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Investigation of Oxygen Vacancies in sputtered GDC thin films probed via *operando* XAS

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In previous works, we reported that Solid Oxide Fuel Cells (SOFCs), having a room-temperature sputtered and then annealed GDC thin film as the cathode/electrolyte barrier layer, had showed a huge increase of the output current (up to +78%) and a decrease of the ohmic resistance (up to -42%) as compared to fully screen-printed industrial SOFCs. We correlated the performance improvement to grain size in the GDC layer as a function of annealing temperature. However, no information on the density and activity of oxygen vacancies in the thin film to correlate with functionality could be extrapolated in these studies.

Element and valence sensitive probes such as X-Ray Photoelectron Spectroscopy (XPS) and X-Ray Absorption Spectroscopy (XAS) enable atomic level characterization of nanostructured granular GDC layers deposited on polycrystalline anode/electrolyte bilayer substrates and the interplay between morphology and stoichiometry in determining the Ce3+/Ce4+ ratio, which in turns regulates their ionic and electronic conductivity.

Here we show the results obtained on three room-temperature RF-sputtered GDC thin films, annealed with the same annealing ramp but at different plateaux temperatures, making use of XPS measurements to study the unreacted surface and the *operando* XAS to monitor the changes in Ce3+/Ce4+ ratio in different reactive atmospheres (i.e. neutral, oxidizing and reducing). The latter were carried out using the ambient pressure cell available at APE-HE beamline (Elettra synchrotron in Trieste, Italy). Our measurements allowed to determine the role of the annealing parameters in the number of available oxygen vacancies available in the oxygen reduction reaction (ORR), highlighting the different modifications induced in the investigated samples by the annealing process.

* 1. Introduction

Partially substituted trivalent rare earth cerium oxides attracted interest in the past years due to their versatility and catalytic properties, which make them well qualified for a wide range of applications[1–3].

In particular, it is now established that the oxygen evolution reaction [4,5] used to generate electricity in Solid Oxide Fuel Cells (SOFCs) depends on the ionic transport through the electrolyte and the so-called barrier layer which is usually a gadolinium doped ceria (GDC) layer. Furthermore, it is well known that, in GDC barrier layer of SOFC, the ion conductivity is related to the hopping of oxygen ions through the oxygen vacancy sites in the lattice and that the mechanism of oxygen vacancy formation consists in the Ce valence change (from Ce4+ to Ce3+) induced by Gd doping [6].

Thus, once the percentage of Gd doping is fixed, the ionic conductivity of the GDC layer can vary depending on the specific structure, granularity, defect incorporation and density of oxygen vacancies induced in the film lattice.

In previous work [7], in the case of room-temperature sputtered GDC barrier layers, we demonstrated that, by reducing the mean GDC grain size by decreasing the post-growth annealing temperature, the complete SOFC shows both a very large increase in the output current and a simultaneous decrease in the ohmic resistance of the SOFC. However, in these studies no information was extrapolated on the density and activity of oxygen vacancies in the thin film. Since the aforementioned GDC layer fabrication process (Coppola et al. 2020; Coppola et al. 2018b) has proved feasible also in the case of industrial scale SOFC (Coppola et al. 2021), it is interesting and noteworthy to achieve a deeper understanding of microscopic differences among sputtered GDC thin film barrier layer as a function of post-growth annealing treatment in view of further optimization of industrial scale SOFCs.

Here we show the results obtained on three RF-sputtered GDC thin films at room-temperature , annealed with the same annealing ramp but at different plateau temperatures, using two different spectroscopic techniques, namely X-Ray Photoemission Spectroscopy (XPS) measurements to study the unreacted surface, and *operando* X-Ray Absorption Spectroscopy (XAS) to investigate the changes in Ce3+/Ce4+ ratio in neutral and reducing atmosphere. XAS measurements were carried out using the ambient pressure cell available at APE-HE beamline (Elettra synchrotron, Trieste, Italy).

* 1. Materials and Methods
		1. Thin Film Deposition

Three Gd0.1Ce0.9O1.95-δ (GDC) thin films of 300 nm thickness were sputtered at room-temperature using an RF-sputtering equipped with a 15 cm diameter 99.999% purity target (Testbourne). The deposition parameters are reported in (Coppola et al. 2018a; Coppola et al. 2018b). The substrate used consists in NiO/YSZ polycrystalline bilayers (SolydEra S.p.A, Mezzolombardo (Italy)) cut into slivers of 5x5 mm2.

Two of the as-grown samples were thermally treated using the annealing ramps described in [7].

All samples are RF-sputtered at room-temperature and have the same composition, but the only difference among them relies in the post-growth annealing ramp plateau temperature:

* Sample GDC800 is annealed with a 800°C plateau temperature
* Sample GDC1000 is annealed with a 1000°C plateau temperature,
* Sample GDC-As- grown
	+ 1. X-ray Diffraction (XRD)

The crystal structure of the deposited thin films was investigated both before and after annealing using a D2-Phaser diffractometer equipped with a Cu-Kα radiation source characterized by a wavelength λ= 1.541 Å. All the spectra were acquired setting 2θ=0.01° as angular resolution and 0.4s as acquisition time.

* + 1. X-Ray Photoemission Spectroscopy (XPS)

The sample surface was analyzed using the XPS core level spectra acquired using a TX400 X-ray photoemission spectroscope equipped with an Al source cathode ( with Kα = 1486,7 eV) available at the Elettra Synchrotron as an offline facility of the APE-HE beamline. The measurements were carried out at a pressure of 10-9 bar and a pass energy of 50 eV. The analyzer mean radius is 200mm. The X-rays hit the sample at 45° with respect to the source. The survey scans were acquired with a channel width of 2.3 mm while a channel width of 1.1 mm was selected for the element-specific scans. The energy calibration of all spectra was performed using the Au 4f reference spectra acquired after each sampling run.

