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Epitaxial Thin Films Obtained by Chemical Solution Deposition for $YBa_2Cu_3O_{7-X}$ (YBCO) Superconducting Architecture

- Abstract of PhD Thesis -

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Abstract of the thesis

This thesis focused on the study of the chemical methods for oxide thin films used in the fabrication of high temperature superconducting architecture. Chemical Solution Deposition is particularly attractive for preparing superconducting architecture because the solution precursor can easily be deposited on a substrate by spinning or dipping. The method is inexpensive, the composition can be easily controlled and modified, providing an atomic level mixing of the elements, reducing the diffusion path up to nanometric scale for obtaining the desired material and, as a consequence, lower synthesis temperatures. Moreover, due to the fact that the solubility of metal-organic compounds in polar or non-polar solvents can be tuned by modifying the organic part of the molecule and because the organic moiety pyrolyzes in oxidizing ambient atmosphere without residue, MOD presents important advantages.

The solutions obtained by chemical solution deposition (CSD) method, contain metal-organic molecules which evaporate to a solid precursor and then decompose to epitaxial or polycrystalline films, during the controled heat treatment. Polycrystalline films are produced when the amorphous film crystallizes. The polycrystalline film is converted to a single crystalline film by the growth of oriented grains formed at interface for the single crystalline substrate.

Chapter 1 is dedicated to $YBa_2Cu_3O_{7-x}$(YBCO) high temperature superconducting materials and describes a theoretical approach on the preparation of oxide thin films using chemical methods as buffer layers in the multilayer architecture of the second generation coated conductors fabrication.

Chapter 2 presents the experimental set up for the synthesis and deposition of the precursor solutions, the controlled/optimized thermal treatment for the fabrication oxide thin films and the investigation techniques used 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.

Chapter 3 describes the fabrication of $La_{0.66}Sr_{0.33}MnO_3$ (LSMO) epitaxial thin films on (00l) $SrTiO_3$ single crystalline substrates using a new simple chemical solution route, with emphasis on the precursor chemistry since the LSMO thin films are considered to be excellent conductive buffer layers for superconducting coated conductors.

The precursor solution for the deposition of epitaxial LSMO thin films has been prepared at room temperature starting from lanthanum acetylacetonate $La(CH_3COCHCOCH_3)_3{\cdot}xH_2O$, manganese acetylacetonate $Mn(CH_3COCHCOCH_3)_3{\cdot}\ xH_2O$, and strontium acetate $Sr(CH_3COO)_2{\cdot}\ xH_2O$ with a purity of 99.9% purchased from Alfa Aesar to yield a 0.4M solution with a 0.66:0.33:1 stoichiometry. These salts were separately dissolved in an excess of propionic acid, C_2H_5COOH, concentrated by the removal of solvents (methanol, water) under vacuum (93 mbarr, 75 ^oC bath temperature) and brought to approximately 5 ml volume coating solution.

For a better understanding of the precursor chemistry, the precursor powder obtained by drying the coating solution was investigated by TG-DTA thermal analyses coupled with a

quadrupole mass spectrometer (QMS) using an atmospheric sampling residual gas analyzer 200 QMS Stanford Research System. The thermal analysis (TG-DTA) of the LSMO gel powder was performed under dynamic air and in oxygen atmosphere, respectively, in the temperature range 20-1000 ^{o}C, at heating rates of 5, 10, 15 ^{o}C/min.

The LSMO precursor solution was spin coated in air onto single crystalline (00l) $SrTiO_3$ (STO) substrates at 3000 rpm for 60 seconds. The as-deposited thin films were thermally treated both in air and in oxygen atmosphere in the temperature range from 800 ^{o}C to 1100 °C for 2 hours, at a heating rate of 5 ^{o}C/min up to 500 ^{o}C (corresponding to pyrolysis) and 10 ^{o}C/min up to the crystallization temperature.

Were performed, in the same temperature range the θ–2θ scans for the films annealed in air, between 800 ^{o}C and 1100 ^{o}C, and in oxygen. They both reveal the presence of the LSMO thin films diffraction peaks corresponding to the (00l) plane family, indicating an epitaxial growth of the LSMO films on STO (001) substrates, without evidence of any secondary phase.

For the films grown in air, a clear shift in the (002) peaks is seen towards higher 2θ values, as the annealing temperature is increased and thus oxygen incorporation is facilitated. The reduction of the out-of-plane lattice parameter as a function of the annealing temperature has been previously reported in LSMO epitaxial thin films grown on STO substrates.

The FWHM of the ω-scans for the (002) LSMO peak constantly decrease as the annealing temperature is increased from 0.079^{o} to 0.054^{o}, close to that observed for the LSMO films grown by PLD. As the temperature is increased at 1100 ^{o}C, the crystallites become larger and exhibit sharp edges indicating an increase of the film crystallinity degree. Surface roughness range from 7.2 nm for the film annealed at 800 ^{o}C to 11.8 nm for the film treated at 1100 ^{o}C.

