THE DEVELOPMENT OF MOD–TFA PRECURSORS FOR THE DEPOSITION OF THICK YBCO FILMS ON METALLIC SUBSTRATES FOR THE SUPERCONDUCTING COATED CONDUCTORS

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1.1. Introduction

In order to scale-up the $YBa_2Cu_3O_{7-x}$ (YBCO) coated conductors technology, the development of a low cost method for the deposition of epitaxial YBCO thick film is essential. The chemical solution deposition (CSD) is promising since this technique fulfils the requirements of the fabrication of coated conductors at industrial level (versatility, low vacuum, inexpensive, high deposition rate, easy control of the stoichiometry, etc.). Until now, the trifluoroacetates metal organic deposition (TFA-MOD) has been the most used CSD method for the YBCO superconducting film deposition. Using this method several groups [1,2,3,4] have obtained high performance YBCO superconducting films with a critical current density (J_c) in the range of J, approximately 2-3 MA at 77 K and zero magnetic field. Nevertheless, the major drawback of the TFA-MOD method consists in the evolvement of hydrofluoric acid, during the heat treatment of the precursor film, which limits the thickness of the film and enhances the pyrolysis time.

A modified TFA-MOD method, using only barium trifluoroacetate, is presented. The yttrium and copper triflouroacetates were replaced by the alcoholic solutions of Cu and Y acetates dispersed in propionic acid. The characterization of the epitaxially grown YBCO films, on both (001) $SrTiO_3$ and $CeO_2/YSZ/CeO_2/Pd$ buffered Ni-5at.%W substrates, using the modified TFA-MOD method is also presented.

2.2. Experimental

The coating solution was prepared starting from yttrium acetate $Y(CH_3COO)_3.4H_2O$, barium trifluoroacetate $Ba(CF_3COO)_2$ and copper acetate $Cu(CH_3COO)_2.H_2O$ corresponding to the 1:2:3 stoichiometry. While the barium 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, then treated with NH_4OH until the solutions became clear. The three solutions were mixed together under stirring and concentrated by the removal of solvents under vacuum. The resulting solution was spin coated both on (001) $SrTiO_3$ and $CeO_2/YSZ/CeO_2/Pd$ buffered Ni-5at.%W substrates at a spinning rate of 4000 RPM for 60 seconds.

The dried (60^0C) precursors were investigated by FT-IR (Fourier Transformed Infrared Spectroscopy), QMS (Quadrupole Mass Spectroscopy), and thermal analyses (DTA and TG). The thermal analysis (TG-DTA) of the YBCO gel powder was performed under dynamic nitrogen atmosphere in the temperature range 20-700°C, at a rate of 10°C/min. The TG-DTA thermal analyses have been coupled with a quadrupole mass spectrometer using an atmospheric sampling residual gas analyzer (200 QMS Stanford Research System). Scanning Electro Microscopy (SEM) and X-Ray Diffraction (XRD) were used for the investigation of the film morphology and crystalline structure, respectively. The temperature dependence of the electrical resistance was determined by a four point method. The YBCO film thickness was measured directly by means of a profilometer on a step patterned film.

