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Characteristics and properties of a magnetron sputtered gadolinia-doped ceria barrier layer for solid oxide electrochemical cells

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ABSTRACT

Gadolinia-doped ceria (GDC) films are synthesized by direct current magnetron sputtering under reactive conditions for hydrogen production by high temperature electrolysis (HTE). First, the sputtering process is investigated by varying the reactive gas flow rate. Working conditions in elemental sputtering mode (ESM) are adjusted to ensure a high incorporation of oxygen while keeping a high deposition rate. Heat treatments in air are found necessary to stabilize the sub-stoichiometric deposited oxide. The main characteristics of the films (crystallinity, chemical composition, porosity, etc.) are studied by Rutherford backscattering spectroscopy (RBS), optical transmission spectroscopy, Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and scratch test and are compared to that of a conventional 2 µm thick GDC layer deposited by screen printing. The sputtered layer appears dense and adherent but kind of blisters are observed when deposited on half-cells. Performances of a thin GDC barrier layer (below 500 nm) sputter deposited on half cells are evaluated. Encouraging results are obtained since performances (i.e. about $-1.70\ A{\cdot}cm^{-2}$ at 1.3 V and 800 °C in HTE mode) are slightly higher to that typically achieved with a classical manufactured cell (i.e. about $-1.65\ A{\cdot}cm^{-2}$ at 1.3 V and 800 °C). A degradation rate of about 9% for 1000 h operation (at 800 °C with a current density of $-0.5\ A{\cdot}cm^{-2}$, GDC layer thickness of 425 nm) is achieved.

1. Introduction

In solid oxide cells (SOC) systems, deleterious reactions often occur between materials used as cell core components. As example, when classical materials are chosen, well-known interfacial phenomena occur between yttria-stabilized zirconia (YSZ, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$) electrolyte and doped-lanthanum cobaltites (LSCF, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$) oxygen electrode leading to diffusion and segregation of Sr and La atoms. Those elements react and induce the formation of highly resistive phases ($La_2Zr_2O_7$ and/or $SrZrO_3$) [1]. The formation of these compounds generates an increase of interfacial resistance with time according to a parabolic rate law, even when the system operates at intermediate temperature (600–700 °C) [2]. Strontium diffusion and $SrZrO_3$ phase formation have been observed using X-ray diffraction during annealing [3]. Reactions at the LSCF/YSZ interface also result in the destabilization of the perovskite-type oxide structure and thus to the deterioration of the ionic conductivity. Thus the ageing behavior of the cells is strongly related to the formation of these interfacial compounds.

Several studies focus on new perovskite-type oxides as electrode material to enhance the performances [1,4–5]. As example, Qiu et al. have studied the reactivity behaviors between other types of LSCF and YSZ and showed that for some compositions (i.e. $Ln_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, Ln = Pr, Nd (y = 0.8)), the by-products of $Ln_2Zr_2O_7$ and $SrZrO_3$ are both suppressed when the cell is sintered at 1000 °C for 100 h [5].

Another well-known and more studied solution to limit the kinetics of the interfacial reaction consists in depositing a barrier interlayer between YSZ and LSCF [6,7]. It has been reported in literature that GDC ($Ce_{1-x}Gd_xO_{2-\delta}$) is a good candidate to reach this goal. This GDC barrier layer can be deposited by many technics as screen printing, spray pyrolysis or magnetron sputtering [8–13]. Jordan et al. have compared SOC with GDC barrier layer deposited either by screen printing or magnetron sputtering, and found that the GDC layer microstructure influences the electrochemical performances of cells with a LSCF oxygen electrode [14]. More recently, Constantin et al. have studied the influence of this buffer layer thickness for a LSCF/GDC/YSZ half-cell. Ageing behavior of the half-cell has been found to be strongly dependent on the GDC thickness, the lowest degradations being recorded for the thinnest layer. A 0.11 µm thick GDC layer allows a strong reduction of the polarization resistance thanks to the blocking effect on strontium

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diffusion, which limits the interface degradation [11].

Many studies investigate the influence of the barrier layer features [15–16]. Uhlenbruck et al. have shown that a thin and dense GDC layer (about 0.4 μm) permits the decrease of the chemical reactivity between LSCF and YSZ and leads to an improvement of electrical properties of the cell in comparison to a thick and porous layer (about 3 μm) [12]. Besides a low porosity, Mai et al. have shown that improved performances are also conditioned by the layer buffering properties, inhibiting $SrZrO_3$ formation [15]. Moreover, when the deposition or post-treatments of the barrier layer takes place at low temperature the detrimental reaction between GDC and YSZ is minimized. It is known that the temperature (higher than 1300 °C) used to sinter a GDC screen printed layer can create between GDC and YSZ an interaction zone with low ionic conductivity [17]. Similar observation is done after heat treatments performed between 1100 and 1500 °C for a GDC layer manufactured by electrostatic spray pyrolysis [18].

In this work, the main objective is to replace the classical screen printed GDC layer by thinner and denser layer manufactured by magnetron sputtering. To reach this goal, the conditions allowing the formation of a thin (below 1 μm) and dense GDC barrier layer by sputtering are investigated. The effect of high temperature annealing (1000 °C) on GDC thin film deposited onto half cells (support of NiO-YSZ cermet coated by a NiO-YSZ functional layer and YSZ electrolyte) is also considered to evaluate the layer behavior and adhesion in conditions that will be used to complete the cell. The thin GDC interlayers are characterized (chemical composition, crystallinity, porosity) and their performances as barrier layers are evaluated and compared to that of screen printed layers.

