

Pulsed-DC reactive magnetron sputtering process for the deposition of solid oxide electrochemical cell layers

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Abstract: Deposition of YSZ and CGO thin films by reactive magnetron sputtering was studied. Evolution of the cathode voltage with the oxygen flow rate evidenced the transition from metal to compound regime and exhibited the well-known hysteresis behaviour. By varying various parameters like substrate temperature, oxygen flow rate, substrate position etc. and by eventually resorting to an annealing treatment, it has been possible to synthesize dense, fully oxidized, crystalline thick films required for the application.

Keywords: reactive magnetron sputtering, gadolinium doped cerium oxide, solid oxide electrochemical cells.

1. Introduction

In high temperature electrolysis (HTE) cells, requiring high working temperatures, it is known that deleterious reactions are able to occur between the constituting layers. As an example, when YSZ (yttria-stabilized zirconia) is used as an electrolyte and LSCF (doped-lanthanum cobaltite) as an electrode, diffusion and segregation of Sr and La have been evidenced [1]. These elements react to form highly resistive phases ($\text{La}_2\text{Zr}_2\text{O}_7$ and/or SrZrO_3) which induces an increase of the interfacial resistance and leads to the degradation of the cell performance with time. It has been demonstrated that the adjunction of a thin barrier layer (typically 200-500 nm) between the electrolyte and the electrode could prevent this phenomenon. Gadolinia doped ceria (CGO) is an interesting candidate for this purpose since it is a good ionic conductor and it is chemically inert towards YSZ and LSCF at the temperatures used both for the cell fabrication and operation [2].

The objective of this work is to add a sputtered thin CGO layer to the high performance electrochemical cells developed by the CEA and elaborated by tape casting and screen printing. This requires optimizing first the CGO film characteristics [3] but also the interface between the screen printed YSZ and the magnetron sputtered layer. To ensure a good adhesion between these layers elaborated by very different techniques, the deposition of an intermediate YSZ layer by magnetron sputtering could be required. For instance, it has been shown that a thin sputtered YSZ film (10 nm) could act as a seed layer for the further growth of CGO. A good transition could also be achieved by synthesizing thick YSZ/CGO bilayers or YSZ-to-CGO gradient composition layers by magnetron sputtering [4]. All these solutions require the ability to perform deposition of both compounds in the same experimental device and to precisely control the corresponding processing parameters.

In that aim, we studied the reactive sputtering of YZr and CeGd targets in argon oxygen mixtures by varying different experimental parameters: the power supply (pulsed DC or high power impulse magnetron sputtering), the oxygen flow rate, the target-to-substrate distance, the substrate bias etc. The present contribution focuses on the optimization of the sputtering/deposition parameters in order to synthesize fully oxidized crystalline oxides, keeping high deposition rates, typically above 1 $\mu\text{m/h}$.

2. Experimental details

Deposits were synthesized in a 35-L deposition chamber (designed by APRIM Vide company, France). Two 4-inch diameter metallic targets (zirconium - yttrium (Zr/Y 82/18 wt%) and cerium - gadolinium (Ce/Gd 80/20 at.%) were used. Each target was powered by a DC pulsed Pinnacle + (Advanced Energy®, USA) or a HiPIMS (Starfire Industries Impulse 2-2) generator allowing independent control of the discharge current, power or voltage. The target surface was 30° tilted with respect to the substrate mechanically maintained on a heatable rotating substrate holder. The flow rates of argon and oxygen were controlled by two Bronkhorst flowmeters. The control of the pressure during the deposition step was allowed by a gate valve placed between the deposition chamber and the turbo-molecular pump.

Deposits were performed onto silicon wafers (100 N type, Institute of Materials Electronic Technology, Poland) and on half cells (NiO-YSZ/ YSZ elaborated by screen printing). The morphology of the deposits was observed by scanning electron microscopy (SEM) (Carl Zeiss SMT, Supra-40, FEG-SEM). Cross section observations were performed on cleaved silicon wafers to evidence the microstructure. Energy dispersive spectrometry (EDS, Bruker XFlash Detector 4010) was used to establish the composition depth profile normal to the substrate surface.

Rutherford backscattering spectroscopy (RBS) was employed to determine the chemical composition and evaluate the oxygen amount over the thickness of the deposits. These experiments were performed at the CEMHTI laboratory with 2 MeV alpha particles extracted from a Pelletron accelerator and at 165° scattering angle. The spectra were treated using the SIMNRA software [5].

The crystalline structure of the films were analysed by X-ray diffraction (XRD) using a Bruker D8 Discover (diffractometer) equipped with a Cu source and in θ -2 θ configuration.

