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Epitaxial growth and characterization of $La_2Zr_2O_7$ multilayers on biaxially textured NiW substrate by chemical solution deposition under highly reducing conditions

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ABSTRACT

The paper presents the growth and characterization of highly textured $La_2Zr_2O_7$ (LZO) multilayer coatings on Ni–5 at.%W (NiW) biaxially textured substrates by chemical solution deposition (CSD) under highly reducing conditions ($Ar + 12\%H_2$) in order to protect the metallic substrate from oxidation. The coating solution consists in a stoichiometric mixture of lanthanum and zirconium acetylacetonates dissolved in an excess of propionic acid. The precursor chemistry was studied by means of infrared spectroscopy, thermogravimetric–differential thermal analyses, Raman spectroscopy and X-ray diffraction carried out on the precursor powder. The as-grown multilayer LZO coating exhibits a sharp in-plane and out-of-plane texture, with the full-width-at-half-maximum of the ω-scans and φ-scans of about 7.2° and 8.0°, respectively, close to that of the NiW substrate. The volume fraction of the *c*-axis oriented grains from the top layer of the coating increases with the number of layers. The LZO coating exhibits a smooth and crack-free surface, appropriate for the further epitaxial growth of a seed layer for the $YBa_2Cu_3O_{7-x}$ (YBCO) deposition. Transmission Electron Microscopy was used to investigate the microstructure of the CSD LZO thin films deposited on flexible NiW substrates. A high density of nanovoids, with a size ranging between 10 and 30 nm, was observed in the LZO layers. YBCO films epitaxially grown by pulsed laser deposition on the CSD LZO buffer layer exhibit critical current densities, J_c, close to 1.6 MA/cm^2 at 77 K and self-field and zero resistance critical temperature ($T_c(R=0)$) of 90.3 K.

1. Introduction

Lanthanum zirconate has been intensively studied over the past years for its catalytic [1,2], optical [3] and electrical properties [4]. Moreover, due to its good lattice match with $YBa_2Cu_3O_{7-x}$ (YBCO), lanthanum zirconium oxide is considered to be a promising buffer layer for YBCO based superconducting coated conductors. It has also been demonstrated by L. Molina et al. [5] that $La_2Zr_2O_7$ (LZO) is an efficient barrier against oxygen diffusion. In the so-called RABiTS approach, the coated conductor consists of a highly biaxially textured Ni-based metallic flexible substrate on which both the buffer layer architecture and the YBCO superconducting films are epitaxially grown [6,7]. In order to obtain a high critical current density YBCO superconducting layer with reduced large angle grain boundaries the substrate texture has to be transferred and improved by buffer layers [8]. The role of the buffer layer architecture, which usually consists of several epitaxial oxide layers, is to avoid the diffusion of oxygen and nickel into the metallic substrate and from the substrate into the YBCO film, respectively, as well as to adapt the thermal, chemical and crystalline properties of the metallic substrate to those of the ceramic YBCO film. Until now, the most used oxide buffer layer architecture is CeO_2/yttria-stabilized zirconia (YSZ)/CeO_2, epitaxially grown by DC and/or RF sputtering, on Ni–5 at.%W (NiW) biaxially textured substrates [9,10]. In spite of the excellent results obtained on the sputtered CeO_2/YSZ/CeO_2 buffer architecture, the development of a non-vacuum and low cost chemical solution deposition (CSD) method for the epitaxial deposition of one or more buffer layers presents a great interest in the field of coated conductor fabrication. Under these circumstances, due to their good chemical compatibility and low lattice mismatch with YBCO, the $La_2Zr_2O_7$ thin films grown by CSD are used as buffer and/or seed layers in the fabrication of low cost coated conductors [11,12]. LZO has a pyrochlore-type cubic structure with a lattice parameter $a = 10.79$ Å. For epitaxy on the (001) plane, according to the coincident site lattice matching condition, the matching distance is 3.81 Å (a quarter of the face diagonal of the *fcc* lattice, $a/2\sqrt{2}$). Thus, the lattice mismatch with YBCO is 0.52% and 1.84% for the *a* axis ($a = 3.83$ Å) and *b* ($b = 3.88$ Å) axis, respectively. In this case, the lattice mismatch between LZO and the most used metallic substrate NiW ($a = 3.54$ Å) is about 7.6%. Nevertheless, it has been demonstrated that LZO can be (001) epitaxially grown on NiW substrates [12,13].

