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Dos Santos Gómez, Lucia; Sanna, Simone; Norby, Poul; Pryds, Nini; Losilla, Enrique R. ; Marrero-López, David ; Esposito, Vincenzo

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Electrochemical stability of (La,Sr)CoO_{3-δ} in (La,Sr)CoO_{3-δ}/(Ce,Gd)O_{2-δ} heterostructures

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Lucía dos Santos-Gómez^{a,b,*}, Simone Sanna^a, Poul Norby^a, Nini Pryds^a, Enrique R. Losilla^b, David Marrero-López^c and Vincenzo Esposito^{a,*}

A modulated coherent (La,Sr)CoO_{3-δ}/(Ce,Gd)O_{2-δ} heterostructure is characterized for the first time for its electronic and chemical properties. 2D-multilayer architectures are deposited on NdGaO₃ (110) single crystal substrate by pulsed laser deposition, resulting in epitaxial structures with in-plane lattice rotation that, via the metal oxides' interfaces, induces mutual structural rearrangements. Our results show that (La,Sr)CoO_{3-δ} thin films of 10-100 nm are chemically unstable when exposed to air at 600 °C during electrical cyclic stress-tests. Conversely, improved stability is achieved confining LSC in the nanometric heterostructure. Remarkably, the chemical stabilization occurs without compromising substantially the electrical properties of the LSC component: the heterostructures show unexpected electrical behaviour with dominant electronic contributions, fast conductivity and mixed ionic-electronic properties, depending on the number of interfaces and the nano-scaled layers.

Introduction

Ionotronics are electrochemically activated ionic-carrier materials and devices that are rapidly defining a new generation of ionic-electronic systems, for energy, electro-mechanics, sensing and advanced electronics.¹⁻⁵ Among the different ionotronic materials, oxygen defective metal oxides (MeO) are emerging as the most relevant for their wide range of functions and tunability of properties. These properties arise from the formation of structural oxygen defects in the crystal that result in the activation of charge electrical carriers of diverse species.⁶ The introduction of electron/hole charge-carriers in MeOs, e.g. by doping, is a distinctive effect of mixed ionic-electronic conductors (MIECs), where mobile electrons are formed to balance the oxygen vacancies and other defective charge carriers in the lattice.^{7,8}

Besides doping and crystalline symmetry, the electrical properties of mixed oxides can be tailored by *nano-scaling*.⁹ Two-dimensional interfaces and nano-scaled structures between different materials have especially received much attention due to the possibility of obtaining physical properties that deviate greatly from bulk material equivalents, including

thermoelectricity, ferromagnetism, superconductivity, and a wide variety of electronic and ionic phenomena than can be detected only at the interfaces.⁹⁻¹⁵

In MeOs heterostructures, e.g. in multilayer thin films stacked at the nanoscale, electronic and ionic properties at interfaces can also be mixed and enhanced by varying layer characteristics and new properties in such heterostructures come from lattice strain and interface mobility effects, resulting even in enhanced chemical stability.¹⁶⁻²⁰

MeOs such as oxygen defective cerium oxide (ceria) fluoride, CeO_{2-δ}, and cobalt-based perovskites are a good example of such tunability. Ceria is a MIEC under reducing atmospheres, where formation of oxygen vacancies are compensated by the formation of polaron defects due to Ce⁴⁺/Ce³⁺ valence changes.²¹ After doping, the electrical properties can be enhanced toward oxide ion conductivity (acceptor doping) or electronic conductivity (donor doping) activated at high temperatures.²² Ceria is also chemically stable and it can lead to new phase stability domains in heterostructures with other unstable oxides.^{16, 23, 24}

Oxygen-deficient perovskites such as La_{1-x}Sr_xCoO_{3-δ} (LSC) are among the most studied MIEC metal oxides. LSC exhibits mixed ionic and electronic conduction by both oxide ions and highly mobile "itinerant" electron holes, in the metallic-like state (LSC conductivity at room temperature is above 2·10³ S cm⁻¹).^{25, 26} The strong potential of LSC especially lies in its fast oxygen surface exchange and diffusivity (K* = 9.67·10¹¹ cm s⁻¹ and D* = 8.0·10¹⁶ cm² s⁻¹), leading to efficient oxygen gas redox cycles, e.g. in reducing oxygen gas in cathode material for solid oxide fuel cells (SOFCs) and oxygen transport membranes (OTM).²⁷⁻³⁴ Despite these remarkable properties, LSC undergoes chemical instability, especially at the solid-gas interface with phase

^a Department of Energy Conversion and Storage, Technical University of Denmark, DTU Risø Campus, DK-4000 Roskilde, Denmark.