3.Results and discussions

3.1Precursor chemistry

The TG-DTA analysis (Figure 1) have revealed that the decomposition of the YBCO precursor takes place in four successive stages. The first weight loss occurs in the temperature range 60-135°C and corresponds to a loss of 1.4 % from the initial weight, evidenced by the endothermic effect at 118°C in the DTA plot. As demonstrated by the QMS measurements (Figure 2), this weight loss can be attributed to the evaporation of the residual water from the dried gel. The second stage between 135-250°C is accompanied by the evolvement of CO_2 (m/z=44), acidic rests (m/z=43) and methanol (m/z=31), as well as by an endothermic peak at 239°C in the DTA plot. The main weight loss (43%) takes place between 250 and 320°C. The gaseous products evolved in this temperature range are CO_2 (m/z=44), acidic rests (m/z=43) and water (m/z=18) due to the combustion of organic moieties, evidenced by a broad exothermic band with three peaks at 321, 330, 353°C respectively, each one representing a decomposition reaction, consistent with the decomposition of the individual metallic precursors. At the same time, complex competitive oxidation processes due to the burning of the organic moieties take place between 250-450°C. CO (m/z=28) evolvement could not be registered due to the overlapping with the nitrogen molecule. Nevertheless, it is presumed to convert to CO_2 during the combustion process. From room temperature to 320°C the total weight loss is about 60 %. Between 460 and 800°C a slight weight gain is registered, associated with the probable oxidation of Cu^{+} to Cu^{2+}.
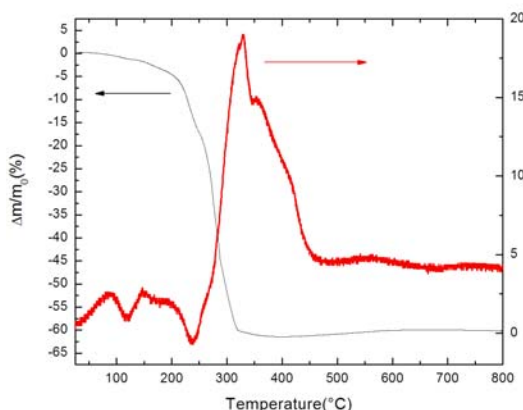

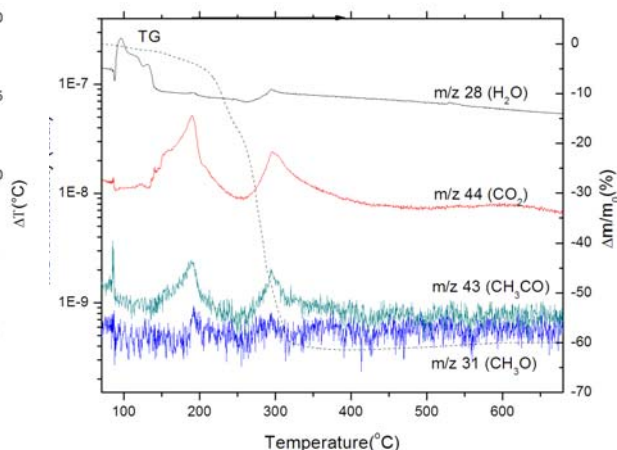Figure 1. DTA and TG curve for YBCO dried   Figure 2. TG-MS results on YBCO dried gel.

The FTIR spectrum of the YBCO powder is shown in Figure 3. A broad band between 3750 and 3100 cm^{-1} is due to the O-H stretching vibrations from the residual alcohol, water and Metal O-H bonds. The peaks at ~3000 cm^{-1} and the peaks in the region between 1500 and 700 cm^{-1} are due to the alkyl groups (C-H), while those corresponding to 800 and 726 cm^{-1} are attributed to the C-F bonds due to barium trifluoroacetate. The sample presents the carboxylate (COO^{-}) characteristic vibration frequencies at 1681 cm^{-1}, as well as the skeletal vibration of propionates at 1076 cm^{-1} found for the yttrium and copper individual precursors only. The peak at 1302 cm^{-1} corresponds to the CH_2 symmetric vibration associated with propionates. The peaks below 660 cm^{-1} are attributed to the Me-O bond stretching vibrations.
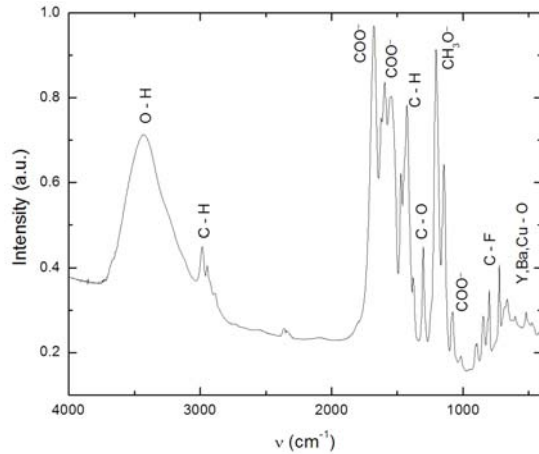
Figure 3. FTIR spectra of the YBCO dried gel at 110 ^{0}C. The sample presents the COO characteristic vibration frequencies at 1681 cm^{-1}, as well as the skeletal vibration of propionates at 1076 cm^{-1}.