2. Experimental details

2.1. Magnetron sputtering device

GDC thin films are synthesized in a 35-L deposition chamber (designed by APRIM Vide company, France) equipped with three circular 4-inch balanced magnetrons. A 101.6 mm diameter cerium–gadolinium metallic target (80/20 at.%) is powered by a DC pulsed Pinnacle + (Advanced Energy®, USA) generator allowing the control of either the discharge current, power or voltage. The target surface is 30° titled with respect to the substrate mechanically maintained on a circular rotating substrate holder. The distance between the center of the target and the center of the substrate holder is 127 ± 2 mm.

The deposition chamber is pumped down to 10^{-4} Pa via a system combining an Edwards XDS5 dry pump and an Adixen ATH 400 M turbo-molecular pump. A gate valve placed between the deposition chamber and the turbo-molecular pump allows the control of the pressure during deposition step. The flow rates of argon and oxygen are controlled by two Bronkhorst flowmeters and the pressure in the deposition chamber is monitored by a cold-cathode (Alcatel ACC1009) and a capacitive (Pfeiffer CCR375) gauge. During the deposition step, the rotation speed of the samples is about 26 rpm.

In all experiments, the argon flow rate is set at 20 sccm. The pressure in the sputtering chamber is adjusted at 1 Pa by a gate valve. The current at the target is maintained at a constant value of 1 A pulsed at 50 kHz (time off 5 μs) to avoid accumulation of the charged species which leads to electrical instabilities.

2.2. Samples preparation

Various substrates: i.e. half cells (NiO-YSZ/YSZ) manufactured by tape casting and screen printing, n-type silicon wafers 100 (Institute of Materials Electronic Technology, Poland) and glass plates (Menzel-Gläser, Germany) are used as substrates.

Heat treatments are performed in air in a furnace (Nabertherm model LT5/13/B180, Germany) at 500 °C and 1000 °C with a heating rate of 1 °C·min^{-1}. Heat treatment at 500 °C in air (temperature maintained during 1 min) is performed to stabilize the sub stoichiometric deposited compound, that means to avoid evolution of its composition (oxygen content) when exposed to air and reduce the stress level in the film. The temperature is chosen on the basis of a preliminary study in which optical transmission measurements have been performed on magnetron sputtered deposits subjected to various heat treatments (not presented in this paper). It has been proved that a heat treatment at a temperature higher than 300 °C is required. However, in working conditions, a cell will be exposed to higher temperatures (about 800 °C). Moreover, the last step of the SOC elaboration process consists in the deposition of the LSCF oxygen electrode which is generally performed by screen printing followed by an annealing at high temperature (> 1000 °C). Therefore, additional treatment at 1000 °C in air (temperature maintained during 1 h) is also realized on samples previously heated at 500 °C to examine the behavior of the GDC films at higher temperature.

2.3. Samples examination

The morphology of the coatings is observed by means of scanning electron microscopy (SEM) (Carl Zeiss SMT, Supra-40, FEG-SEM) equipped with energy dispersive spectroscopy (EDS, Bruker XFlash Detector 4010) to assess the composition. The acceleration voltage is set at 3 kV for micrographs and 15 kV for EDS measurements. Cross section observations are performed on cleaved half cells to evidence the microstructure. The SEM micrographs are obtained using the secondary electrons collected on a tilted detector in order to further the observation of the topography. To quantify the porosity of the GDC barrier layer, image analyses are performed with Image J software on micrographs at four different magnifications (×1k, ×2k, ×5k and ×10k). Each reported data is an average value calculated from three measurements performed on each micrograph.

The oxygen content is estimated on thin films (about 300 nm) deposited on silicon wafers by Rutherford backscattering spectroscopy (RBS) using a 2 MeV He ion beam produced in a Pelletron accelerator (facility of CEMHTI laboratory, Orleans). To avoid evolution of the oxygen content, the as-deposited films are stored under vacuum. The samples are exposed to air < 6 h before their RBS analysis. The spectra are treated using the SIMNRA software to determine the oxygen concentration profile [19].

Raman spectroscopy is used to get insight into the composition and the crystalline quality structure of the thin films before and after annealing, compared to a classical screen printed GDC layer. Many papers report of the characterization of GDC layers by Raman spectroscopy [20–21]. The analyses are carried out at room temperature in backscattering configuration using an InVia Reflex Renishaw system. The spectra are collected under a microscope (50×) using a 514.5 nm excitation wavelength. The Raman-scattered light is dispersed by a holographic grating with 1800 lines/mm and detected by a charge-coupled device (CCD) camera. Raman spectra are recorded on the GDC films deposited on glass plates, thus preventing the detection of parasitic signals from the other components of the cell. As the thickness of the GDC layer manufactured by screen printing is higher (about 4 μm thick), no overlapping can occur and thus, the Raman spectra are collected directly on half cells. Spectra are fitted using the WiRE 3.4 software (Renishaw, England). The Raman peak shift and the full width at half maximum (FWHM) are determined. Each reported data is an average value calculated from three spectra recorded at different positions on the sample.

For a cross check of the oxidation and crystallization state, optical transmission measurements are performed on deposits realized on glass plates with a spectrophotometer in the 400–1000 nm range (Agilent Technologies, Cary60 UV–Vis).

Adhesion between YSZ substrate and GDC barrier layer is evaluated by scratch test (Anton Paar, Austria). Those tests are performed by applying a progressive (i.e. linearly increasing) load. The load rate is