^b Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía, 29071-Málaga, Spain.

^c Universidad de Málaga, Departamento de Física Aplicada I, Laboratorio de Materiales y Superficie, 29071-Málaga, Spain.

* Corresponding authors: vies@dtu.dk, lucia_2_santos@uma.es

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separation and carbonation. This is mainly due to SrO segregation that, in MIEC perovskites, can heavily affect the performance of a variety of electrochemical conversion devices both bulk- and thin-film-based.^{34, 35} LSC performance appears, however, improved in composite materials with respect to the pure phase. CGO/LSC composites are, *e.g.*, functional in electrochemical applications and especially for oxygen reduction reactions (ORR) in SOFC cathodes.^{23, 36-40} LSC membranes with CGO coating show high values of K^* , which improves ORR kinetics.⁴⁰ On the other hand, nano-composites and vertically aligned CGO/LSC nanostructures (VANs) show exceptionally high cathodic activity in thin film-based SOFCs.^{36, 37} Develos-Bagarinao *et al.* have also proposed a dense, columnar CGO-LSC multilayer as a functional cathode for thin film-based SOFCs, achieving enhanced oxygen exchange properties.⁴¹ Other effects can also occur at the MIEC and ionic conductor interface, inducing a reciprocal electrostatic attraction between oxygen defects and mobile electrons at near-interface phases.⁴²

In this work, we present planar heterostructures, *i.e.* thin film-multilayer, with alternating thin layers of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ and acceptor-doped cerium oxide (Gd-doped CeO_2). Highly textured heterostructures are here epitaxial structures with high coherence between the layers is obtained by depositing on single crystal substrates (NdGaO_3) with a compatible structure. Several architectures, varying thickness and number of interfaces, are proposed. This is especially to shed light on chemical stability and electrochemical properties at the LSC/CGO solid-solid interface at different degrees of interfacial interaction. The multi-interface modulation is also the key to explore possible “nano-effects” occurring at the materials and their interfaces, as already reported for other ceria-based heterostructures with enhanced electrical properties and/or chemical stability.^{4, 9, 16, 23}

Experimental

Materials synthesis and methods

Thin film-based heterostructures of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO) were deposited on (110) NdGaO_3 (NGO) substrates by pulsed laser deposition (PLD). Different $[\text{LSC/CGO}]_N$ samples were prepared by modulating the thickness and the number of LSC/CGO bilayers (N). The total thickness of the heterostructures was controlled by varying the deposition time. For simplicity, the heterostructures are hereafter labelled as $x\text{-CGO}[\text{LSC/CGO}]_N\text{NGO}$, where x is the total thickness of the heterostructure. Two different kinds of architectures were deposited: $[\text{LSC/CGO}]_N\text{NGO}$ with LSC termination and $\text{CGO}[\text{LSC/CGO}]_N\text{NGO}$ with CGO at the air termination. Lattice mismatch between the crystals was calculated as described elsewhere.⁴³

For the deposition, a KrF excimer laser (Coherent Lambda Physik GmbH) with a pulse-duration of 25 ns and a wavelength of 248 nm was focused on the LSC and CGO targets. These were placed in a multi-target carousel. The laser fluence was kept constant at 2 J cm^{-2} , the substrate-target distance was 80