3.2 YBCO film growth and characterization

To obtain epitaxial YBCO superconducting films the precursor films undergo a two step heat treatment. First, they were heat treated up to 400°C under humidified oxygen (about 17 Torr H$_2$O and balance oxygen) as follows: up to 80°C with 10°C/min, up to 200°C with 2°C/min, up to 250°C with 0.5^{o}C/min and finally to 400°C with 10°C/min, and then cooled to room temperature in the same nominal gas environment (Figure 4). The high temperature thermal treatment (Figure 5) has been performed at 800°C and 850°C, at a rate of 10°C/min, for about two and one hour, respectively in an environment of humid oxygen and nitrogen (about 17 Torr H$_2$O, oxygen pressure 70 miliTorr and balance nitrogen) and another 10 minutes in the dry mixture of oxygen and nitrogen (70 miliTorr oxygen and balance nitrogen). The film was cooled to about 450°C in the same nominal gas environment at a rate of 10°C/min, held at this temperature for 1 hour in oxygen and subsequently cooled to room temperature.
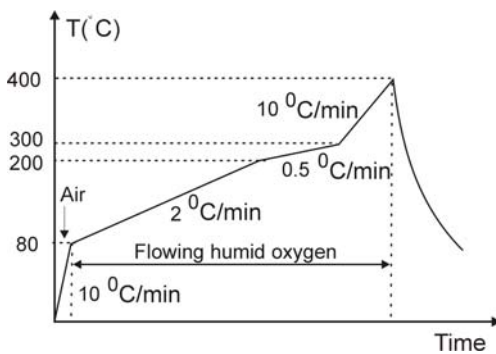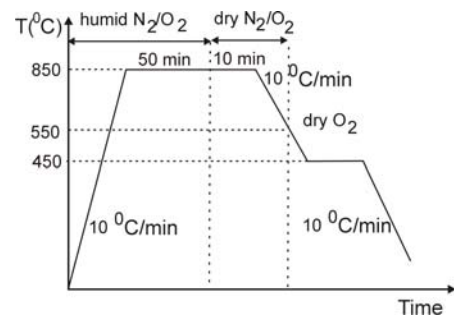

Figure 4. Pyrolysis heat treatment.

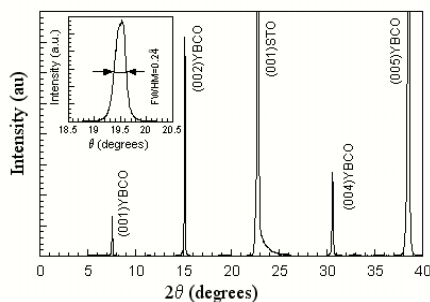*Figure 5. Crystallisation heat treatment.*

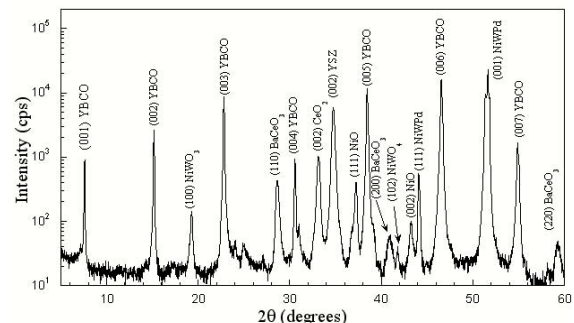*Figure 6. X-ray diffraction pattern of YBCO film on (100) SrTiO$_3$ substrate.*

Figure 7. X-ray diffraction pattern of YBCO on CeO$_2$/YSZ/CeO$_2$/Pd buffered Ni-5at.%W substrate.

