Use of polymeric compounds to produce thick YBCO films by TFA-MOD process

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Abstract. One route to achieve thick YBCO layers by a single deposition on single crystal substrates (LAO) has been to modify the viscosity of the solution by using different polymeric agents in precursor solutions. A screening investigation of several polymers with different molecular weights has been performed to choose the best additive based on the following criteria: to increase viscosity, to avoid any chemical reaction with the precursors and to keep the same decomposition temperature as compared to the pyrolysis of the TFA precursors. Solution viscosity, thermal and thermo-gravimetric analysis measurements have been used to characterize the TFA solutions with the additives. An increase of the YBCO films thickness of 100% ($\geq 600$nm) has been demonstrated keeping a high $J_c \geq 1.1$ MA/cm$^2$ (77K).

1. Introduction
Superconducting power transmission cables are regarded as one of the most promising applications of high temperature oxide superconductors. In this point of view, high temperature superconducting thin/thick films, especially YBa$_2$Cu$_3$O$_7$ (YBCO), deposited on various substrates have attracted much attention in recent years because of their unique properties of high quality film, high critical temperature ($T_c$) and high critical current density ($J_c$). The chemical solution deposition techniques are very promising compared with the more expensive physical ones. The choice to use trifluoroacetate (TFA) precursors has been based on the objective to avoid BaCO$_3$ phase which is very stable. Indeed, the main advantage of this approach is to lead to BaF$_2$ as a final product, after decomposition of the metal-organic precursors: BaF$_2$ is then more easily converted to oxide. Physical deposition techniques, like pulsed laser deposition (PLD), are effectively used to produce thick films [1]. It has been also demonstrated the routinely preparation of 2 $\mu$m thick YBCO films by the method of photo assisted MOCVD [2]. However, it has been shown that a strong dependence of the critical current density with the film thickness exists, whatever the technique: PLD [3, 4], sputtering [5] or the BaF$_2$ process [6]. Beside this, most of the researchers working with solution deposition process developed a multiple deposition approach. The YBCO deposition was usually repeated two or three times along with heat treatment [7, 8]. It has been shown the feasibility of a 1$\mu$m thick YBCO layer by a single deposition and it has also been demonstrated the increase of the $I_c$ with the film thickness and a relatively lower dependence of the $J_c$ with the thickness [9]. We
have taken advantage of the flexibility of the MOD process in terms of solution modification and successfully increased the TFA solution viscosity by adding a polymeric compound. Several organic products have been investigated. In this paper, we demonstrate a new methodology to achieve the preparation of thick YBCO layers by a single deposition on single crystal LaAlO$_3$ (LAO) substrates using organic additives to modify the solution viscosity. The main idea was to increase the viscosity of the TFA solution and then increase the YBCO film thickness.

2. Experimental
The detailed preparation of the coating solution for the TFA-MOD method is reported in another paper [10]. The "mother solution" has been modified by adding a certain percentage of the studied additive. The solutions were deposited onto 5*5 mm (00l)-oriented LaAlO$_3$ (LAO) single-crystal substrates by means of a spin coater or dip coater. Substrates were cleaned in successive ultrasonic baths of acetone and methyl alcohol with cleaning cycles typically lasting 5 min. Substrates were finally dried with pure N$_2$ gas. A spinning rate of 6000 rpm and an acceleration time of 1 second were used in depositing the precursor films by spin coating. The samples were spun for 2 min. Spin and dip coating experiments were performed in a controlled atmosphere to minimize water contamination. The dip coating technique offers the opportunity to vary the withdrawal speed (from 1.3 to 25.4 cm/min in our case). The viscosity of each freshly prepared solution was systematically measured with a rheometer Haake RheoStress 600. Two different expressions show the dependence of the thickness with the viscosity, according to the method of deposition considered. In both cases spin [11] and dip coating [12], the film thickness is proportional to the viscosity. The aging of the solutions was also analysed by systematic measurements of the viscosity after a determined period of time. The film thickness after pyrolysis and/or after growth was determined through direct measurements with a profilometer. Surface morphologies were also observed by optical microscopy (after pyrolysis) and more deeply by Scanning Electron Microscopy (SEM) after growth. X-Ray Diffraction (XRD) was used to ascertain the phase purity and determine the texture quality. Electrical resistivity and $J_c$ inductive measurements were used to investigate the superconducting properties of the films.

3. Results and discussion
The determination of the best additives has been made taking into account two major parameters: the increase of the viscosity and the thermal decomposition of the prepared solution.

