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ZrO_2 tape as flexible substrate to artificially nanostructured materials

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A B S T R A C T

We associate tape casting and magnetron sputtering techniques to engineer flexible nanostructures using ZrO_2 green tape as substrate. We systematically investigate the structural, magnetic and electrical properties of NiFe/Cr/NiFe trilayer nanostructures, with variable thickness values of the NiFe and Cr layers, grown onto rigid glass and flexible ZrO_2 tape substrates. We verify the mirroring of these properties in the trilayer nanostructures, irrespective on the kind of employed substrate. The fact that the trilayer nanostructures can be reproduced in distinct substrates corresponds to an important advance for their applicability. The results place the ZnO_2 green tape as an attractive candidate for application flexible substrate in the development of electrical and magnetic sensor elements with high sensitivity to mechanical stress.

1. Introduction

Low-cost thin ceramic membranes present interesting properties and find a wide range of applications in the fields of electronics and chemical processing technology. The most widely used techniques for the fabrication of these membranes are hot pressing, hot rolling and tape casting. Thin ceramic materials have been developed intensively in the last decades by the tape casting method, which is a low-cost process and particularly indicated for the production of multilayered ceramic composite materials and solid oxide fuel cells (SOFC) [1–7]. Tape casting is a widespread colloidal processing that has as advantage the production of homogeneous green structures. This process consists basically in forming slurry and in casting it through a doctor-blade on a generally moving surface [8,9]. The suspension is comprised by a dispersion of a ceramic powder in a solvent, with the addition of binders, plasticizers and dispersants [10–13]. In the last years, aqueous-based tape casting has been investigated in order to avoid health and environmental concerns [9,14–18]. The use of additives in the slurries affects directly its behavior as well as the properties of the tape cast substrates. A tape casting slurry must be adjusted in order to produce tapes with no defects, microstructural homogeneity and high mechanical strength after sintering. Thus, the composition and the rheological behavior of the aqueous slurries must be characterized and optimized in order to obtain green tapes, cracks and defects free with high and homogeneous green structure.

Yttria-stabilized zirconia (YSZ) is intensively used as the electrolyte material in SOFC due to its high ionic conductivity and chemical stability [18–20]. In particular, the YSZ is the most widely used electrolyte material for oxygen sensor and fuel cell applications. Pure zirconia ZrO_2 cannot act as a good electrolyte owing to its poor ionic conductivity and phase transformation (monoclinic/tetragonal) on heating associated with a large volume change. Doping of ZrO_2 with a small amount (3–10 mol%) of a divalent or trivalent oxide can stabilized cubic fluorite phase and, in the process, increases its oxygen vacancy concentration leading to an enhanced ionic conductivity. This makes stabilized zirconia suitable for the use as electrolyte material, while the Yttria (Y_2O_3) is the most commonly used dopant for stabilizing zirconia for the aforementioned applications [21].

At the same time, the functionalization of these tapes through insertion of metals and/or non-metallic alloys by using magnetron sputtering technique emerges as an attractive tool. The magnetron sputtering technique enables the growth of nanostructures in the single film or multilayer geometry for distinct technological applications. Traditionally, thin films are grown onto rigid amorphous or oriented substrates, and electrical and magnetic properties are explored for distinct purposes. In recent years, flexible substrates, with specific mechanical and electrical properties, have attracted considerable interest, mainly for flexible electronics devices [22–25]. In this sense, flexible tapes with distinct compositions, such as ZrO_2, arise as a promising candidate as substrate. On the other hand, this same integration between tape casting and magnetron sputtering techniques can be used to functionalize the tape before sintering, changing the mechanical and electrical properties of the

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resulting ceramic materials. However, until this moment, a comparison of the structural and electrical and/or magnetic properties of nanostructures grown onto conventional rigid and flexible tape substrates has not been reported yet, an achievement fundamental for future applications.

In this work, we associate tape casting and magnetron sputtering techniques to engineer flexible nanostructures and perform a systematic investigation of the structural, magnetic and electrical properties of NiFe/Cr/NiFe trilayer nanostructures, with variable thickness values of the NiFe and Cr layers, grown onto rigid glass and flexible ZrO_2 tape substrates. We verify that structural properties and magnetic and electrical responses are reproduced, irrespective on the kind of employed substrate. The results place the ZnO_2 tape as an attractive candidate for application as flexible substrate in the development of electrical and magnetic sensor elements with high sensitivity to mechanical stress.

2. Experimental procedure

For the study, we consider a set of $Ni_{81}Fe_{19}/Cr/Ni_{81}Fe_{19}$ trilayer nanostructures, with variable thickness values of the NiFe and Cr layers, grown onto rigid glass and flexible ZrO_2 tape substrates. Fig. 1 shows and schematic representation of the investigated samples, as well as the remarkable flexibility of the ZrO_2 tape substrate.

To obtain the flexible ZrO_2 tapes, slurries are prepared with 55 wt.% YSZ powder (3YSZ), 3 mol% Y_2O_3-stabilized ZrO_2 (Tosoh Corporation, Japan) with average particle size of 400 nm, 22 wt.% deionized water used as solvent, and 1 wt.% dispersant (Darvan 821A, Vanderbilt), and using alumina ball milling for 24 h. Subsequently, 20 wt.% binder (Monowilith LDM-6138, Clariant), 0.5 wt.% antifoam (Antifoam A, Sigma–Aldrich) and 1.5 wt.% surfactant (coconut diethanolamide, Stepan) are added to the mixture and the suspension is mixed for 30 min. The slurries are cast with a CC-1200 Mistler tape caster at 25 °C and 5 $cm \cdot min^{-1}$. The thickness of the tapes is around 125 μm.

