sign is not apparent in the ceramic sample that presents temperature dependence and conductivity values very close to previous results in air by other authors (Fig. 3). Also the measurements in Ar atmosphere for the same films show a thermal activation up to $\approx 500$ °C followed by a maximum and a slight decrease up to 760 °C (Fig. 4). This reduction of conductivity with increasing temperature is observed in all the films in the high-$T$ range ($T>450$ °C) for both atmospheres–more clear for the measurements in Ar– and is attributed to a carrier concentration depletion as the films start loosing oxygen and decrease oxygen stoichiometry. A similar behaviour has been reported in many oxide perovskites, for instance in (Sr,Ca)FeO$_{3-x}$ [17] and (La,Sr)(Fe,Co)O$_{3-x}$ [18].

The ionic transference number for oxygen in Sr$_3$Fe$_6$O$_{13+y\alpha}$ is known to be of the order of $10^{-3}$ to $10^{-4}$ [20], so almost all the contributions to conductivity come from electronic carriers and depend on the oxygen partial pressure, $p$O$_2$. In our films, for each thickness and temperature the conductivity in Ar ($p$O$_2 \approx 10^{-5}$ bar) is lower than in pure O$_2$, indicating a $p$-type transport by electron holes, as reported for bulk samples in the high-$p$O$_2$ range [5]. Adiabatic small-polaron hopping has

![Fig. 2. Impedance spectrum of a 234-nm-thick film at 531 °C in argon. The points corresponding to $10^6$ Hz frequencies ($n=1, 2, \ldots, 7$) are indicated by solid circles.](image)

![Fig. 3. Temperature dependence of total conductivity $\sigma$ in O$_2$ in our Sr$_3$Fe$_6$O$_{13+y\alpha}$ ceramic sample and four films with the indicated thickness. The results for bulk samples in air according to different authors are shown for comparison (dotted line: Ref. [17], dashed line: Ref. [18]).](image)

![Fig. 4. Temperature dependence of total conductivity $\sigma$ in Ar for the same films as in Fig. 3. The more resistive samples are beyond our measuring range below $\approx 300$ °C.](image)
been proposed as the conduction mechanism in Sr$_4$Fe$_6$O$_{13+x\alpha}$ and other strontium ferrites [21]. In the Emin-Holstein model for the small-polaron hopping in the adiabatic approximation [22] the carrier concentration is constant and the temperature dependence of conductivity arises from the thermal activation of the mobility, yielding

\[ \sigma(T) = \frac{A}{T} \exp(-E_a/(kT)), \tag{1} \]

with \( k \) as the Boltzmann constant, and \( A \) is a preexponential factor that depends on the carrier concentration, the distance between hopping sites and the frequency of the longitudinal optical phonon that propels the polaron hopping over the potential barrier of height \( E_a \) (activation energy). In Fig. 5 we represent \( \ln(\sigma T) \) versus reciprocal \( T \) for the measurements in oxygen of Fig. 3. The linear dependence in the low-T range strongly supports the assumption of the polaronic mechanism for conduction, and allows us to determine \( E_a \) and \( A \) for each sample. The fit of Eq. (1) to all the measurements in O$_2$ in the 100–450 °C range and for the ceramic sample is presented in Table 1. It includes the results of some samples with intermediate thickness, not shown in Figs. 3 and 5 for the sake of clarity. The resulting activation energies in the range 0.20–0.30 eV are typical for adiabatic small-polaron hopping. Fig. 6 represents the thickness dependence of the preexponential factor \( A \) taken from Table 1.

A clear dependence of \( \sigma \) with film thickness is apparent from Figs. 3 and 4. The highest conductivity in O$_2$ (Fig. 3) is achieved in the 10 nm-thick film. Then the values decrease monotonously by increasing the thickness, remaining still one order of magnitude higher than the ceramic ones in the 313-nm-thick sample. The behaviour as a function of thickness in Ar atmosphere is similar: the thinner the film is, the higher is the conductivity (Fig. 4). Other authors have reported thickness-dependent transport properties in epitaxial films of some perovskite oxides, and different mechanisms have been suggested [9,23,24].