mm and the repetition rate was 10 Hz. The optimum oxygen partial pressure and substrate temperature during the deposition were 10^{-2} mbar and 750 °C, respectively. The CGO target was prepared by uniaxially pressing the commercial powder (Rhodia) into disks of 3 cm of diameter at 125 MPa and sintering at 1400 °C for 4 h. The LSC target was prepared by solid-state reaction, from La_2O_3 (Sigma-Aldrich, 99.99%), SrCO_3 (Alfa Aesar, 99.99%) and Co_3O_4 (Sigma-Aldrich, 100%) in stoichiometric amounts. La_2O_3 was previously calcined at 1000 °C for 2 h to achieve de-carbonation.³⁴ All reagents were mixed in an agate mortar for 25 min and heated at 1000 °C for 1 h. After that, the powders were ground in a ball mill for 2 h, pressed at 80 MPa and sintered at 1300 °C for 5 h to reach nearly full density ($> 95\%$). Commercial NGO (110) single crystal (Crystal GmbH) of 500 μm thickness was used as substrate. The substrates and targets were cleaned with acetone and ultrasonic procedure before deposition. Since the films were deposited under a constant oxygen partial pressure of 10^{-2} mbar, the as synthesized samples were expected to be highly oxygen defective, and thus partially reduced. To achieve full oxidation, and thus equilibrium, all samples were heated at 600 °C for 1 hour in air before the electrical characterization. Moreover, θ - 2θ scan were measured before and after the electrical measurements to evaluate the stability of the samples.

Thin film characterization

The phase purity of both CGO and LSC targets was investigated by X-ray powder diffraction (XRD), using a PANalytical X'Pert PRO diffractometer with monochromatic $\text{CuK}_{\alpha 1}$ radiation. The structural characterization of the layers was carried out in an ω - 2θ rocking curve and θ - 2θ scans on a Rigaku Smartlab triple-axis diffractometer with a rotating Cu anode as a source, operating at 200 mA and 50 kV and using a one-dimensional multi-layered optic to collimate and monochromatize the X-ray beam point-source, $\lambda = 1.5418 \text{ \AA}$.

The microstructure of the films was observed by Field Emission scanning electron microscope (FEI, Helios Nanolab 650), equipped with a Tomohawk focused ion beam (FIB), and transmission electron microscope (FEI Talos F200X) coupled with dispersive X-ray spectrometer (EDS). Different electron-transparent lamellas were prepared by following a similar procedure described elsewhere.⁴⁴

In-plane conductivity of the samples was carried out by the four-probe Van der Pauw method by using silver-gold ink and Au wires for the electrical connections. The measurements were carried out in synthetic air between room temperature and 600 °C, during the heating and cooling cycles to test the reproducibility of the data.

Impedance spectra were also acquired in the 2-probe symmetric configuration with a Solartron 1260 frequency response analyser by applying an AC amplitude of 200 mV in the 0.01 Hz – 1 M Hz frequency range in air. Accuracy and reliability of the in-plane measurement for multi-layers are discussed in previous publications.^{17, 23} Measurement on pristine NGO crystal substrates were carried out to appraise

the contribution of the substrate on the electrical measurements.

XPS measurements were recorded on a PHI 5000 VersaProbe II. X-ray source: Al 1486.6 eV mono at 47.5 W; beam diameter was 200.0 μm with a 1.4 V 20.0 μA neutralizer and a FAT Analyser mode. For the ionic milling, a 20kV10nA3x3 C60 sputter source was used in 42 alternating cycles. A Multipak-V9.3 software package was used for data analysis. The recorded spectra were fitted using Gaussian-Lorentzian curves to determine the binding energy of the different elements. The Sr 3d peak was deconvoluted to two main contributions. The Sr 3d area ratio and doublet separation were constrained to 1:0.66 and 1.7 eV, respectively.

Results and discussion

Pristine structural and microstructural features

Due to the dissimilar crystallography of the materials, epitaxial growth of CGO fluorite and LSC perovskite layers on the NGO perovskite (110) substrate has to be engineered *via* mutual crystallographic structural arrangements to result in a coherent interface. Cubic CGO fluorite (space group $Fm\bar{3}m$) has a lattice parameter of $a = 5.426 \text{ \AA}$ and this value is quite different to the value of the cubic LSC perovskite (space group $Pm\bar{3}m$, $a = 3.84 \text{ \AA}$) and the NGO substrate (orthorhombic, space group $Pbnm$ with $a = 5.4276 \text{ \AA}$, $b = 5.4979 \text{ \AA}$, $c = 7.7078 \text{ \AA}$). However, in the pseudo-cubic notation, NGO (110) can be represented such as a distorted perovskite structure with lattice parameter of approximately $3.86 \text{ \AA}$ ($b^* = c/2 = 3.8539$

and $a^* = 1/2\sqrt{(a^2 + b^2)} = 3.8628 \text{ \AA}$). Therefore, it is possible to describe the epitaxial relationship between LSC and NGO (110) as cube on cube growth.