* + 1. *Operando* X-Ray Absorption Spectroscopy (XAS)

XAS spectra were acquired in *operando* using the ambient pressure cell present at the APE-HE beamline of the Elettra Synchrotron. A detailed description of the cell and the silicon nitride membrane used during the experiment can be found in [11]. a two-contact measurement (one contact on the membrane, the other one on the sample) allowed to obtain the XAS total electron yield (TEY) signal. The spectra were acquired in neutral (1 bar He gas) and reducing (1 bar H2 gas) atmospheres at temperatures ranging from room temperature up to about 300 °C.

* 1. Results

The GDC800, GDC1000 and GDC-As-grown samples were preliminary studied using XRD measurements both before and after the annealing treatment. The obtained results are shown in Figure 1.



Figure 1 XRD spectra of the analysed samples: sample GDC-As-grown (black line), sample GDC800 (pink line) and sample GDC1000 (blue line). Dashed burgundy lines are in correspondence of the angular positions of the bulk GDC reflections in terms of Miller indices found in literature[12].

By comparing the XRD spectra it is evident that the as-grown sample shows GDC peaks at lower angular positions than the values reported in literature and thus the evaluated c-axis parameter is higher than the literature values, being ≈ 5.45 Å. However, both annealed samples show all the visible peaks at bulk angular positions corresponding to the expected calculated value of the c-axis ≈ 5.41 Å. Therefore, no structural differences induced by the different plateau temperatures of the annealing ramp are evident from the XRD spectra. Moreover, it is not possible to extrapolate a difference in the oxygen content induced in the GDC lattice by the annealing ramp in GDC800 and GDC1000 samples.

On the contrary, the comparison among the XPS spectra (Figure 2) of the three samples highlights the actual differences induced by the post-growth treatment. In particular, by looking at Figures 2b and 2c it can be noticed that the three samples are characterized by different relative intensities of the features associated to different valence states (in case of Ce) and different types of surface oxygen (namely lattice oxygen, vacancies and OH- species) [1].



Figure 2 XPS spectra of samples GDC800 (pink line), GDC1000 (blue line), GDC-As-grown (black line). In a) the survey scan performed on the whole energy range is displayed while in b) and c) details of the Ce 3d3/2 and 3d5/2 and O 1s core levels are shown respectively.

The above results allow us to conclude that, even if no structural difference is highlighted by XRD, on the contrary, the GDC800 and GDC1000 samples present different amounts of Ce3+ and Ce4+ (and therefore a different amount of oxygen vacancies in the lattice) and this result is accordingly accompanied by differences in the O 1s core level spectra.

The second part of the experiment consisted in *operando* XAS spectra acquisition performed on the same samples previously mentioned. The results obtained at Ce M4,5 absorption edge for the GDC800 and GDC1000 samples are summarized in Figure 3.



Figure 3 a) In operando XAS evolution of the Ce M5 absorption edge of the GDC800 sample in He/H2 atmosphere over exposure time and at different temperatures. Red arrows indicate the peak related to the Ce3+ formation, while the blue arrow indicates the main peak associated to the oxidized Ce (Ce4+); b) In operando XAS evolution of the Ce M5 edge of the GDC1000 sample in He/H2 atmosphere over exposure time.

The XAS spectra shown in Figures 3a and 3b allow to verify the different reactivity of samples annealed with different plateau temperatures and characterized by different initial Ce3+/Ce4+ ratios and therefore a different amount of oxygen vacancies. Indeed, while GDC800 sample is characterized by an evident evolution of the features associated to Ce3+ and Ce4+ as a function of the atmosphere and temperature at which it is exposed during the XAS measurement, on the contrary, the sample annealed at higher plateau temperature is characterized by a very poor evolution of the Ce M5 XAS spectra. This last observation indicates a better oxygen ionic conductivity and surface exchange rate of GDC800 sample compared to GDC1000, providing a first hint on the nature of the behavior of samples studied in [7].

* 1. Conclusions

Sputtered GDC thin films deposited on industrial substrates and annealed at different temperatures were structurally and spectroscopically characterized by XRD, XPS and *operando* XAS. XRD showed that the analyzed samples are characterized by the same lattice parameter, thus not allowing to distinguish any differences in the oxygen content induced by the annealing temperature. Conversely, XPS and XAS measurements highlight the presence of dissimilarities in the thermally treated thin films with different annealing ramps, mainly in terms of oxygen content. In fact, XPS performed on the surface of unreacted samples allows to attribute a higher amount of Ce3+, and thus a higher number of oxygen vacancies, to the GDC800 sample. On the contrary, the GDC1000 sample is characterized by a greater quantity of Ce4+.

The variation of the Ce3+/Ce4+ ratio that characterizes the GDC thin films studied here is reflected in the evolution of the absorption spectra at the Ce M5 edge probed via the *operando* XAS. The sample annealed at lower temperature, i.e. GDC800, is characterized by a higher ionic mobility, being characterized by the highest changes in the shape of the Ce M5 edge in both oxidizing and reducing atmospheres. These results are in agreement with the results presented in (Coppola et al. 2018b; Coppola et al. 2020) and may provide hints on the annealing-induced microscopic changes of GDC thin films that positively contribute to the final performance of SOFCs.

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