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IBA of ZrO_2:Yb/Si thin films produced by the spray pyrolysis method

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Abstract

A spray pyrolysis method was used to produce thin films of ZrO_2 doped with different Yb concentrations on Si(100). The films of these ionic semiconductors have potential applications as solid electrolytes in modern ceramic fuel cells of second generation. The determination of the atomic composition of the films is very important because it strongly affects the chemical and thermal stability, as well as electrical properties of the films. A combination of two Ion Beam Analysis (IBA) methods was applied to obtain the atomic composition of the films. A nuclear reaction analysis (NRA) method using a low energy deuterium beam was applied to measure the oxygen content of the films. Heavy ion Rutherford backscattering (HI-RBS) method using a $^{12}C^{3+}$ beam was applied to measure the Yb and Zr atomic profiles of the samples. X-ray diffraction (XRD) and ellipsometry were also employed to determine structural properties and refractive index of the films, respectively. The IBA, XRD and the ellipsometry supply a wide range of information about the film layers, which can be used for qualification as well as for feedback to the films production.

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1. Introduction

The preparation of thin films of solid oxide electrolytes by different techniques has become very important for second-generation solid oxide fuel cells (SOFCs) [1–3]. Due to its high ionic conductivity at high temperatures and chemical stability in both oxidizing and reducing atmospheres, yttria stabilized zirconia (YSZ) has been the most widely studied material as solid oxide electrolyte for SOFCs. However, other rare earth elements (Yb, Ce, Gd, etc), has also been investigated as zirconia dopants for such applications [1–3]. A number of studies have shown that the ionic conductivity of stabilized zirconia, which is attributed to the mobility of oxygen vacancies created by the stabilizer dopant, is maximum for a certain dopant level (typically 8–20%) and that it tends to be highest as the ionic radius of the dopant closely matches that of Zr^{+4} host cation [3,4]. Tablets and/or bars prepared from compactation and sintering of fine grained powders of stabilized zirconia with ytterbia (YbSZ) have been reported to have a conductivity higher than that of YSZ [2,5]. However, to our knowledge, there are scarce reports on the preparation, composition and structure of YbSZ thin films [6].

In this work, we report the preparation of YbSZ thin films with different content of Yb, by the spray pyrolysis method. The atomic composition of the YbSZ films was measured using IBA methods. There are different IBA methods able to provide the film stoichiometry of the Yb and Zr oxides. We selected a combination of two IBA methods as the most favorable: (a) a RBS/NRA method using a low energy deuterium beam was applied to obtain the oxygen concentration through nuclear reactions (NR) produced on oxygen nuclei. This method lacks good mass separation and has a poor depth resolution; (b) a HI-RBS method using a $^{12}C^{3+}$ was applied to measure the

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Zr and Yb concentration profiles. This method has a good mass separation and excellent depth profile resolution. Other complementary material analysis techniques used were XRD and ellipsometry in order to obtain the crystallographic properties and ellipsometry to measure the refractive index and thickness of the films, respectively.

2. Experimental details

The YbSZ films were deposited by the ultrasonic spray pyrolysis method, which has been used recently for the preparation of pure zirconia (ZrO_2) and YSZ thin films [7,8]. The substrates used to deposit the films were single crystalline silicon (1 0 0) n-type, 0.1–2.0 Ω cm The precursor solution was prepared by dissolving a fixed amount (0.025 M) of zirconium (IV) acetylacetonate [Zr(acac)$_4$ = $Zr(C_5H_7O_2)_4$] from Sigma-Aldrich Chemicals, in anhydrous methanol. The dopant level of Yb_2O_3 was controlled by adding different concentrations of ytterbium acetate hydrate [$Y(acet)_3(H_2O)_x = Yb(C_2H_3O_2)_3(H_2O)_x$] (also from Sigma–Aldrich), to the precursor solution. The molar concentration of $Yb(acet)_3(H_2O)_x$ were 0.0025 M (YbSZ1), 0.005 M (YbSZ2), 0.0075 M (YbSZ3) and 0.01 M (YbSZ4). The substrate temperature (Ts) was kept constant at 425 °C, air gas carrier was used as and director gas flow rates, were fixed at 3.5 l/min and 1.5 l/min, respectively. The deposition time (t_d) was adjusted to 30 min to obtain films with similar thickness in the range of 900–1100 nm.