Several reasons may account for the higher \( \sigma \) values of the films relative to the ceramic. First, the highly anisotropic transport properties expected in Sr$_4$Fe$_6$O$_{13+x\alpha}$, according to the paths that have been suggested for the charge diffusion. In fact, the conduction of electron carriers takes place along the FeO$_2$ planes in the perovskite layers [5], while that of oxygen ions is dominant along the non-perovskite blocks [3,20]. Both contributions give rise to an increased mixed conductivity perpendicular to the \( b \) axis, that is to say along the measuring direction in our \( b \)-oriented epitaxial thin films. In addition, the high crystal quality of the latter minimizes the losses across the high-angle grain boundaries that are significant in ceramic samples.

In a lower extent, the minority presence in the films of isolated SrFeO$_3$ precipitates with higher conductivity might originate an apparent increase in their measured conductivity. Our SEM and TEM observations along with compositional analyses indicate that the concentration of the SrFeO$_3$-\( x \) inclusions is very low. In particular, it is much below the percolation limit — the one at which the inclusions form continuous conducting pathways. In these conditions we can estimate the conductivity of the two-phase material by

\[ A = \exp(-E_a/(kT)) \]

Table 1 Preexponential factor \( (A) \) and activation energy \( (E_a) \) resulting from the fit of Eq. (1) to the conductivity measurements in O$_2$ in the 100–450 °C range, as a function of the film thickness and for the ceramic sample

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>( A ) ((\Omega^{-1} \text{ cm}^{-1} \text{ K}))</th>
<th>( E_a ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>( 1.80 \times 10^6 )</td>
<td>0.24</td>
</tr>
<tr>
<td>24.5</td>
<td>( 1.88 \times 10^6 )</td>
<td>0.31</td>
</tr>
<tr>
<td>38.2</td>
<td>( 1.59 \times 10^6 )</td>
<td>0.30</td>
</tr>
<tr>
<td>56.3</td>
<td>( 7.22 \times 10^5 )</td>
<td>0.26</td>
</tr>
<tr>
<td>80.0</td>
<td>( 4.45 \times 10^5 )</td>
<td>0.23</td>
</tr>
<tr>
<td>156</td>
<td>( 2.50 \times 10^5 )</td>
<td>0.24</td>
</tr>
<tr>
<td>234</td>
<td>( 1.31 \times 10^5 )</td>
<td>0.22</td>
</tr>
<tr>
<td>313</td>
<td>( 9.70 \times 10^4 )</td>
<td>0.22</td>
</tr>
<tr>
<td>Ceramic</td>
<td>( 5.71 \times 10^3 )</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Fig. 5. \( \ln(\sigma T) \) versus reciprocal temperature (in O$_2$) in our Sr$_4$Fe$_6$O$_{13+x\alpha}$ ceramic sample and the four films with the indicated thickness. Straight lines represent the fits of Eq. (1) to the data in the 100–450 °C range.

Fig. 6. Thickness dependence of the preexponential factor \( A \) (in double logarithmic scale) taken from Table 1. The approximate value of the critical thickness \( t_c \) has been indicated by an arrow.
Maxwell-Wagner approximation, which in this limit is valid regardless of the inclusions’ shape [25]:

$$\frac{\sigma_t}{\sigma_m} = 1 + 3\nu\left[\frac{\sigma_i - \sigma_m}{\sigma_i + 2\sigma_m}\right].$$  \hspace{1cm} (2)

Here $\nu$ is the volume fraction of the inclusions, and $\sigma_m$, $\sigma_i$ and $\sigma_t$ stand for the conductivities of the matrix, inclusions and whole film, respectively. According to the conductivity values for SrFeO$_3-\delta$ and Sr$_4$Fe$_6$O$_{13-\delta}$ samples [17], it is $\sigma_i \gg \sigma_m$, and so

$$\left[\frac{\sigma_i - \sigma_m}{\sigma_i + 2\sigma_m}\right] \approx 1,$$  \hspace{1cm} (3)

which gives

$$\frac{\sigma_t}{\sigma_m} \approx 1 + 3\nu.$$  \hspace{1cm} (4)