The X-ray θ–2θ scans (Figures 6 and 7) both for the YBCO/STO and YBCO/CeO$_2$/YSZ/CeO$_2$/Pd/Ni-W films present only (00l) YBCO peaks indicating that the films have a high degree of epitaxy with the *c*-axis perpendicular to the substrate. As it can be seen from figure 7, besides the peaks corresponding to the YBCO/ CeO$_2$/YSZ/CeO$_2$/Pd/Ni-W structure, the X-ray diffraction pattern exihibits also the peaks corresponding to NiO, NiWO$_4$ and BaCeO$_3$. The nickel oxide and the NiWO$_4$ compound are mainly formed during the deposition by PLD of the first CeO$_2$ layer [5], while the BaCeO$_3$ is formed at the interface between the CeO$_2$ cap layer and the YBCO film during the growth thermal treatment at 850^0C. The peaks corresponding to Pd are not observed, indicating that Pd is completely diffused into the Ni-W substrate during the deposition at high temperature, both of the CeO$_2$ cap layer and the YBCO film. The formation of a superficial layer of Ni-W-Pd solid solution is confirmed by the peaks very close to the Ni-W (200) reflection. The ω-scan of the (005) peak for the YBCO/STO film has a full-width at half-maximum (FWHM) of 0.24 °, close to that observed in the YBCO films grown by PLD. The rocking curve (Figure 8) through the (002)Ni-W, (002)CeO$_2$, (002)YSZ peaks along the transverse direction (TD) and (005)YBCO peak along the rolling direction (RD) have an out-of-plane FWHM of 8.2°, 4.2°, 4° and 1.9°, respectively. The improvement of the CeO$_2$ texture is an effect of the Pd film, which has a sharper texture with respect to the Ni-W substrate [5]. On the other hand, the lattice mismatch between CeO$_2$ and Pd is 1.6%, much smaller than that between CeO$_2$ and Ni of 8.4%. The YBCO film grown at 850^0C on the CeO$_2$/YSZ/CeO$_2$/Pd/Ni-W architecture has an excellent out-of-plain texture with $\Delta\omega$=1.9^0 for the (005) reflection.
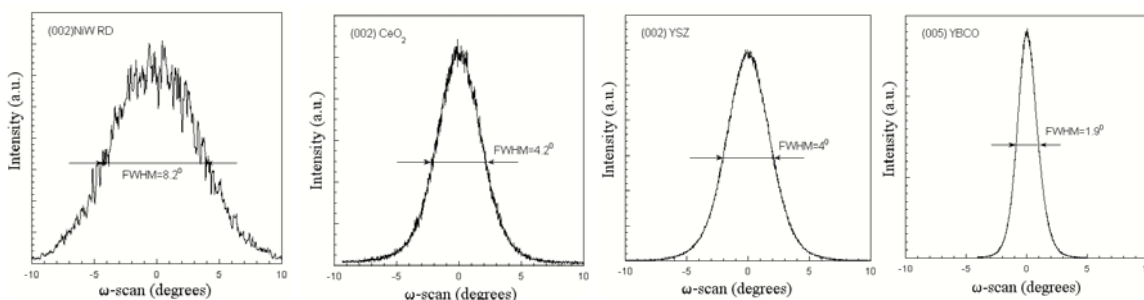

Figure 8. φ -scan through the (002)Ni-W, (002)YSZ, (002)CeO$_2$ and (005)YBCO peaks.