To complete the oxidation process and improve the crystallization level, the samples were heat treated in air after deposition. This was carried out either in a conventional furnace (Nabertherm LT5/13/ B180, Germany) at 500 °C with a heating rate of 1 °C·min⁻¹, or in a rapid thermal annealing (RTA) system at 1°C/sec. The cooling rate of the samples in both devices was not controlled.

3. Results and discussion

Reactive sputtering of YZr target: a multistep process

It is well known in reactive magnetron sputtering that the deposition process turns from metal to compound regime as the reactive gas flow rate increases (hysteresis behaviour when the oxygen flow rate decreases is also known) [6]. This transition is clearly visible on figure 1 when following the evolution of the YZr target voltage (for a fixed discharge current) as function of the oxygen flow rate.

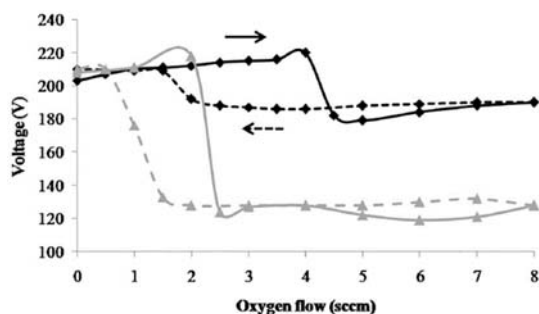


Fig 1. Evolution of the YZr target voltage for increasing (continuous lines) and decreasing (dashed lines) oxygen flow rate for 1.25 A discharge current, 1 Pa total pressure and 20 sccm argon pressure. Black lines stand for room temperature deposition and grey ones for 550°C.

This behaviour has been widely studied and is due to the poisoning of the target, and then to a radical change in sputtering/deposition parameters, when the amount of reactive gas in the reactor is sufficiently high. In metal regime, the deposition rate is high, but the films, even if containing high level of oxygen close to the transition, remains metallic. In the compound regime, films are dense, amorphous and fully oxidized, but the deposition rates are

dramatically low (one order of magnitude less than in the metal regime) [6].

A way to keep a high deposition rate and ensure complete oxidation and crystallization of the films is to work in the metal regime, at high flow rates (staying before the transition) and to perform a post-annealing treatment. The main drawback of this procedure is that delamination could occur, especially in the case of thick layers (above 500 nm). To avoid this, we tried to perform YSZ deposition by heating the substrate at 550°C. The corresponding cathode voltage evolution is plotted in figure 1, clearly showing that the transition between metal and compound regimes occurs at lower oxygen flow rates. This has been related to an enhanced reactivity versus oxygen of the target that is indirectly heated by the substrate holder at 550°C [7]. Thus, performing deposition in the metal regime at 550°C requires to choose an oxygen flow rate lower than at room temperature, typically 1 sccm instead of 3 sccm.

XRD analysis was performed on 1.5 µm thick YSZ films synthesized in both conditions, i.e. 3 sccm oxygen flow rate and room temperature (cdt1) and 1 sccm oxygen flow rate at 550 °C (cdt2). Corresponding patterns are presented in figure 2. RBS measurements (note shown here) exhibited that the incorporated oxygen amount is similar on both films, close to 65 %. On figure 2 no peaks are observed for cdt1 showing that the films are amorphous (or nanocrystallized). For the application well crystallized YSZ is required to ensure good ionic conductivity of the electrolyte. When the substrate is heated (cdt2) peaks appear on the XRD pattern belonging to cubic (or tetragonal) YSZ phase and to pure Zr one. Thus, even if the crystallisation of the film is enhanced, part of the deposited Zr is not oxidized, which is not desired.

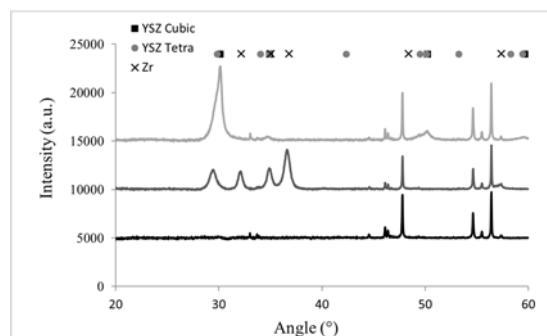


Fig. 2. XRD patterns of as deposited YSZ films elaborated in various deposition conditions. Black line: 3 sccm oxygen flow rate, room temperature, dark grey line: 1 sccm oxygen flow rate, 550°C and light grey line: 1 sccm, 550°C multistep process.