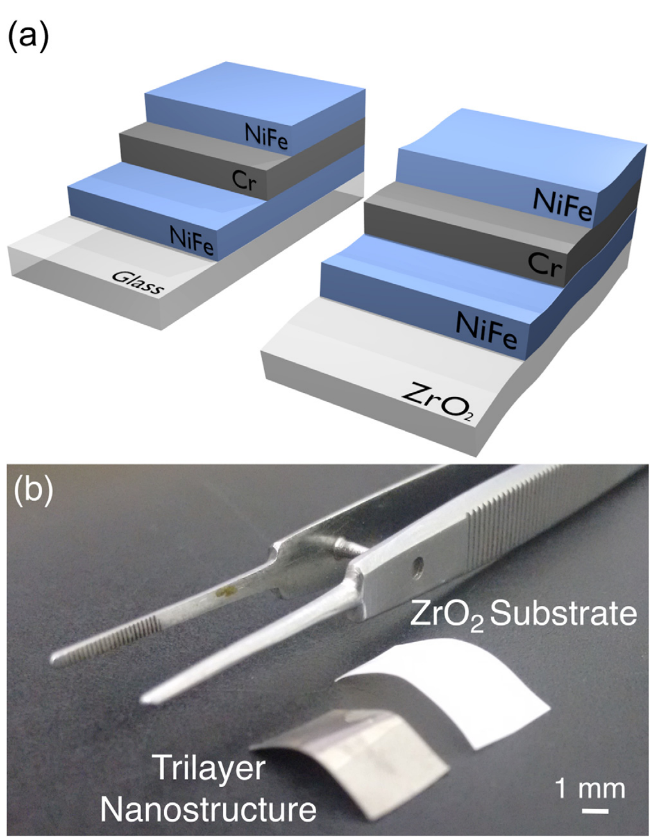

Fig. 1. (a) Schematic representation of the NiFe/Cr/NiFe trilayer nanostructures grown onto rigid glass and flexible ZrO_2 tape substrates. (b) Flexible ZrO_2 tape substrate and a trilayer nanostructure grown onto this substrate. Notice the remarkable flexibility of the substrate.

The stability of the yttria-stabilized zirconia slurries is analyzed by means of rheological characterization through viscosity curves. The viscosity experiments are carried out using a Haake Viscotester-Thermo Fischer Scientific viscosimeter with cone and plate geometry, at room temperature, and with shear stress between 0 and 1000 s^{-1}. Scanning electron microscopy micrographs, not shown here, present similar features to the ones found for the same material in Ref. [14].

With respect to the NiFe/Cr/NiFe trilayer nanostructures, the samples are produced by magnetron sputtering, with normal incidence, onto rigid glass and flexible ZrO_2 tape substrates with dimensions of 4×4 mm^2. The films are deposited using the following parameters: base vacuum of 5.0×10^{-6} Torr, deposition pressure of 3.0 mTorr with a 99.99% pure Ar, and dc source with currents of 40 mA and 60 mA used for the Cr and NiFe layer deposition, respectively. Under these conditions, the deposition rates are 0.47 Å/s for Cr and 0.59 Å/s for NiFe alloy. Table 1 presents the complete set of trilayer nanostructures investigated in this work.In order to verify the magnetic and electrical properties with respect to the thickness of the NiFe layers, all the samples present total thickness of $[2t_{NiFe} + t_{Cr}] = 300$ nm, while the values of the thicknesses for the NiFe and Cr layers, t_{NiFe} and t_{Cr}, respectively, varies continuously.

The structural properties of the trilayer nanostructures onto distinct substrates are verified by X-ray diffraction (XRD), which verify the structural character of the films and preferential growth direction. The measurements are obtained using a Rigaku Miniflex II diffractometer, in the Bragg–Brentano ($\theta - 2\theta$) geometry, with $Cu - K_\alpha$ radiation.

The magnetic behavior is investigated through magnetization curves measured at room temperature using a Lake Shore model 7404 vibrating sample magnetometer, with maximum in-plane magnetic field of ±300 Oe. In particular, the curves are acquired along the two lateral directions of the samples to verify the magnetic behavior of the trilayer nanostructures.

Finally, the electrical properties of the samples are studied through $I - V$ curves. In this case, the electrical response is obtained using a 238 – Keithley High Current Source-Measure Unit through the measurement by four point probe method.

3. Results and discussion

First of all, we perform the rheological characterization of the 3YSZ suspension. Fig. 2(a) shows the viscosity curve as a function

Table 1
Thickness t_{NiFe} and t_{Cr} values of the NiFe and Cr layers composing the trilayer nanostructures grown onto rigid glass and flexible ZrO_2 tape substrates.

Sample	t_{NiFe} (nm)	t_{Cr} (nm)	t_{NiFe} (nm)
T1	75.00	150.00	75.00
T2	82.50	135.00	82.50
T3	90.00	120.00	90.00
T4	97.50	105.00	97.50
T5	105.00	90.00	105.00
T6	112.50	72.50	112.50
T7	120.00	60.00	120.00
T8	127.50	45.00	127.50
T9	135.00	30.00	135.00
T10	142.50	15.00	142.50