NGO is an optimal substrate due to its lower electronic conductivity. An epitaxial growth minimizing the strain between LSC and NGO is also possible. Moreover, as shown in previous literature, while bulk LSC crystallizes with orthorhombic structure at temperatures (T) below 600°C , the LSC cubic form is stable at higher T , and the cubic phase is retained as metastable by cooling at lower T .⁴⁶ Such an effect occurs when the LSC crystallite size is in the nanometric range, avoiding the rhombohedral-cubic phase transformation.⁴⁶ For the CGO layer, previous work showed that CGO can easily accommodate cubic perovskites by lattice strain with respect to the cube on cube configuration *via* a 45° -rotation of the cell during deposition.⁴⁷ Figure 1 shows the results of the structural analysis and a schematic representation of the as deposited $[\text{LSC}/\text{CGO}]_N/\text{NGO}$ heterostructures. Figure 1a displays XRD patterns in the θ - 2θ scan mode of the samples with $N=2$ and 50 nm of thickness. The pattern well represents all the samples with different thicknesses and number of layers. The overall diffraction shows the presence of the NGO substrate and multilayer with CGO (200) and LSC (011) orientations at $2\theta = 34^\circ$. Diffraction peaks corresponding to the (200) and (011) reflections of CGO and LSC, respectively, are clearly observed. The diffraction pattern confirmed that the CGO cells are arranged with an in-plane 45° -rotation, as expected.⁴⁷ For a finer structural characterization, the ω - 2θ rocking curves of the samples were also performed on the

Figure 1. (a) θ - 2θ X-ray diffraction pattern of as-deposited 50nm-CGO[LSC/CGO]_{N=2}/NGO, (b) rocking curve of x-CGO[LSC/CGO]_N/NGO ($N=2$ and 5) with different thickness ($x=50, 100$ and 300 nm), (c) reciprocal space map of the (113) asymmetric reflections for the sample 100nm-CGO[LSC/CGO]_{N=5}/NGO and (d) schematic representation of the deposited heterostructures.

50nm-, 100nm- and 300nm-CGO[LSC/CGO]_NNGO (N = 2 and 5) samples (**Figure 1b**). Satellite peaks of CGO and LSC are visible at higher and lower angles with respect to the main reflection peaks, indicating high-quality of the heterostructures.^{16, 18, 48, 49} The values of full width at half maximum (FWHM) are between $0.5^\circ < 2\theta < 1.3^\circ$ (**Figure 1b**), suggesting a high degree of crystallinity and low structural and microstructural mosaic disorder in the films. Especially, the crystallinity of the films improves by decreasing N and increasing the thickness. This effect is likely due to the theoretical mismatch between CGO and LSC is 0.92%. As consequence, increasing N increases the average mismatch between the two lattices. Moreover, the distortion of the cell parameters at the interface and at the near-interface is lower for thicker layers, where the lattice relaxes. As result, the number of distorted cells is reduced when the thickness of the layers is increased.

Figure 1c shows the reciprocal space map (RSM) for the 100nm-CGO[LSC/CGO]_{N=5}NGO, where the asymmetric reflections of (113) plane is also distinguished. A peak is clearly observed and, due to the large lattice mismatch between CGO towards NGO and LSC, it is attributed to CGO layers.