To enhance the incorporation of oxygen inside the deposit performed in the metal regime and promote the crystallisation level, we developed a multistep process composed of successive deposition steps followed by in situ-annealing treatments in pure oxygen atmosphere. Evolution of the deposition parameters (total pressure,

target current and substrate temperature) during such a process (constituted of 3 steps) is shown on figure 3. During the deposition steps, the target is powered and the oxygen pressure is set at 1 Pa. The annealing steps are carried out in pure oxygen at 10 Pa (15 sccm), the target power supply being off. It is seen from the zoom (b) presented in figure 3, that the oxygen consumption by the freshly deposited metallic film can be detected on the time evolution of the pressure inside the reactor.

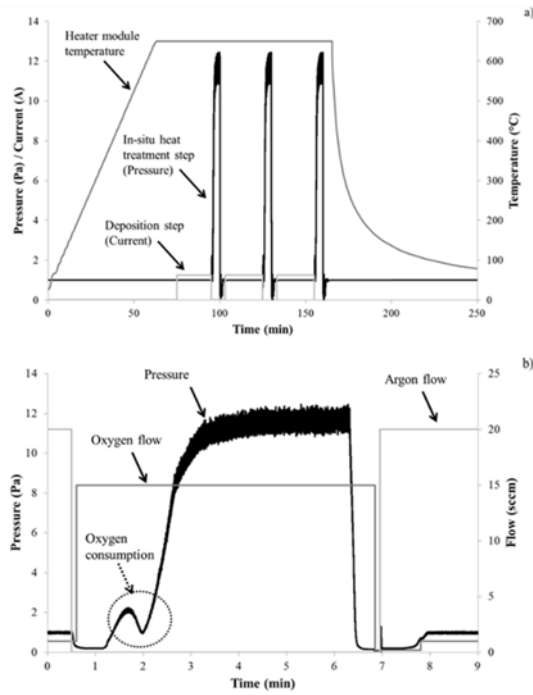


Fig. 3. a) Evolution of the substrate temperature, the total pressure and the target current during a 3 steps process. b) zoom on the evolution of the total pressure and gas flow rates during one annealing step.

Studying the time evolution of the oxygen pressure during the annealing steps of films of various thicknesses has been found a convenient way to optimize the oxidation process of the metallic film. This is illustrated in figure 4.

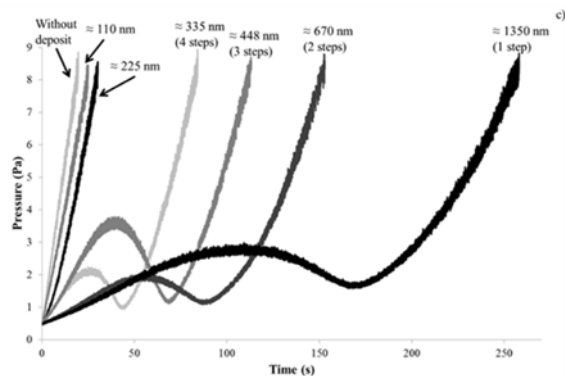


Fig. 4. Time evolution of the pressure inside the vacuum chamber during the annealing step (argon gas is turned off and oxygen flow rate is set at 15 sccm) depending on the thickness of the freshly deposited ZrY film.

Indeed, the oxygen consumption lasts longer for thicker metallic films. The oxidation step could be considered complete when the pressure starts to increase again. The abrupt rise observed for thicknesses below 300 nm, indicates that the oxidation of the whole film is almost instantaneous. The peak observed for higher thicknesses reveals the competition between oxygen consumption and injection inside the vessel. For 1.3 μm thickness, about 3 minutes are required to oxidize the whole film.

The diffraction pattern of an YSZ film synthesized using the multistep process is given in figure 2. It clearly exhibits the required well crystallized cubic phase. This is a very promising result even if asymmetry of the peaks indicates the presence of the tetragonal phase too.

Reactive sputtering process of CeGd target: preferential orientation

On figure 5 is plotted the voltage evolution of the CeGd target with respect to the oxygen flow rate for 1 A and 1 Pa.

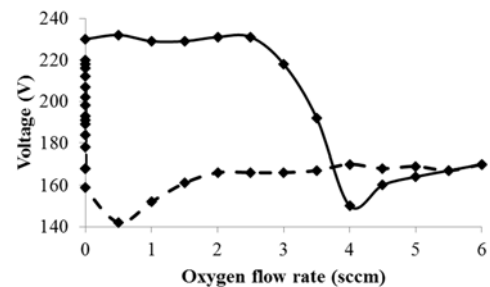


Fig 5. Evolution of the CeGd target voltage for increasing (continuous lines) and decreasing (dashed lines) oxygen flow rate for 1 A discharge current, 1 Pa total pressure and 20 sccm argon pressure.

