**YBa$_2$Cu$_3$O$_{7-x}$ films prepared by TFA-MOD method for coated conductor application**

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**Abstract.** The epitaxial growth of YBCO films both on (001) SrTiO$_3$ (STO) and Ni-W biaxially textured metallic substrates prepared by metal-organic deposition (MOD) using a trifluoroacetic acid (TFA) solution is reported. The degree of epitaxy of the YBCO films was investigated by X-ray diffraction and scanning electron microscopy (SEM). The as deposited films exhibit good morphological and structural properties. The $\omega$-scan of the YBCO films grown on (001) SrTiO$_3$ single crystal substrate and on Pd/CeO$_2$/YSZ/CeO$_2$ buffered biaxially textured Ni-5at%W (Ni-W) tapes has a full width at half maximum (FWHM) of 0.12° and 3.4°, respectively. The $\phi$-scan of (113) peak of YBCO film grown on Ni-W substrate has FWHM of 6.1°. The YBCO/STO film has a zero resistance critical temperature of $T_c(R=0)=92$ K and a critical current density $J_c>2$ MA/cm$^2$ at 77 K and in zero magnetic field.

1. Introduction

The scaling up of the YBCO film deposition represents the main challenge in the field of second-generation coated conductors fabrication. Due to their composition versatility, wide flexibility in processing conditions, precise stoichiometric control and their relative simplicity (low cost non-vacuum method), the chemical solution deposition (CSD) methods for epitaxial thin films fabrication have gathered a constant scientific interest for the development of superconducting materials. In the early time, there were three commonly used methods applied for the YBCO deposition [1, 2, 3]: 1) sol-gel process using alkoxides and 2-methoxyethanol as reactant and solvent; 2) hybrid processes that use chelating agents such as acetylacetone or diethanolamine to reduce alkoxide reactivity and 3) metal-organic decomposition (MOD) techniques that use high molecular weight precursors and water-insensitive carboxylates, 2-ethylhexanoates, etc. [4]. It has been demonstrated that the trifluoroacetate (TFA) precursors are most suitable for the epitaxial YBCO deposition [5]. In the TFA-MOD method, a fluorine containing coating solution decomposes to fluorides which, in turn, undergo different chemical reactions during the high temperature firing process (700-800 °C) in controlled atmosphere to convert to oxides [6, 7, 8]. The main advantage of the fluorine-containing precursors for the superconducting YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) films consists in their carbonate free decomposition and, as a consequence, no barium carbonate occurs as an intermediate phase, which can interfere kinetically with the formation of the superconducting YBCO phase, altering its transport properties.
In this paper, we report on the structural and morphological characterization of epitaxial YBCO films grown both on (001) SrTiO$_3$ single crystal substrates and Pd/CeO$_2$/YSZ/CeO$_2$ buffered biaxially textured Ni-W tapes, by the TFA-MOD method.

2. Experimental details

The precursor solutions for YBCO were prepared by sonicating the mixture of Y, Ba and Cu acetates in a 1:2:3 cation ratio with a stoichiometric quantity of trifluoroacetic acid in de-ionized water. The resulted solution was slowly dried at low temperature (50 °C) both in air (TFA1) and under vacuum (TFA4) to form a glassy blue resin. Methyl alcohol was then added to dissolve the resin and to adjust the concentration of the metal ions in the final solution to 1.52 mol/dm$^3$.

The precursor solution was deposited both on (001)-oriented SrTiO$_3$ (STO) single crystals and on Ni-W/Pd/CeO$_2$/YSZ/CeO$_2$ templates by spin coating. The samples were spinned at 4000 rpm for about 120 s. The resulted gel films were treated in two heating stages in order to obtain the YBCO superconducting films. In the first stage, the precursor films were slowly heated at 400 °C in a humid oxygen atmosphere (25 °C dew point) in order to decompose the precursors in metal oxy-fluorides. From 400 °C to room temperature the samples were cooled in stagnant humid oxygen. The as resulted oxyfluoride films were subsequently transformed in YBCO by annealing at 800 °C in humid nitrogen-oxygen gas mixture (dew point 30 °C) with a partial oxygen pressure of 5×10$^{-3}$ atm. The heat treatment used in this work is the same as that reported by McIntyre et al. [6]. The thickness of the YBCO films obtained under these conditions is of about 200 nm.

3. Results and discussion

3.1 Morphological properties

The surface morphology of the YBCO film grown on STO is shown in figure 1a. Needle-like particulates represent $a$ or $b$-axis oriented YBCO grains. These particulates are also observed in the YBCO films grown by PLD on single crystal substrate. 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.