The in-plane ($a_{x,y}$) and out-of-plane (a_z) lattice parameters are calculated from the RSM by the following equations:

$$a_{x,y} = \frac{2\pi\sqrt{h^2 + k^2}}{q_{x,y}} \quad (1),$$

$$a_z = \frac{2\pi\sqrt{l^2}}{q_z} \quad (2),$$

where $q_{x,y}$ and q_z are related to the in-plane (x-y) and out-of-plane (z) parameters of the diffracted wave-vector. The lattice parameters were calculated as $a_{x,y} = 4.90 \text{ \AA}$ and $a_z = 5.56 \text{ \AA}$ for CGO. These values are slightly different to those reported for the bulk CGO ($a = 5.426 \text{ \AA}$) (ICSD 182976), indicating that the CGO lattice is strained to adapt the large lattice mismatch with LSC and NGO.⁵⁰ Such results also suggest that the interfaces generate a compressive strain in CGO layers and, consequently, a tensile strain in the LSC layers. **Figure 1d** schematically represents the results obtained by the XRD characterization, reporting the theoretical lattice mismatches calculated for the orientations revealed by XRD: NGO vs 45°-rotated-CGO with a lattice mismatch of 0.59 % and CGO vs 45°-rotated-LSC with a lattice parameter mismatch of 0.92%. For the chemical and microstructural characterization, the films were extensively analysed by a combined use of FEI-SEM and HR-TEM, especially to cover different features and size scales.

Electrical characterization

Heterostructures with and without CGO-termination (top-layer) were tested to investigate conduction mechanisms and contributions. While measurements carried out on the pristine substrate indicate no contributions from the NGO crystal, it is known that CGO in air is a nearly pure ionic conductor with a negligible electronic (n-type polaron hopping) contribution at temperatures below 600 °C.⁵¹ In an in-plane measurement configuration, the CGO top-layer termination is thus expected to block electrons for the charge transfer at the sample/electrode interface. The CGO[LSC/CGO]_NNGO configuration can thus avoid short cuts-effects, *i.e.*, a pure

metallic resistive electric behaviour by the “itinerant” charges in the LSC top layer and, for the DC-measurement, should polarize the electrodes forming double-charged layers at the oxygen ionic conductor/electrode interface, by blocking the electronic component. On the other hand, the [LSC/CGO]_NNGO samples, *i.e.* LSC-terminated heterostructures, help to clarify the contribution of the LSC-interface to the conduction mechanisms and estimate the LSC thin layer degradation observed in the samples. By using these two configurations, different heterostructures were prepared by varying both the number of bilayers and the total thickness of the samples (N = 2 and 5; and the thickness were 50, 100 and 300 nm). **Figure 2** shows the Arrhenius plots in the direction parallel to the interfaces (*in-plane* conductivity) for the heterostructures with N = 2, overall thickness of 50 nm (**Figure 2a**) without and with CGO top-layer and comparison with the pure compositions (**Figure 2b**). The samples exhibit electronic properties with some unexpected features. Despite the similar electrical behaviour, **Figure 2a** shows that the 50nm-[LSC/CGO]_{N=2}NGO sample exhibits lower conductivity than the same sample with the CGO top layer. This is unexpected, especially at low temperatures, where LSC has a dominant electronic contribution and CGO is not an electronic conductor. A deeper analysis indicates that, while the CGO-terminate are stable, degradation of LSC termination that occurs at the first stage of the measurements (details in Figure S1). On the other hand, **Figure 2b** shows the electrical behaviour of 50nm-CGO[LSC/CGO]_{N=2}NGO sample compared to other thin films: conductivity of a LSC single layer (blue line), made in the same PLD conditions, and CGO thin film (red line) from reference 52. Conductivity of the pure LSC film resulted stable and comparable with the value of the 50nm-CGO[LSC/CGO]_{N=2}NGO sample. This evidence suggests that thin LSC-thin films behave differently than thick LSC layers. The Arrhenius plots also show that the CGO layer situated directly below the electrodes does not perform as electron blocking layer and the electron transport occurs by passing the more resistant CGO film, performing better overall conductivity than the exposed LSC top-layer.

Figure 2. a) Arrhenius plot of heterostructures with N=2, overall thickness of 50 nm and with and without CGO top layer measured in air in the RT-600 °C temperature range. b) Comparison between the conductivity of 50nm-CGO [LSC/CGO]_{N=2}NGO (black line), LSC 50 nm thin film fabricated under the same experimental conditions (blue line) and CGO film (red line) in air.⁵²

Figure 3. Conductivity of (a) x-CGO[LSC/CGO]_{N=2}NGO and (b) x-CGO[LSC/CGO]_{N=5}NGO heterostructures with different thicknesses measured in air from RT to 600 °C.