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So far, several techniques have been used for the deposition of $La_2Zr_2O_7$ thin films, including both physical [14] and chemical methods [11]. Among these, the chemical solution deposition (CSD), comprising methods such as sol–gel routes and metal-organic deposition, offers a number of advantages over the vapor deposition techniques. The CSD methods [15–19] are versatile, non-vacuum methods that do not require expensive equipment and allow an easy control of stoichiometry, suitable for large scale fabrication. Moreover, the solubility of metal-organic compounds (metal alkoxides, carboxylates, β-diketonates, etc.) in polar or non-polar solvents can be tuned by modifying the organic part of the molecule, since the organic moiety pyrolysis under oxidizing atmosphere takes place without residue. The main drawback of the CSD processing is the need for a supplementary pyrolysis step to decompose the organic species from the precursor film prior to the film crystallization [20].

In case of the epitaxial deposition on biaxially textured Ni-based metallic substrates, the substrate oxidation during the deposition of LZO buffer represents an obstacle towards large scale application. Therefore, in contrast with previous works [11,13,14,19], this paper presents the results on the epitaxial deposition of LZO multilayer coatings on NiW biaxially textured substrates under severe reducing atmosphere ($Ar + 12\%H_2$). Moreover, due to the fact that the quality of the LZO epitaxial thin films strongly depends on the chemistry of the precursor solution, on the thermal treatment and on the reactions that take place during the decomposition of the precursor, a special attention has been given to the precursor chemistry. The coating solution was concentrated by distillation under controlled temperature and pressure conditions, highly reproducible for the scale-up. The YBCO film was epitaxially grown by PLD on the LZO template. The good structural, morphological and superconducting properties of the YBCO film demonstrate the high potential of the as-deposited LZO film for coated conductor applications.

2. Experimental details

2.1. Precursor solution preparation

The LZO precursor solution for the deposition of epitaxial thin films has been prepared at room temperature starting from lanthanum (III) 2,4-pentadionate and zirconium (IV) 2,4-pentadionate with a purity of 99.9% purchased from Alfa Aesar, according to a procedure previously described [21]. The reagents were separately dissolved in an excess of propionic acid and mixed in stoichiometric quantities corresponding to a La:Zr = 1:1 ratio to form lanthanum and zirconium propionates. The as-obtained solution was concentrated by distillation under severe conditions (P = 5000 Pa, T = 75 °C) up to a $[La^{3+}] = [Zr^{4+}] = 0.4$ mol l^{-1} concentration. The advantage of using propionic acid consists in its intrinsic ability to dissolve metal pentanedionates in high concentrations. The viscosity of the precursor solution, measured at 20 °C over a period of six months using a Haake RheoStress 600 rheometer, was $\eta = 2$ mPa·s^{-1}.

2.2. Thermal analyses and infrared spectroscopy

The thermal decomposition behavior of the powder obtained by drying the solution at 80 °C both in air, and in reducing $Ar–12\%H_2$ atmosphere was investigated by means of thermogravimetric–differential thermal analyses (TG–DTA) in the temperature range of 50–1000 °C at a heating rate of 10 °C/min. To identify the infrared active functional groups, the precursor solution and the obtained powder were characterized by Fourier transform infrared spectroscopy (FT-IR) using a Perkin Elmer FT-IR spectrometer. The Raman spectrum of the precursor powder annealed at 1000 °C was recorded using a Bruker Senterra Micro-Raman spectrometer equipped with an Ar laser operating at 532 nm and 20 mW.