The LSMO films grown under oxygen atmosphere show the (002) LSMO peaks that are very close to the ideal value bulk, and do not radically change position as a function of temperature. This is an indication that they are much more relaxed from a structural point of view than the air grown samples, and that oxygen incorporation is attained even at low temperatures. Furthermore, the width of the (002) LSMO diffraction peak is narrower for the film annealed at 1100 ^{o}C (FWHM=0.22^{o}) than for the 800 ^{o}C annealed one (FWHM=0.34^{o}) , indicating a higher degree of crystallinity of the films treated at higher temperatures, as confirmed by the AFM surface morphology studies. Surface roughness, which can be associated with crystallinity, has low values of 3.11 nm and 2 nm respectively for the 800 ^{o}C and 900 ^{o}C treated films and much higher values, of 11.19 nm and 13.4 nm, for the 1000 ^{o}C and 1100 ^{o}C treated ones.

The electrical properties of the LSMO films were determined by performing R vs. T measurements on the samples deposited in air and in oxygen atmosphere at 1000 ^{o}C. The Curie temperature of the film annealed in oxygen was determined as the maximum of the dR/dT curve and it was found to be around 320 K. For the film grown in air, the Curie temperature was determined through M(T) measurements to be around 360 K. Lower structural quality of the 1000 ^{o}C oxygen annealed sample, having a FWHM of the (002)

LSMO peak of 24°, with respect to a FWHM of 0.21°, for the air grown one, may be an indication of the existence of structural defects.

Epitaxial LSMO thin films were successfully grown on STO(100) monocrystalline substrate using a propionate-based metalorganic deposition (MOD) solution route. The nature of the coating solution and the decomposition of the precursor powder was investigated by FT-IR spectroscopy, TG-DTA and quadrupole mass spectrometry. The as-obtained LSMO thin films exhibit good structural and electrical properties. The Full-Width-Half-Maximum (FWHM) of the ω-scan for the (002) peak is of about 0.06°, close to that observed in the LSMO films grown by physical deposition techniques. The Curie temperature of the LSMO thin films is 320 K and 350 K for the films annealed in oxygen and air, respectively.

Chapter 4 presents the preparation $YBa_2Cu_3O_{7-x}$(YBCO) epitaxial thin films by chemical solution deposition.

In this chapter, two new solutions YBCO-Prop (acid) and YBCO-TEA (neutral) with further reduced fluorine content were put forward using Ba–TFA and non-fluorine Y and Cu salts as precursors. In these solutions, the fluorine content is reduced with 70% of that in the all-TFA solution. The coating solutions for two methods were prepared starting from yttrium acetate $Y(CH_3COO)_3 \cdot 4H_2O$, barium trifluoroacetate $Ba(CF_3COO)_2$ and copper acetate $Cu(CH_3COO)_2 \cdot H_2O$ corresponding to the 1:2:3 stoichiometry.

For YBCO-Prop (acid) method the Ba trifluoroacetate was dissolved in methanol, the Y and Cu acetates were separately dispersed in methanol, treated with an excess of propionic acid (C_2H_5COOH), and further neutralized with NH_4OH until the solutions became clear. The three solutions were mixed together under stirring and concentrated by the removal of solvent under vacuum. The as-prepared solution was spin coated on the substrate at spin rates of both 3000 and 4000 rpm for 60 s.

The precursor films were heat treated in two stages following the same procedure independent of the substrates employed. In the first stage, the samples were heat treated up to 400 °C under humidified oxygen (about 17 Torr H_2O). The second thermal treatment was performed at 850 °C, with a rate 10 °C min^{-1}, for 1 h in an environment of humid oxygen and nitrogen and another 10 min in a dry mixture of oxygen and nitrogen. The film was cooled to about 450 °C in the same nominal gas environment with a rate 10 ◦C min^{-1}, kept at this temperature for 45 min in oxygen, and subsequently cooled to room temperature.

The thermal decomposition and phase evolution of the precursor powder has been investigated by thermal analysis using thermogravimetric (TG) and differential thermal analysis (DTA), thermogravimetric analysis coupled with quadrupole mass spectrometry (QMS) and X-ray diffraction (XRD).

Precursor powders for individual components were, analyzed by thermogravimetric analysis (TGA) and differential thermal analysis (DTA), MS, IR to determine their decomposition mechanism.

For example, a new copper propionate complex was synthesised and characterized for application as precursor for CuO based oxide thin films deposition. The XRD has revealed that the copper propionate complex $[Cu(OOCCH_2CH_3)_3]_2 \cdot H_2O$ has the binuclear molecular

structure connected by a Cu· · ·Cu bond of 2.6 Å and bridging bidentate carboxylates groups. The FT-IR spectroscopic analysis acknowledges the molecular structure of the propionate complex, as determined by XRD on propionate single crystal. The thermal decomposition of the copper propionate to CuO was investigated both in air and in nitrogen atmosphere. Regardless from the atmosphere, the TG curves have revealed that the mass increase in the temperature range from 350 ^{o}C to 600 ^{o}C is due to the oxidation of Cu and Cu_2O, which indicates that reduction of Cu(II) to Cu(I,0) during the decomposition of copper propionate. The result is significant for in situ preparation of Cu_2O/Cu nanocomposite thin films. The X-ray diffraction pattern at 1000 ◦C presents only the peak of CuO, demonstrating that at this temperature the metallic copper is completely oxidated.