The low activation energy values calculated for the samples are between 0.01 and 0.03 eV with a dominant semi-metallic/metallic behavior. Such low values are a nearly thermal independent electric transport from RT to 300 °C, which, consistently with the “itinerant” charges, matches the LSC properties, dominating over the expected CGO pure ionic conductivity. These values are similar to the activation energy of single LSC film (0.03 eV), confirming that the conductivity is dominated by LSC and showing that CGO does not block conduction at low temperatures.^{23, 24} A transition to metal-like properties also results at higher temperatures for both samples. Such behavior is particularly clear for the CGO-terminated sample that achieves a total conductivity of *ca.* 350 S cm⁻¹ with a peak-like transition at 300 °C.

As a possible explanation of such an effect is that both the interfaces and the CGO layers contribute to the conduction mechanism, supplying itinerant electrons to the charge transport. Presence of pinholes in CGO top layers was not detected by the TEM and SEM observations. The reproducibility of the results collected on the samples, *e.g.* with different number of interfaces and thicknesses, also indicated a high quality of the samples⁵³.

Figure 3 shows the Arrhenius plots in air for the heterostructures with *N* = 2 (**Figure 3a**) and 5 (**Figure 3b**) as a function of layer thickness (50, 100 and 300 nm). It can be noted that, since the effect of the conductivity across interfaces is more pronounced, the conductivity values increase as the thickness decreases. Particularly, the conductivity values at 600 °C of the sample with *N* = 2 vary from 290 to 80 S cm⁻¹ when the thickness is decreased from 50 to 300 nm, respectively. Thus, the conductivity is 3.6 times higher when the thickness is reduced from 300 to 50 nm. Moreover, this difference is even greater at temperatures below 200 °C. Similar behaviour was also observed for the sample with *N* = 5. This is possibly explained by the fact that the interface conductivity dominates when the layers are extremely thin. When the thickness of each individual layer is increased a strong contribution of the bulk of these layers appears and the effect of the interface conduction mechanism is not appreciable. Furthermore, the thickness of each individual electron-insulating CGO layer is increased, when the total thickness of the sample increases, which generates a

decrease in the total conductivity. This fact is also confirmed by activation energy values, which range from 0.032 to 0.340 eV for 50nm-CGO[LSC/CGO]_{N=5}NGO and 300nm-CGO[LSC/CGO]_{N=5}NGO heterostructures, respectively. It is a remarkable change of activation energy of $\Delta E_a = 0.308$ eV as a consequence of the increase of ionic activation energy. The increase in activation energy of ionic migration is thus activated by the 2D-nanometric confinement with possible space charge effects and polarization of the interfaces.⁹ On the other hand; it can also be observed that for the thinner samples (100 and 50 nm) the conductivity is directly related with *N* (**Figure 3a and 3b**). The conductivity ranges from 100 to 240 S cm⁻¹ at 600 °C for 100nm-CGO[LSC/CGO]_{N=2}NGO and 100nm-CGO[LSC/CGO]_{N=5}NGO, respectively (*i.e.* 2.4 times higher). Such an effect is explained as an increase in the number of interfaces, which affects the concentration and mobility of charge carriers and, consequently, the electrical properties. For the thicker samples, *i.e.* the 300nm-CGO[LSC/CGO]_{N=5}NGO and 300nm-CGO[LSC/CGO]_{N=2}NGO, the electrical behaviour is closer to the CGO bulk contribution, as compared to the pure CGO reference, and the number of CGO layers with higher thickness increases the resistance considerably.

To summarise the conductivity results, the conductivity of LSC/CGO heterostructures is controlled by the thickness and the number of interfaces. However, the individual film thickness appears to be the dominant factor in the samples, causing a higher conductivity variation and varying the nature of the conductivity in CGO layers. This occurs when they are reduced in the nanometric range of 10-20 nm. In this case samples show dominant electronic conductivity even at low temperature. Change of conductivity at high activation energy due to Ce³⁺/Ce⁴⁺ small polaron hopping were not registered and LSC contribution is dominant. On the other hand, clear evidence of a change of conductivity due to strain effects measured in the LSC and CGO layers was not detected at such high conductivity.

