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Nanostructured YSZ thin films for solid oxide fuel cells deposited by ultrasonic spray pyrolysis

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Abstract

Nanostructured thin films of yttria-stabilized zirconia (YSZ) have been prepared on single-crystalline silicon substrates by ultrasonic spray pyrolysis using zirconium acetylacetonate and yttrium acetylacetonate hydrate as metallo-organic precursors dissolved in anhydrous methanol. The morphology, structure and electrical properties were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and impedance spectroscopy (IS). The substrate temperature was optimized for obtaining smooth, dense and homogeneous nanocrystalline films with grains sizes as small as 10 nm. The influence of thermal annealing on structural properties of films was studied. The activation energy measured for electrical conduction through the grains (1.14 eV) was similar to that obtained in bulk of YSZ, but for conduction through the grain boundaries it acquires a value of 0.79 eV, increasing the total conductivity of the material up to 0.033 S/cm at 650 °C. These activation energy values are related to the small grain size and the close boundaries obtained at the optimized conditions. The obtained films are good candidates for applications as electrolytes in solid oxide fuel cells (SOFC) operating at relatively low temperatures.

Keywords: YSZ; Nanostructure; Ultrasonic spray deposition

1. Introduction

Yttria-stabilized zirconia (YSZ) is commonly used as electrolyte material in solid oxide fuel cells (SOFC) and oxygen sensors due to its chemical and thermal stabilities, and its high oxygen ionic conductivity at high temperature [1–4]. However, in order to improve the performance of these devices, a lower operation temperature is desired. One approach to reduce this temperature is to increase the ionic conductivity of the YSZ electrolyte by decreasing its thickness as much as possible [5–9]. Some studies in this direction show that the ionic conductivity of YSZ can be enhanced by preparing cubic or tetragonal polycrystalline films with grain sizes in the nanometer range [8,9].

Several physical and chemical processes have been employed to prepare YSZ thin films, including pulsed laser ablation, electron-beam evaporation, sol–gel, polymeric precursor spin coating, spray pyrolysis in its three versions; electrostatic, pneumatic and ultrasonic, and others [6–25]. Among them, the spray pyrolysis techniques are very attractive for the industry of planar SOFCs, because they allow the deposition of a wide variety of ceramic films over large areas. Besides, they are probably the cheapest and simplest processes. Each one of the spray pyrolysis versions has advantages and drawbacks in terms of complexity and quality of deposit. Electrostatic spray deposition (ESD) has been widely used for preparing YSZ and other ZrO_2 based films [7,12–16]. This technique produce almost mono-dispersed and fine drops, however, the effect of preferential landing characteristic of the charged droplets can lead to porous and/or cracked films.

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Pressurized spray deposition is reported as a more adequate technique to deposit dense films compared to the ESD technique, however, there is less control on the microstructure of the deposited films due to a higher dispersion in droplet sizes [15]. Although in several papers an optimization of the ESD process parameters has been made to prepare dense YSZ films, their electrical properties were not reported in some of these cases [12–16]. Ultrasonic spray deposition (USD) allows a smaller and homogeneous droplet size than electrostatic or pressurized spray. This technique allows the deposition of homogeneous thin films with excellent physical properties [17]. USD using different solvents and precursors has been used for obtaining high quality ZrO_2 [18,19] and YSZ films [20–23]. For example, Matsuzaki et al. deposited thin films of YSZ using yttrium and zirconium octylates and substrate temperatures in the range from 873 to 1023 K. Although these YSZ films were dense, they have cubic crystalline structure with columnar growth and grains with sizes in the range from 73.5 to 265 nm. However, their electrical properties were not reported [20]. Beltrán et al. [22] used inorganic precursors and rapid thermal annealing at 900 °C to obtain crystalline YSZ films with cubic phase and activation energy for ionic conduction of 1.3 eV. Wang et al. [21] and Ramirez et al. [23] obtained better electrical properties in films deposited using yttrium and zirconium acetylacetonates at lower substrate temperatures (525–700 °C). In the former case the YSZ films deposited at 600 °C had a mixture of monoclinic and tetragonal crystalline phases with grain sizes from 80 to 120 nm, and the activation energy for ionic conduction was of 1.08 eV. In the latter case, YSZ film deposited at 525 °C had a cubic crystalline structure, with average grain size of ~22 nm and activation energy for ionic conduction of 1.0 eV. However, in both cases the effect of lower substrate temperatures on the microstructural and electrical properties of the films has not been investigated [21,23].