The YBCO film deposited by spin coating under the conditions described above has the thickness of about 0.6 μm. The surface morphology of the YBCO film grown on the CeO$_2$/YSZ/CeO$_2$/Pd/Ni-W architecture is shown in Figure 9. A surface free of cracks, but with some holes can be seen. In spite of the voids, the *c*-axis oriented grains are well connected over the pores, as it can be seen from the high magnification SEM image (Figure 9 right). The spherical particulates are nanocrystallites of CuO [3]. It is to be noted that no needle-like particulates representing *a* or *b*-axis oriented YBCO grains were observed. The high magnification SEM image reveals that the voids are at the surface of the YBCO film and, therefore, the film can be considered electrically continuous. The films grown on STO have the same morphology. At the same time, the morphology of the YBCO film is similar with that of the film grown by the trifluoroacetate precursors (TFA-MOD) [6].
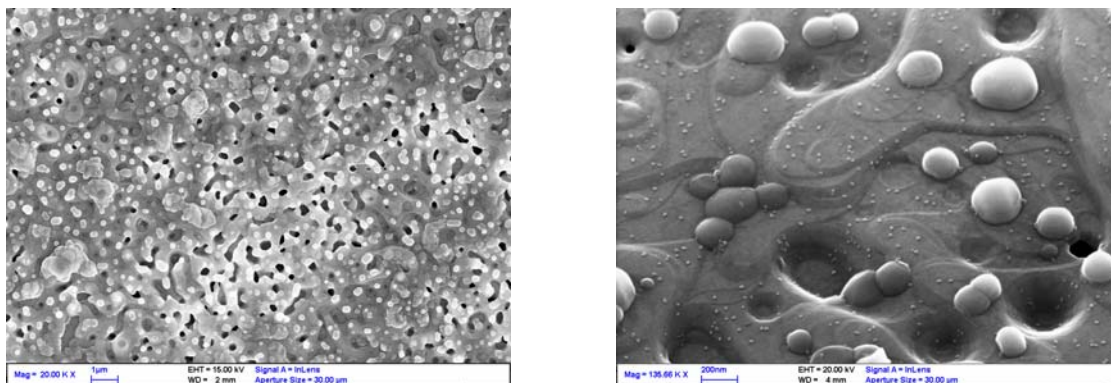
Figure 9. SEM image of YBCO film grown on CeO$_2$/YSZ/CeO$_2$/Pd buffered Ni-W substrate at 850^{0}C at two different magnifications (left 20.00 K X and right 135.66 K X).

The electrical resistance versus temperature for the YBCO films grown at different temperatures is presented in Figure 10. The YBCO film grown on STO at 800^{0}C exhibits a lower critical temperature (T$_c$(R=0)=88K) and a nonlinear behavior in the normal state with the ratio R(300)/R(100)=2. On the contrary, the films grown at 850^{0}C on both STO and NiW exhibit a linear behavior of the electrical resistance in the normal state with the ratio R(300)/R(100) of 3 and 3.3, respectively, close to the intrinsic value of the optimally doped YBCO. The zero resistance critical temperature (T$_c$(R=0)) is 91.3 K and 91.6 K, respectively. Nevertheless, the films grown at 850^{0}C have a two step transition, indicating a multiphase system. This behavior is more evident for the YBCO film on NiW, where two sharp transitions (ΔT=1 K) can be observed, one with the T$_{conset}$=94.7 K and another one with the T$_{conset}$=92.5 K. The volume fraction of the two phases, estimated from the resistance change, is of about 50%. The presence in the film of a high amount of phase with high transition temperature (T$_c$(R=0)=93 K) should improve the superconducting carrying capacity. The critical current density versus magnetic field at 40K for the YBCO film grown on (100) SrTiO$_3$ at 850 ^{0}C is presented in Figure 11. The critical current density was derived from the M(B) curves at different magnetic field using the Beam critical state model.
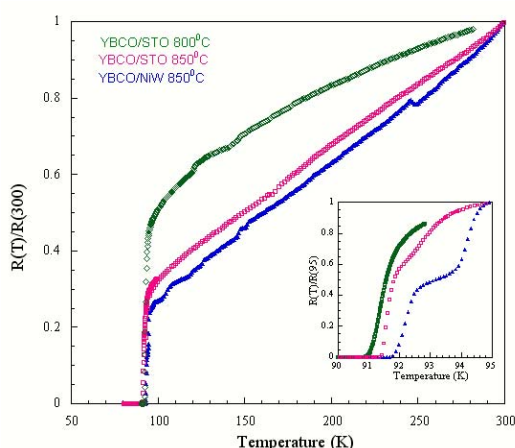

