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## PhD Thesis

# Multifunctional Epitaxial Oxide Thin Films for Coated Conductors Fabrication

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The aim of this thesis consists in the study of epitaxial oxide thin films used as buffer layers by chemical methods in the fabrication of high temperature superconducting coated conductors based on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

The PhD thesis contains five major chapters with the references at the end of each chapter.

**Chapter 1** is dedicated to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  high temperature superconducting materials for coated conductors. A coated conductor (CC) consists of a metallic substrate, one or several oxide buffer layers and a superconducting layer which must develop a biaxial texture of high quality, with intergrain misorientation smaller than  $\sim 4\text{-}6^\circ$ . The crystallographic texture can be achieved by different techniques applied to the substrate (Rolling Assisted Biaxial texture, RABiT) or to the buffer layers (Ion Beam Assisted Deposition, IBAD). Finally, the deposition of the oxide and superconducting layers can be based on vacuum deposition techniques (Laser ablation, evaporation etc.) or on non-vacuum chemical processes (Chemical Vapour Deposition (CVD), Chemical Solution Deposition (CSD)). The key is to prepare a textured substrate adequately buffered with oxide layers which transmit, totally or partially, the underneath structure to the superconducting layer.

**Chapter 2** presents the synthesis of the precursor solutions including the fundamentals of Chemical Solution Deposition and Polymer Assisted Deposition methods. The thermal treatment of the oxide thin film used as buffer layers in the multilayer architecture of the second generation coated conductors and the investigation techniques are also presented.

The deposition of the precursor is performed by coating, while the thermal treatment is carried out in a quartz tube furnace under optimized heat treatment schedule and controlled atmosphere. The investigation techniques used are: thermal analyses (TG-DTA), mass spectrometry, infrared spectroscopy, X-ray diffraction on powder, optical microscopy and NMR relaxometry for the aging study of the precursor solutions. The experimental description for the preparation of the  $\text{BaZrO}_3$ ,  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{CeO}_2$  buffer layers and for YBCO-BZO nanocomposite

thin films by both metalorganic decomposition and polymer assisted deposition are also described.

The chemical methods for the deposition of thin films are cheap, accessible and easy to control, they ensure the molecular level homogeneity of the precursors, relatively high deposition rates, adequate for scaling-up. Chemical Solution Deposition appears to be the best candidate for the large-scale production of CCs and, in general, for functional oxide thin films. The major advantages of CSD are the low investment costs of the technology, the possibility to deposit over large areas and the excellent film composition control at molecular level through the control of the stoichiometry of the precursor solution.

**Chapter 3, Chapter 4 and Chapter 5** comprise the original part of the doctoral thesis.

**Chapter 3** presents the investigations on the epitaxial growth of BaZrO<sub>3</sub> (BZO) thin films on (100) MgO substrates using a propionate-based MOD solution route. The X-ray  $\theta$ -2 $\theta$  scan and  $\phi$ -scan measurements have demonstrated that the BZO thin films grown in the temperature range from 600 °C to 1000 °C exhibit a cube-on-cube epitaxy on the (100) MgO substrate. The Full-Width-Half-Maximum (FWHM) for the  $\omega$ -scan and  $\phi$ -scan of 0.29° and 0.46°, respectively are comparable with those obtained for the BZO films grown by physical vapor deposition techniques. The films grown at lower temperatures (600, 700, 800 and 900 °C) have a porous structure, while the film grown at 1000 °C has an uniform and compact morphology. The RMS roughness of the film is temperature dependent, varying from 3.63 nm to 5.25 nm for the film annealed at 600 °C and 1000 °C, respectively.

A special attention has been given to the thermal decomposition mechanism of the precursors. Thus, a new barium acetato-propionate complex has been synthesized by dispersing the barium acetate in methanol, reacting with propionic acid and neutralized with ammonia. This means that the barium acetate is partially transformed for barium propionate. The X-Ray diffraction on the single crystal precursor has revealed that the molecular formula of the new precursor is [Ba<sub>7</sub>(CH<sub>3</sub>CH<sub>2</sub>COO)<sub>10</sub>(CH<sub>3</sub>COO)<sub>4</sub>·5H<sub>2</sub>O], having four crystallographically different barium ions coordination. One of them has the coordination number 8 and three of them 9. Ba(1) is surrounded by two bridging tetradentate ligands, while Ba(2) is surrounded by two carboxylate groups, coordinated by two different types chelating bidentate and bridging tridentate. Ba(3) is

surrounded by two water molecules and one bridging tridentate carboxylate group and, Ba(4) by one carboxylate group, with chelating bidentate type coordination. The barium acetato-propionate precursor is a three dimensional channel-type polymer that crystallizes in the monoclinic system, space group P2(1)/c, with the following cell parameters:  $a=15.338(6)\text{\AA}$ ,  $b=15.748(6)\text{\AA}$ ,  $c=14.128(6)\text{\AA}$  and  $\beta=95.826(7)$ . The crystallographic data were indexed in the Cambridge Crystallographic Data CENTER under Nr. CCDC 814595.