3.1. Viscosity characterization.
Different families of additives have been used, which have different organic functions, leading to the modification of the viscosity of the TFA solution in different ways. A fundamental property of the additive is to be chemically inert to the TFA solution. This property has eliminated several compounds. The measurements of viscosity have allowed us to distinguish two polymeric compounds: polyvinylpyrolydone (PVP) and the polyethylene glycol (PEG). Figure 1 shows the values of viscosities obtained with 10% of PVP and PEG. And with this single result, it seemed obvious that PVP is the best candidate to increase the viscosity of the TFA solution.

3.2. Thermal decomposition.
The TGA data of the PEG and the PVP have been recorded under the same conditions, and are presented in figure 2. The PEG is totally decomposed at 200°C; whereas the PVP requires more energy, finishing its decomposition at 650°C. It has been shown previously that TFA precursors are all decomposed at 310°C. The TGA results, combined with the viscosity measurements, have determined the PEG as the most promising additive to produce thick YBCO films with the TFA-MOD process. TGA (figure 3) and DTA data were obtained for the gels dried from the TFA precursor solution without additive and the same solution with PEG.
The thermal decomposition processes were clearly different for the two gels (figures 4 and 5). The DTA of the gel without PEG (figure 4) displays three major exotherms. The first extends from 200°C to 270°C, the second lies between 290 and 300°C and finally the last exotherm appears at 310°C. The two last exotherms are very close. This observation is consistent with the possible decomposition of the Y(TFA)$_3$, Ba(TFA)$_2$ and Cu(TFA)$_2$ separately. The TGA shows two major weight losses. The first one probably corresponds to the decomposition of Cu(TFA)$_2$. The second and third one, more abrupt, are in agreement with the nearly simultaneous decomposition of the two others precursors.

The solution fabricated with PEG (figure 5) displays a single major exotherm, of which the maximum is approximately at 260°C. From DTA experiments we conclude that all decomposition
occurs in a smaller temperature range. And TGA data shows a more abrupt weight loss. The main result of this experiment is the evident positive influence of the additive on the decomposition of the TFA precursor solution. The temperature range of decomposition becomes sharper.

3.3. YBCO film preparation and characterization.
Several additives have been used to prepare divers solutions. From the previous results of viscosity and thermal decomposition, the further investigation has focused on the use of PVP and PEG. The two solutions have been spin or dip coated on LAO single crystals. The polyvinylpyrrolidone leads to layers with defaults like cracks or dewetting, due to too high evaporating point of this compound. Different solutions with different quantities of PEG$_{8000}$ have been prepared. With 50% of PEG$_{8000}$, the thickness of the deposited layers reaches a critical limit that irremediably causes cracks during the pyrolysis step. 40% of PEG$_{8000}$ in the TFA solution seems to be the highest quantity that can be used to produce thick and continuous YBCO films. Nevertheless, the superconducting properties of these layers are low and SEM investigations showing a porous layer have explained this result. An optimization of the growth process should solve this difficulty. The results obtained with 30% of PEG$_{8000}$ are the more promising of the series investigated. The YBCO films, 600 nm thick, show very few pores, much more homogeneous than with 40% of PEG. The reproducibility of the good morphology of the 30% PEG$_{8000}$ films has been demonstrated. Their characterization by XRD reveals a good epitaxial growth on LAO single crystals. Concerning the superconducting properties, we have systematically measured the critical current density (J$_c$) of each sample. Thus, we have determined a dependence of the J$_c$ with the thickness. Results are represented in figure 6. It appears clearly that the critical current density is higher than 1 MA/cm$^2$ at 77K and no thickness dependence of J$_c$ can be detected within the investigated range, in agreement with previous results in TFA YBCO films.

4. Conclusions
The feasibility of growing thick YBCO films by a single deposition chemical process has been demonstrated, using organic compounds as additives to modify the viscosity of the solution. Polyethylene glycol gives the most promising results and high quality films up to 600 nm have already been obtained. The physical properties are not damaged by this modification and a
Figure 6. Critical current density at 77K of YBCO-PEG_{8000}-TFA films vs. film thickness

A reproducible value can be reached ($J_c = 2 \times 10^6$ A/cm$^2$). With higher quantities of PEG, higher film thickness has been obtained after pyrolysis but further improvements of growth conditions are required.

Acknowledgments
This work has been financed by the EU within the scope of the SOLSULET project, contract No G5RD-CT2001-00550, by the Spanish CICYT (MAT02-02642) and by the Generalitat de Catalunya (2001-SGR-00336 and CeRMAE).

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