Figure 10. Electrical resistance versus temperature for the YBCO film grown on (100) SrTiO$_3$ at 800 ^{0}C (green) and 850^{0}C (red) and for the YBCO film grown at 850^{0}C on CeO$_2$/YSZ/CeO$_2$/Pd buffered Ni-5at.%W substrate (blue).
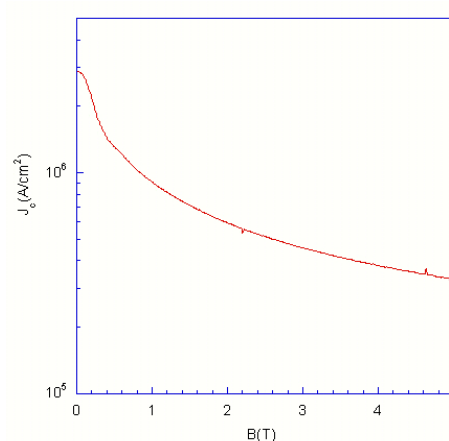
Figura 11. Critical current density vs magnetic field at 40K for the YBCO film grown on (100) SrTiO$_3$ at 850 ^{0}C.

3. <u>Conclusions</u>

A modified TFA-MOD method for the deposition of YBCO films was studied. With respect to the conventional TFA-MOD, the yttrium and copper trifluoroacetates were replaced by the alcoholic solution of Cu and Y acetates dispersed in propionic acid. The method presents several advantages such as: eliminates the evolvement of hydrofluoric acid and, as a result, permits the deposition of thicker YBCO films, overcomes the problems related to the sublimation of copper trifluoroacetate and shortens the conversion time of the precursor film. The YBCO film grown both on (100) $SrTiO_3$ and CeO_2/YSZ/CeO_2/Pd buffered Ni-5at.%W substrate exhibits good morphological, structural and superconducting properties with T_c(R=0) greater than 91K and an out-of-plain texture with   . of 0.24^0 and 0.19^0 , respectively.

References

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[5] **G. Celentano, V. Galluzzi, A. Mancini, A. Rufoloni, A. Vannozzi, A. Augieri, <u>T. Petrisor</u>, <u>L. Ciontea</u> and U. Gambardella,**   *"YBCO coated conductors on highly textured Pd-buffered Ni-W tape"*, Journal of Physics: Conference Series 43 (2006) 158–61.

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2. **V. Galluzzi, A. <u>Augieri,</u> <u>L. Ciontea</u>, G. Celentano, F. Fabbri, U. Gambardella, A. Mancini, <u>T. Petrisor</u>, N. Pompeo, A. Rufolonu, E. Silva, A. Vannozzi**, *"YBa2Cu3O7-δ films with BaZrO 3 inclusions for strong-pinning in superconducting films on single crystal substrate",* IEEE Transactions on Applied Superconductivity 17 (2), pp. 3628-3631 (2007).

3. **A. Vannozzi, A. Augieri, G. Celentano, <u>L. Ciontea</u>, F. Fabbri, V. Galluzzi, U. Gambardella, A. Mancini, <u>T. Petrisor</u>, A. Rufoloni**, *"Cube textured substrates for YBCO coated conductors: Influence of initial grain size and strain conditions during tape rolling"*, IEEE Transactions on Applied Superconductivity 17 (2), pp. 3436-3439 (2007).