The kinetics of the thermal decomposition of the YBCO precursor powder was studied under different atmospheres such as air, oxygen and humid oxygen from ambient temperature to 1000 °C. During the decomposition of the precursor powder several intermediates phases were detected (Cu, Cu_2O, CuO and $B_{1-x}Y_xF_{2+x}$) and, as a result, a mechanism for the formation of the mixed oxide as proposed. Thermogravimetric analysis of the precursor powder show 4 wt.% additional weight loss, under dry conditions. These results are very important for obtaining dense YBCO superconducting films with high critical current density.

The θ–2θ scans for the as-obtained YBCO films reveal the presence of the YBCO diffraction peaks corresponding to the (00l) plane family, indicating an epitaxial growth of the YBCO on the STO (001) substrates, without evidence of any secondary phases. The analysis of the YBCO surface morphology investigated by SEM reveals a rather low porosity of the films. The critical current density, Jc, was determined from magnetization measurements assuming the Bean critical state model as a function of the temperature. The value at 77 K is 1.5 MA/cm^2.

The YBCO-TEA (neutral) method involves the use yttrium acetate [$Y(OOCCH_3)_3$], barium trifluoroacetate [$Ba(OOCF_3)_2$] and copper acetate [$Cu(OOCH_3)_2$] in stoichiometric metal ratio (1:2:3). In order to remove the crystallization water of the reagents, a preliminary drying procedure was carried out using a thermostatic vacuum dryer. These powders were dissolved in a mixture of methanol/triethanolamine-TEA (solvent and chelating agent) with the cation concentration of 1.5 mol l^{-1}. The addition of TEA was important because it greatly improved the solubility of the copper acetate precursor powder in methanol. The formation of mixed carboxylate-TEA copper (II) complexes has been previously described. The rheometric and spectroscopic properties of the precursor solutions were also studied.

The solutions were coated on the single-crystal substrates with (001) orientation 5 × 5 mm^2 ($LaAlO_3$) substrates by spin coating, were cleaned with methanol and then dried under N_2. The deposition was performed at controlled ambient temperatures (20-23°C) and in a glove box where a N_2 flow has enabled absolute humidity below 10%. The spin rate was increased from 0 up to 6000 rpm in about 1 second and was held for 2 minutes. After spinning, the films were calcined in a fast pyrolysis process at 310 ◦C in humid oxygen. Finally the films are annealed at 810 ^{o}C in a mixture of humid nitrogen and oxygen, and then post-annealed at 450 ^{o}C in dry oxygen.

The surface of a single-layer pyrolyzed film was observed under optical microscopy. No pores and cracks are observed on the film surface. However, still some remaining in homogeneities is present that need further elimination.

The two-dimensional XRD characterization of the YBCO film on the (001)$LaAlO_3$ substrate after crystallization was performed. As can be seen, the Chi - integrated XRD pattern spectrum mainly shows only the (00l) YBCO reflections, indicating that the YBCO film is epitaxially grown on the (001)$LaAlO_3$ with a [*00l*]//[*00l*] epitaxial relationship between the substrate and the film, no grains with the *a/b*-axis oriented perpendicular to the substrate are observed.

The morphology of the YBCO film was examined by SEM. At 7KX magnification the film morphology has a plate like aspect. It should be noted that the coalescence of the film is quite good. Nevertheless, pores are also observed. The high magnification (50 KX) image reveals clearer this porosity, which needs further investigation. We believe that the pores are due to the gases generated by the reaction with H_2O vapors during the film growth step.

YBCO epitaxial thin films were successfully grown by spin-coating the new coating solution. The preparation of the precursor is inexpensive and environmentally friendly. A new solution was prepared starting from Ba–TFA and non-fluorine Cu and Y salts as precursors. The generation of fluorinated compounds is greatly reduced. The SEM analysis has revealed a YBCO film still a bit porous. From this reason, further experiments have to be carried out on the thermal treatment of the as deposited film.

Chapter 5 reports on the preparation and characterization of a bilayer system on (001) $SrTiO_3$ substrates consisting of a $YBa_2Cu_3O_7$ (YBCO) superconducting layer grown on a conducting $La_{0.66}Sr_{0.33}MnO_3$ (LSMO) buffer layer. Films were prepared by an all-chemical solution deposition approach using acetate and acetylacetonate precursors for LSMO (chapter 3) and acetate and trifluoroacetates for YBCO (chapter 4). YBCO films grown by YBCO-Prop method on top of the LSMO surface exhibit an excellent morphology and a transition temperature of 75 K.