In the present work, ultrasonic spray deposition was used to deposit YSZ films at substrate temperatures lower than those previously used. In addition to ultrasonic mist, the influence of short distance of nozzle to substrate and a second gas injection zone in the nozzle was analyzed in order to improve the structural and electrical properties of the films. A study of the influence of temperature and deposition time on the morphology of the films was made. The electrical properties of the obtained films were measured and compared with previous reports.

2. Experimental

An experimental setup similar to that shown in reference [21] was used. However, in the present case the nozzle is equipped with a gas injection tube at the top of the nozzle (Fig. 1). This system allows to introduce a director gas for increasing or modifying the velocity of the droplets arriving on the heated substrate without altering the flow rate of the aerosol carrier gas. The diameter of the nozzle was 16 mm and the distance nozzle-substrate was fixed to 20 mm. Films were deposited onto (100) n-type, 200 Ω cm single-crystalline silicon slices in order to perform electrical measurements at high temperatures. The substrates were ultrasonically cleaned, with trichloroethylene, acetone, methanol and 5% HF solution in order to remove the native oxide. The spray solution was 0.025 M of zirconium (IV) acetylacetonate [$Zr(acac)_4 = Zr(C_5H_7O_2)_4$] from Sigma-Aldrich Chemicals and 0.01 M of yttrium acetylacetonate hydrate [$Y(acac)_3(H_2O)_x = Y(C_5H_7O_2)_3(H_2O)_x$], dissolved in anhydrous methanol. The carrier gas and director gas flow rates, air in both cases, were fixed at 3.5 l/min and 1.5 l/min, respectively. The temperature of the heating plate (Ts) was controlled in the range of 300–475 °C, and the deposition time (t_d) was varied between 5 and 25 min.

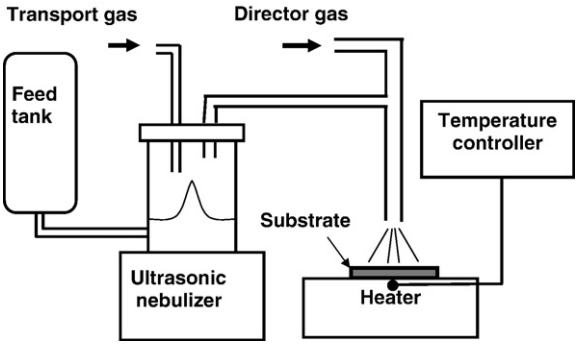

Fig. 1. Experimental setup used for ultrasonic spray deposition.

SEM images were obtained with a XL 30 FEG/SIRION with focused ion- and electron-beam, energy dispersive X-ray spectroscopy, and energy dispersive angle X-ray GENESIS 4000. An atomic force microscope (AFM) (Jeol, JSPM-4210) was used to analyze the surface of the samples. X-ray diffraction (XRD) spectra were obtained with a Siemens D-500 diffractometer using the CuK_α wavelength (1.54056 Å). The X-ray source was operated with a voltage of 25 kV and a current of 30 mA, to produce an intense X-ray beam whose incidence angle was 1°. The XRD spectra were obtained for 2θ angles in the range from 2° to 70° with steps of 0.020°. Considering the small thickness of the film, a long integration or step time (6.9 s) was used in order to obtain high quality XRD spectra. Under these experimental conditions the total acquisition time of each spectrum was around 11 h.

The thickness of the films was measured with a Sloan Dektac IIA profilometer. For this purpose a small part of the substrate was covered with a cover pyrex glass to form a step during deposition. The thickness of films was also measured by ellipsometry with a Gaertner 117A ellipsometer using the 633 nm line from a He–Ne laser. Both methods, ellipsometry and profilometry, gave similar thickness values for films deposited at the same conditions.

AC measurements were carried out using a Solartron 1260 Frequency Response Analyzer in combination with 1287 electrochemical interface over the range 0.1 Hz$<f<$32 MHz and for temperatures between 25 and 650 °C. A parallel pattern of two gold electrodes was sputtered on the film surface to be used as electrodes [21,26].

3. Results and discussion

Fig. 2a shows the dependence of the thickness of the film deposited at 425 °C as a function of deposition time. As can be