The atomic concentration profiles of the YbSZ films were measured using two particle accelerators at the Instituto de Fisica of the Universidad Nacional Autonoma de Mexico. A 3 MV 9SDH-2 NEC Pelletron equipped with a SNICS-II ion source produced a 10.0 MeV $^{12}C^{3+}$, which was used for the HI-RBS technique. A single ended 5.5 MV Van de Graaff (HVECO CN model) produced a 1300 keV $^2H^+$ beam to bombard the films in order to measure the O and C concentrations by NRA. The NR ^{16}O (d,p$_0$) ^{17}O, $^{16}O(d,p_1)^{17}O$, $^{16}O(d,\alpha_0)^{14}N$ and $^{12}C(d,p_0)^{13}C$ NR peaks in the spectra can be used to measure the O and C if their NR cross sections are well determined. A 500 μm thick surface barrier detector (SBD) equipped with standard electronics set at $\theta = 165°$ angle was used to measure the particles energy. The incident beams bombarded the samples at 90° angle relative to the target surface. For the $^2H^+$ beam experiments, no energy absorbing foil was placed in front of the SBD in order to measure the energies of the NR particles and also the $^2H^+$ elastic backscattered energies from the target nuclei. The elastic energies of the $^2H^+$ on Si nuclei substrate was used to deduce the total beam particles and the SBD solid angle. These parameters were used for the analysis of the energies spectra. A Gaertner 117A ellipsometer using the 632 nm line from a He–Ne laser was used to measure the refractive index and films thickness. A Siemens D-500 diffractometer was used to perform XRD of the films. This spectrometer used the Cu Kα1 wavelength (1.54056 Å). The incidence angle of the X ray beam with respect to the film surface was of 2°. The XRD spectra were obtained for 2θ angles in the range from 20° to 105° with steps of 0.02°.

3. Experimental results and discussion

Fig. 1 shows the experimental spectrum (dots) produced by a 1.3 MeV $^2H^+$ beam bombardment on the sample YbS1. There are two well-defined regions in the RBS spectrum: (1) the $^2H^+$ backscattered on Si nuclei from the film substrate and a peak (60–80 channels) due to the $^2H^+$ backscattered from Zr and Yb nuclei. The counting yield from Yb and Zr overlaps to form the peak since this method does not have a good mass separation. However, this method has a good sensitivity to measure the C and O concentrations on the samples through NR. The ^{16}O (d,α_0)^{14}N, $^{16}O(d,p_0)^{17}O$, $^{16}O(d,p_1)^{17}O$ and $^{12}C(d,p_0)^{13}C$ NR peaks are indicated in the high energy region of the spectrum. The DataFurnace (DF) code [9] was applied to fit the energy spectra in order to obtain the atomic film profiles. The code fits simultaneously the elastic (RBS) and NR regions of the spectrum (solid line). DF is an automatic fitting code that generates its own layer structure. NR cross sections obtained from the Ion Beam Analysis Nuclear Data Library [IBANDL] were introduced in the DF to obtain the O and C concentrations [10–12]. It may be observed in the Fig. 1 inset the overlapping of the ^{16}O (d,α_0)^{12}C and ^{16}O (d,p$_0$)^{17}O NR particle yield, however DF is able to provide the O concentration. The $^{16}O(d,p_1)^{17}O$ NR peak is on top of a pile-up tail of backscattered $^2H^+$ deuteron and it was not used because it reduces the accuracy of the NRA measurement. Table 1 shows the atomic O concentrations for the 4 films analyzed. The ^{12}C (d,p$_0$)^{13}C NR peak can be partially attributed to the beam induced

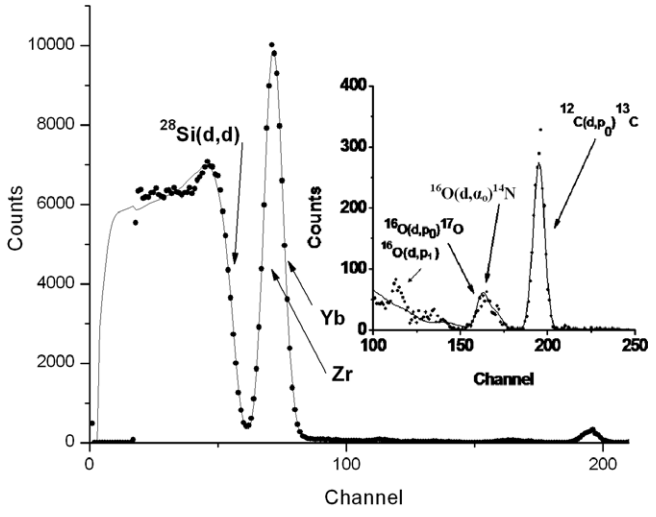

Fig. 1. The figure shows a typical experimental spectrum (dots) produced by a 1300 keV $^2H^+$ beam bombardment of the YbS1 sample. The surface barrier detector was set at 165° angle. DataFurnace code (solid line) fitted simultaneously the elastic and NR regions of the spectrum. $^{16}O(d,\alpha_0)^{14}N$, $^{16}O(d,p_0)^{17}O$ a and $^{12}C(d,p_0)^{13}C$ NR cross section from IBANDL web site were used to fit the NR region of the spectrum.