For increasing oxygen flow rates, the transition from metal to compound regime is clearly visible on the graph. However, the transition back occurs only when the oxygen flow rate is turned off and after a quite long sputtering time (around 45 min) in pure argon, since the time between each measure point is 3 minutes. This behaviour reveals the very strong affinity of Ce and Gd with oxygen and makes the control of the process very critical. One has to avoid at the best the CeGd target to get poisoned, reason why we decided to work without heating the substrate.

In order to protect the CeGd target from oxidation, the location of the oxygen gas inlet was modified from the top (between the target and the substrate) to the bottom of the vacuum chamber and various positions of the substrate was

also tested. From the curves presented in figure 6 it appears that, surprisingly, the target-to-substrate distance has an influence on the hysteresis when the oxygen inlet is located between the target and the substrate. This was not expected since the position of the transition is related to the target poisoning and should not depend on this parameter. We think that this is due to geometrical effect specific to our experimental setup: when the distance is low, the oxygen flux stays more confined in the target surroundings, leading to an accelerated oxidation process of its surface.

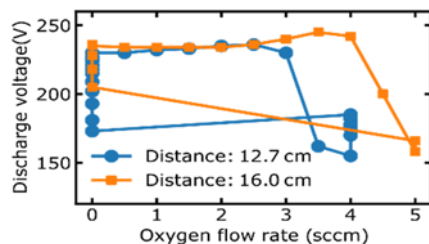


Fig. 6. CeGd target voltage evolution with the oxygen flow rate: hysteresis curves for two target-to-substrate distances at 1 Pa and 1 A and for the oxygen inlet located between the target and the substrate.

From the above result on the sputtering regime, two working conditions were chosen to stay below the transition: short distance – 2 sccm (cdt1) or long distance – 3 sccm (cdt2). They lead to different deposition conditions: low (cdt1) or high (cdt2) oxygen to metal atom flux ratio, respectively. The corresponding as deposited films exhibited different features, showing that the growth mode was different. In cdt1 a sub-stoichiometry in oxygen is obtained (57 at%) and the crystallinity is poor, the deposition rate is high (48 nm/min); in cdt2 the stoichiometry is close to that expected for a fully oxidized compound (67 at%), a [200] preferential orientation is evidenced and the deposition rate remains high (40 nm/min).

The interesting result is that after a short annealing at 500°C that was necessary in this case because of the low deposition temperature, fully oxidized dense films exhibiting two different preferential orientations were synthesized. The corresponding diffraction patterns are shown in figure 7.

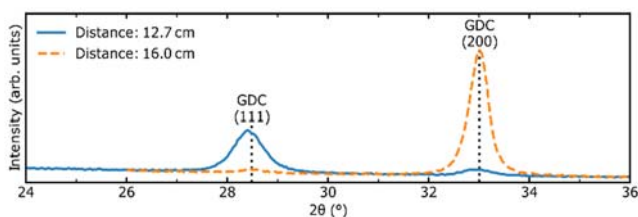


Fig. 7. XRD patterns of CGO thin films deposited at 1 A, 1 Pa and at two target-to-substrate distances, after annealing at 500°C.

Thus, thanks to the different deposition conditions found out in the present work and leading to the growth of different $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_x$ films, it was possible to obtain after the annealing step, two CGO films with the main difference lying on their preferential oxidation. It will be very interesting to study the properties of these films as diffusion barrier inside the electrochemical cell.

4. Conclusion

By coupling the monitoring of the sputtering process (target voltage, pressure evolutions etc.) with characterization of the deposits, we managed to find out appropriate conditions leading to thin films with desired properties. Depending on the element affinity with oxygen it was necessary to adapt the experimental parameters, but finally YSZ and CGO thick, dense and well crystallized films could be obtained with deposition rate above 1 $\mu\text{m/h}$.

In the case of YSZ an original multistep process has been developed which allows to avoid the post-oxidation step usually required. This process promotes the progressive incorporation of O inside the metal lattice at moderate temperature, preventing from delamination mechanism often observed when oxidation is performed abruptly at high temperature starting from metal deposits.

Reactive sputtering of CeGd has to be handled with care, since these elements are very sensitive to oxygen. No heating of the substrate was used, to protect the target surface from poisoning, thus a post-annealing step was required. It has been shown that performing the deposition of the initial sub-stoichiometric $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_x$ at various distances allows to achieve different oxidized states that will be interesting to test.

Acknowledgements

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