Therefore the measured conductivity in this very diluted composite material differs from the actual Sr$_4$Fe$_6$O$_{13-\delta}$ conductivity only by a constant factor close to unity (given that $\nu \ll 1$). This is consistent with the fact that the temperature dependence of the measured conductivity in our films is similar to the one observed in bulk Sr$_4$Fe$_6$O$_{13-\delta}$ samples (Fig. 3), but quite different from that of SrFeO$_3$ [17]. More important, since we have not observed any correlation between the concentration of SrFeO$_3-\delta$ inclusions and the film thickness, it follows that the observed thickness-dependent conductivity (Figs. 3–5) is not related with the presence of the precipitates.

The structural details of our epitaxial films may help to clarify the thickness dependence of their conductivity. Previous crystallographic investigations in Sr$_4$Fe$_6$O$_{13-\delta}$/SrTiO$_3$ [12] and our more recent results on Sr$_4$Fe$_6$O$_{13-\delta}$/NdGaO$_3$ show a variation of the cell parameters with thickness. The epitaxial in-plane compressive stress “forces” the thinner, fully strained films to match the cell parameters of the substrate. Above a critical thickness $t_c$ such strain is partially released upon increasing thickness and the in-plane cell parameters of the film progressively increase, approaching those of the bulk material. The in-plane strain $\varepsilon_{xx}$ is defined as the difference between the pseudocubic lattice parameters of bulk and film in the $a$–$c$ plane, relative to the bulk parameter. Fig. 7 shows the thickness dependence of $\varepsilon_{xx}$ in some of our Sr$_4$Fe$_6$O$_{13-\delta}$/SrTiO$_3$(001) and Sr$_4$Fe$_6$O$_{13-\delta}$/NdGaO$_3$(001) epitaxial films deposited at 10$^{-2}$ mbar O$_2$ pressure and 750 °C substrate temperature. A $t_c$ value around 30–40 nm is observed.

It is clear that the compression of the films along the $a$–$c$ planes by epitaxial strain increases the overlap of the electron orbitals of the iron and oxygen atoms, thus leading to a higher degree of covalency of the Fe–O–Fe bonds. This feature has been reported to increase the electron-hole mobility in small-polaron conductors such as Sr$_4$Fe$_6$O$_{13}$ and other strontium iron oxides [21] or doped strontium iron perovskites [26]. In our case the strain, and so the overlap and the hole mobility, increases by decreasing the film thickness. Indeed, the similarity of Figs. 6 and 7 strongly suggests that the lattice contraction imposed by the epitaxy has a direct effect on the preexponential factor $A$, the thickness dependence of the former (Fig. 7) giving rise to a thickness dependence of the latter (Fig. 6).

Beyond this point it is difficult to establish quantitative estimations. Within the Emin-Holstein model [22] the factor $A$ is proportional to the frequency $\nu$ of the longitudinal optical phonon that carries the polarons. Although we expect an increase in the frequency $\nu$ along the compressed $a$–$c$ planes in our epitaxial films, it cannot account for the more than one order of magnitude increase in conductivity between the 313-nm-thick film and the 10-nm-thick film observed in Figs. 3 and 4. Most probably other factors have an influence on the thickness dependence of conductivity, for example the activation energies, that are higher for the thinner films — excluding the 10-nm-thick film.

Further experimental work is underway in order to elucidate the unclear aspects of the conductivity of Sr$_4$Fe$_6$O$_{13-\delta}$. One of the most interesting points has to do with the intriguing oxygen superstructure modulation observed both in thin films [12] and in ceramic samples [27,28] that could affect the carrier concentration and so the transport properties.

4. Conclusion

The electron-hole conductivity in epitaxial Sr$_4$Fe$_6$O$_{13-\delta}$/NdGaO$_3$ films in oxygen and in argon has been measured, and interpreted as the hopping of small polarons in the adiabatic approximation. The total conductivity of the epitaxial films has been found to increase with decreasing the thickness. The thickness-dependent in-plane compressive strain imposed by the epitaxy is suggested to cause this correlation.

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