The thermal analyses coupled with mass spectrometry of the zirconium precursor resulted from the reaction of zirconium acetylacetonate with propionic acid demonstrates the fact that the zirconium 2,4-pentanedionate is completely transformed in zirconium propionate  $\text{Zr}_6(\text{CH}_3\text{CH}_2\text{COO})_{10} \cdot 9\text{H}_2\text{O}$ . As a serendipitous consequence of a magnetic field, when the as-obtained precursor solution was subjected to nuclear magnetic resonance (NMR) relaxation time measurements, we have obtained single crystals. Zirconium precursor single crystals have been grown over a period of 2-3 weeks. Due to the high complexity, the molecular structures need supplementary refinement.

An important part of this chapter is dedicated to the development of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{-BaZrO}_3$  composite thin films by chemical solution deposition. Barium zirconate is the most attractive material to induce artificial pinning centers in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) thin films in order to increase the critical current density. The main reasons for using BZO as artificial pinning centers in YBCO are: (a) BZO has a high melting temperature with respect to YBCO and so the growth kinetics should be slow, leading to small particles, (b) zirconium does not substitute in the YBCO structure and (c) although BZO can grow epitaxially with YBCO, it has a large lattice mismatch (approximately 9%), so strain between the phases could introduce defects for enhanced pinning. The chemical synthesis route provides an atomic level mixing of the elements, reducing the diffusion path up to nanometric scale for obtaining the desired material.

A study was performed on YBCO with addition of different volumes of BZO corresponding to 5, 7.5, 10 and 15 % mol to the YBCO. The X-ray analysis on the composite thin films deposited on the (100) $\text{SrTiO}_3$  (STO) substrates has revealed that the BZO nanoislands are epitaxially grown throughout the YBCO film. All the samples show critical temperature higher or close to 89 K, with narrow transition regions. Moreover, as revealed by SEM and AFM images, the presence of BZO considerably improves the morphology of the YBCO film. The YBCO sample with no BZO nanoparticles addition shows the presence of  $c$  and  $a$  axis oriented grains,

while the samples with addition of the BZO nanoparticles, show only the *c* axis oriented grains. The BZO addition resulted in an improvement of the critical current density,  $J_c$ , up to 3 MA/cm<sup>2</sup> for the YBCO-10%mol BZO, while the pure YBCO exhibits a critical current density of 1 MA/cm<sup>2</sup>.

**Chapter 4** presents the investigation of the epitaxial deposition of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> multilayer coating on Ni-5at.% W biaxially textured substrates by a chemical solution deposition. Due to its good chemical compatibility and low lattice mismatch with YBCO, the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (LZO) thin films grown by CSD are of great interest as buffer and/or seed layers in the fabrication of low cost coated conductors. It was shown that CSD using a simple propionic acid based precursor solution is appropriate to grow LZO films with a high degree of epitaxy both on (100)STO monocrystalline and Ni-W biaxially textured substrates. The FWHM of the (400)LZO  $\omega$ -scans is of about 0.11°. The multilayer LZO coating exhibits a sharp in-plane and out-of-plane texture with the FWHM of the  $\omega$ -scans and  $\phi$ -scan of about 7.2° and 8.0°, respectively, close to that of the Ni-W substrate. The value of the FWHM depends only slightly on the number of layers and, as a consequence, the method can be successfully used to grow thick epitaxial LZO coatings. The volume fraction of *c*-axis oriented grains increases with the number of LZO layers. The as-grown LZO multilayer coating exhibits a smooth and crack-free surface, suitable for the further epitaxial deposition of the YBCO film.

It is to be noted that the morphological and structural properties of the films are appropriate to be used as buffer layers. Anyway, further investigations are necessary to improve both the shelf life of the coating solutions, and the deposition process of the oxide films.

**In Chapter 5** it was demonstrated the possibility of preparing epitaxial CeO<sub>2</sub> thin films on YSZ single crystals from a novel water based cerium based coating solution, using a new chemical method called Polymer Assisted Deposition (PAD). PAD differs from the conventional CSD techniques because of the water-soluble polymer which plays a significant role in preparing high-quality films. The polymer actively binds the metal and serves to both encapsulate the metal and to prevent chemical reaction that can lead to the formation of undesired phases and maintain an even distribution of the metal in solution. These solutions can remain stable for months even when multiple metals are used resulting in complex oxide compounds. Another advantage of

PAD is that the use of polymers of high molecular weight allows the removal of any unwanted anions or cations by filtering through an Amicon ultrafiltration unit. The polymer used to form the stable and homogeneous precursor solution plays an important role in the formation of this material. The precursor gel was characterized by thermal analyses to establish the optimum thermal treatment and FT-IR spectroscopy to verify the complexation process. Thermal analysis has revealed that most of the decomposition of the organics and nitrates in the precursor film occurs below 370 °C. The ceria thin films were characterized by XRD, pole figures, AFM and TEM measurements. Highly textured CeO<sub>2</sub> layers were finally obtained. The films heat treated at a slow heating rate obtained from both solutions (0.1 and 0.2 M) are oriented and present an adequate roughness.

Depending on the thermal treatment schedule, oriented and good CeO<sub>2</sub> thin films morphologies can be obtained. The process parameters for the PAD process can be used to tune the grains size by modifying the CeO<sub>2</sub> nucleation, essential for the further growth of the YBCO superconducting layer.