To have a better understanding of the conductivity mechanisms, electrochemical impedance spectroscopy was carried out at low temperatures, especially to estimate the different electric contributions at the Air/Electrodes/Electrolyte interfaces. **Figure 4** shows the Nyquist and Bode plots of the CGO[LSC/CGO]_{N=2}NGO (50 nm

Figure 4. (a, c) Nyquist and (b, d) the corresponding Bode plots of different heterostructures and temperatures.

and 100 nm) at 200 °C compared to [LSC/CGO]_{N=5}NGO (100 nm, no CGO-termination). The impedance data are normalized by the geometrical factors of the samples to represent the specific properties of the materials. The 100nm-[LSC/CGO]_{N=5}NGO sample was the only LSC-terminated sample showing steady electrical behaviour after degradation. The EIS results indicate a rather different electrical behaviour between the samples with and without the CGO-termination. Particularly, the LSC-terminated sample shows larger constraint in the bulk conductivity at high frequency with fast relaxation of the capacitive effects at low frequency. Nearly an opposite effect is observed for the CGO-terminated samples: at 200 °C the peak relaxation frequency for LSC-terminated is in the range of MHz, while for CGO-terminated it is between 10 and 100 KHz, depending on the thickness (**Figure 4b**). Faster mechanisms for LSC are generally expected while large impedance at the high frequency could be related to the degradation of the film after the measurement. Interestingly, the CGO-samples show rather different impedance contributions than expected at such low temperatures. **Figure 4c** and **4d** show that the mechanisms are thermally activated and for higher temperatures, up to 500 °C, the impedance is separated in two contributions. The typical relaxation times and conductivity, however, are different from those generally reported for CGO thin films⁵⁴, indicating the presence of LSC-related low temperature effects in the heterostructure. Despite the low temperature, no capacitive-like effects due to charge blocking factors at the electrode/CGO interface were registered.⁵³ This confirms the electronic nature of the conductivity at the CGO top layer.

Chemical stability

To better understand the electrical properties of the heterostructures, pristine and electrically measured samples were compared in a post-mortem fashion, *i.e.* before and after the electrical measurements. **Figure 5** shows views of 50nm-[LSC/CGO]_{N=2}NGO and 50nm-CGO[LSC/CGO]_{N=2}NGO samples, with and without CGO top layer after thermal cycling and electrical measurements. It is clearly observed that the sample without CGO termination exhibits evidences of degradation

Figure 5 FEI-SEM micrographs of the top view of (a) 50nm-[LSC/CGO]_{N=2}NGO and (b) 300nm-CGO[LSC/CGO]_{N=2} heterostructures. HR-TEM of the cross section of (c) 50nm-[LSC/CGO]_{N=2}NGO and (d) 300nm-CGO[LSC/CGO]_{N=2} heterostructures after thermal cycles (aged sample/post mortem).

and phase separation at the surface (**Figure 5a**), where the LSC top layer is discontinuous and multiphase. Degradation in LSC is generally observed at the LSC surface as effect of a spontaneous SrO-segregation and/or its successive carbonation, where CO₂ gas is present in the atmosphere.³⁴ However, due likely to the reduced size of the material, the degradation in LSC was present in the whole top layer, when the material was directly exposed to the atmosphere under the electrical measurements, while the inner LSC layers of the heterostructures remain unchanged (**Figure 5b**). EDS analysis confirm a strong degradation of LSC top layer with presence of Sr- and Co-enriched phases in the near-interface and the top of the superficial layer, respectively. Conversely, both the CGO- and the LSC-layers confined in the heterostructures remain chemically stable and no openings/pinholes on the CGO layer right under the LSC top-layer were detected. The chemical composition of the LSC layers was further characterized by XPS in a depth-profile mode especially to track the evolution of the Sr at the exposed surface and the inner layers (see Figure S2). The XPS plots confirm that LSC termination has Sr-enriched species as SrCO₃, SrO and Sr(OH)₂ while inner LSC layer at the heterostructure are chemically unchanged.