Furthermore, the YBCO grains are connected over pores. This explains the high value of the critical current density ($J_\text{c}>1$ MA/cm$^2$ at 77 K and zero magnetic field) of the YBCO/STO films. The spherical particulates are nanocrystallites of CuO [8]. The morphology (figure 1b) of the YBCO/ CeO$_2$/YSZ/CeO$_2$/Pd/Ni-W films is very similar with that on single crystal. Nevertheless, the density of voids and spherical particulates is considerably greater. The high magnification SEM image reveals that the voids are at the surface of the YBCO film and, therefore, the film can be considered continous.

3.2 Structural properties

The X-ray $\theta$-2$\theta$ scans for the YBCO/STO film presents only (00l) peaks indicating that the film has a
high degree of epitaxy with c-axis perpendicular to the substrate. The \(\theta-2\theta\) scan of YBCO (005) peak has a full width at half maximum (FWHM) of 0.12°, close to that observed in the YBCO films grown by PLD. The XRD pattern of \(\theta-2\theta\) scans for YBCO/CeO\(_2\)/YSZ/CeO\(_2\)/Pd/Ni-W is presented in figure 2a. As for the YBCO/STO film, the XRD pattern exhibits only the (001) YBCO peaks. No (k00) reflections, due to \(a\)-axis oriented grains, were observed. The (002) to (111) peak intensity ratio is of about 10\(^2\) for both films. 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 YBCO film. However, 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. Due to the oxidation of the substrate, in the regions where the buffer layer was not deposited (under the clamps), NiO and NiWO\(_4\) peaks are also observed.

The rocking curve (figure 2b) through the (002)Ni-W, (002)YSZ, (002)CeO\(_2\) and (005)YBCO peaks have an out-of-plane FWHM of 8.8°, 4.2°, 3.8° and 3.4°, respectively. The small values of the FWHM for the YSZ and CeO\(_2\) with respect to the Ni-W substrate is correlated with the Pd film [9, 10]. The pole figures have revealed the presence of a well developed single component \([100][001]\) cube texture both for the Ni-W substrate and for the YBCO film. The in-plane crystallographic relationship of the structure is \([100]YBCO||[110]CeO\(_2\), \([110]YSZ||[100]Ni-W\). The FWHM of \(\varphi\)-scans of (113)YBCO, (111)CeO\(_2\), (111)YSZ and (111)Ni-W peaks are 6.1°, 6.3°, 6.4° and 7.5°, respectively.

3.3 Superconducting transport properties

In figure 3a the \(\rho(T)\) curves for two YBCO films deposited on STO starting from different TFA precursor solutions are reported. Both samples exhibit a linear decrease with RRR=\(\rho(300 \text{ K})/\rho(100 \text{ K})\) > 3 and a very low resistivity close to the intrinsic value of the optimally doped YBCO. The high quality of the YBCO films are confirmed by the \(T_c\) values (90.7 K) and the reduced transition widths (\(\Delta T\sim 1.5 \text{ K}\)) (see inset from figure 3a). Accordingly, both samples show similar \(J_c\) values and magnetic field dependences. In figure 3b \(J(B)\) curves at three different temperatures for the YBCO TFA4/STO are plotted. The \(J_c\) values as high as 1 MA/cm\(^2\) are reported at 84 K, reaching 2.7 MA/cm\(^2\) at 77 K. The drop of the \(J(B)\) in the low field region is balanced by a reduced sensitivity of \(J_c\) at higher fields. The YBCO films deposited on buffered Ni-W metallic substrates showed similar high \(T_c\) up 90.5 K with slightly broader transitions (\(\Delta T\sim 2-2.5 \text{ K}\)) still indicative of a remarkable homogeneity of the film.

4. Conclusions

The YBCO films with a high degree of epitaxy were grown by the TFA-MOD process, both on (100)SrTiO\(_3\) single crystal and Pd/CeO\(_2\)/YSZ/CeO\(_2\) buffered Ni-5at.%W. The X-ray study revealed that the Pd film has a better in-plane and out-of-plane texture with regard to the Ni-W substrates. This explains the excellent structural properties of the YBCO film grown on the as buffered substrate. The SEM investigation have revealed that the YBCO film on Ni-W has a good surface with well connected c-axis oriented grains that suggests good transport properties. The present study has demonstrated that
the CeO$_2$/YSZ/CeO$_2$/Pd buffer layer architecture is adequate for the manufacturing of long YBCO tapes on Ni-W substrates. The future activity will be focused on the preparation and electrical characterization of long YBCO superconducting tapes.

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![Figure 3](image-url)