2.3. $La_2Zr_2O_7$ thin film deposition and characterization

The LZO precursor solution was deposited by spin coating at room temperature both on (001) $SrTiO_3$ (STO) single crystals, and {100}⟨100⟩ biaxially textured NiW substrates, at a spinning rate of 4000 rpm for 60 s. Further details on the preparation of the cube textured NiW tapes are presented elsewhere [22,23]. Prior to the deposition, the metallic substrates were cleaned in acetone and isopropanol. The thermal treatment of the LZO precursor film was carried out in air at 900 °C for the films deposited on STO single crystalline substrates, while the films deposited on NiW substrates were thermally treated in an $Ar–12\%\ H_2$ atmosphere (20 l/h) at 950 °C. Both films were heated at a rate of 10 °C/min up to the crystallization temperature where they were kept for 1 h. After annealing, the samples were cooled down to room temperature at a rate of 10 °C/min. Multiple coatings were used to increase the thickness of the LZO layer. Each layer was heat treated under the same conditions as the film deposited directly on the NiW substrate.

The YBCO film was epitaxially grown on the as-prepared LZO template by the pulsed laser deposition (PLD) technique. More details on the YBCO deposition by PLD can be found elsewhere [24]. The crystalline properties of the films were investigated by X-ray diffraction and pole figures carried out using a Bruker AXS D8 Discover diffractometer in a high resolution (HRXRD) configuration and a Seifert XRD 3003 four-circle diffractometer using the Cu Kα1 radiation. The morphology of the films was investigated by Scanning Electron Microscopy (SEM) at an operating voltage of 10 kV using a LEO 1525 field-emission high-resolution scanning electron microscope and by Atomic Force Microscopy (AFM) using a Veeco D3100 atomic force microscope in the contact mode. Transmission Electron Microscopy (TEM), both in the High Resolution (HRTEM) and Scanning (STEM) mode, was performed on a Jeol JEM 2200FS microscope, equipped with a field-emission gun operating at an acceleration voltage of 200 kV and a CEOS spherical aberration corrector of the objective lens allowing to reach a spatial resolution of 0.9 Å. The Z-contrast STEM measurements were acquired using an electron probe of 1 nm in size, in the High-Angle Annular Dark Field (HAADF) mode. To carry out spatially-resolved chemical analysis by Energy Dispersive X-ray Spectroscopy (EDXS) in the STEM-HAADF mode, a Jeol JED 2300 spectrometer equipped with a 30 mm^2 Si (Li) detector was used. The chemical quantification was performed using the Cliff–Lorimer method, which is considered as a good approximation for thin films [25]. The transport critical current density (J_c) and the zero resistance critical temperature ($T_c(R = 0)$) of the YBCO films were measured by the DC four-probe method. The critical current density was derived from the V–I characteristics using the 1 μV/cm criterion.

3. Results

3.1. Precursor characterization

As shown in Fig. 1a and b, the decomposition processes of the precursor powder annealed both in air, and in reducing $Ar–12\%H_2$ atmosphere were investigated. For the precursor powder annealed in air, the thermal decomposition is characterized by four weight loss steps associated with a total mass loss of about 58% at 1000 °C, in agreement with the theoretical loss expected from the conversion of lanthanum zirconium propionate to LZO. In the first region, from 50 to 145 °C the DTA curve exhibits one endothermic peak at 115 °C due to the dehydration of the precursor powder. The TG curve is consistent with the DTA one, and the total weight loss in the first region is about 4%. In the second region, from 145 to 275 °C, the DTA curve shows an endothermic peak which corresponds to the melting of the propionate precursor. In the third region, from 275 to 650 °C, the DTA plot exhibits three exothermic peaks due to the stepwise thermal decomposition of the organic matter,