A finer analysis of the LSC-layer at the core a cross section of CGO-terminated heterostructure was carried out by high-resolution STEM, especially to evaluate the distribution of species by EDS in the different individual layers (see Figure S3). The STEM analysis on post-mortem image and elemental mapping of the 50nm-CGO[LSC/CGO]_{N=2}NGO heterostructure reveal an alternating layered heterostructure on a NGO (110) single-crystal substrate. Large scale observations of the sample after test showed neither pinholes nor inclusions, *e.g.* macro-particulate from the PLD and well-defined and continuous layers of the two materials are clearly visible. The interfaces between adjacent layers remain clean and free of

Figure 6. (a) HR-TEM image of the [LSC/CGO]NGO layers and (b) a sketch of the epitaxial relation between the NGO, CGO and LSC structures.

delamination or wrinkles. The total film thickness of the 50nm-CGO[LSC/CGO]_{N=2}NGO heterostructure is consistent with the designed value expected by the PLD calibration for CGO and LSC. The average thickness of each individual layer of CGO and LSC is *ca.* 11 and 6 nm, respectively. These results confirm the chemical stabilization effects of the CGO termination heterostructures.

As for the FEI-SEM observations, the STEM EDS elemental mapping also reveals a clear distinction of the different elements (see Figure S3). Both CGO and LSC single layer phases at the heterostructures are clearly identified. Within the limitations of the chemical analysis, the elements are alternated at the layers as expected.

For the structural features of the heterostructures, **Figure 6** shows a magnification of the HR-TEM micrograph of a post-mortem 50nm-CGO[LSC/CGO]_{N=2}CGO sample, including an overlaid representation of the lattice structures on the individual layers and their crystallographic orientations. The HR-STEM micrographs in **Figure 6a** confirmed that CGO and LSC layers grow in a highly coherent structure on top of each other. The figures also show that the heterostructure has a precise periodic lattice structure with controlled interfaces at the atomic level, confirming the X-ray diffraction results of the **Figure 1**. Detailed magnifications in **Figures 6b-6d** show that the CGO lattice rotation effectively matches the lattice mismatch between the substrate and the LSC layers with the CGO ones. The main reflections for both NGO and LSC can be indexed according to the cubic unit cell with a ~ 4.0 Å. The theoretical lattice parameters of LSC (3.84 Å) is lower than this value, implying that LSC layers are strained to adapt the lattice parameters to the CGO ones, creating a tensile strain in the LSC layers. The distortion of the cell is also measured in the case of CGO layers. As discussed for the XRD results, the change in the lattice is likely due to the CGO layers trying to adapt to the lower lattice parameters of the adjacent layers. The lattice parameters of CGO perfectly match with those obtained by the analysis of the reciprocal space map ($a_{x,y} = 4.90$ and $a_z = 5.56$ Å). The schematic of the epitaxial growth of

the atomic layer and between the NGO, CGO and LSC structures both indicating a 45°-rotation of the CGO lattice with respect to the NGO and LSC lattice and emphasize the lattice strain in the in plane directions due to the lattice mismatch. It is worth emphasizing that the HR-STEM on the sample after the electrical measurements shows an excellent stability of the structural feature, deposited the long thermal treatments and heating-cooling cycles.

To check the stability of the samples in the long range, θ -2 θ scan were measured before and after the electrical measurements. **Figure 7** shows that the samples terminated with CGO were structurally stable without observing any remarkable difference in the heterostructure arrangement.

Conclusions

Highly coherent LSC/CGO heterostructures on NGO (110) substrate have been fabricated due to the reciprocal structural readjustment of the CGO and LSC that undergo to out-of-plane compressive and tensile lattice strain, respectively. The heterostructures have presented novel properties: an unexpected dominant electronic conductivity, where CGO component and interfaces are dominated by electronic conduction with a semi-conductive behaviour at low temperatures and quasi-metallic for $T > 400$ °C. Such metallic-like properties are controlled by the thickness and the number of bilayers. Remarkably, while LSC thin films of below 10 nm undergo severe degradation, LSC is stable in the CGO-terminated heterostructure. Moreover, absence of blocking effects at the CGO/electrodes interface at low temperatures below 500 °C suggest that CGO can be used to shield LSC without compromising the properties of the material.

Conflicts of interest

There are no conflicts to declare.

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Figure 7. 2θ X-ray diffraction pattern of 100nm-CGO[LSC/CGO]_{N=2}NGO sample before and after the electrical characterization.

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