Fast calcination of purified Trifluoroacetate metal-organic precursors for high critical current YBa$_2$Cu$_3$O$_7$ thin films

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Abstract. A new processing schema is proposed to fasten the metal-organic decomposition step required to grow high critical current YBa$_2$Cu$_3$O$_7$ thin films based on Trifluoroacetates (TFA). AFM and optical microscope study of quench samples at different temperatures have been performed to determine the temperature window where strong stresses are generated. The thickness evolution with the temperature has been observed and linked to the final microstructure. The influence of the gas flow and temperature annealing ramp for two different types of solution has been investigated. We demonstrate that high critical current YBa$_2$Cu$_3$O$_7$ thin films, i.e. $J_c = 3\text{MA/cm}^2$, with thickness of 300 nm can be grown with a new fast calcination process lasting only 60 min. This fastened calcination process allows to enhance the coated conductor production rate without the need of any modification of the metal-organic precursor solutions.

1. Introduction
Nowadays, metalorganic deposition process using trifluroacetates (TFA) has become one of the most promising methods for fabrication of YBa$_2$Cu$_3$O$_7$ (YBCO) coated conductors because good reproducibility and high critical current density films are achieved at low cost [1-4]. The growth of superconducting epitaxial YBCO films by means of chemical solution deposition process is a complex one which involves three different stages- the pyrolysis step, the growth process, and finally an oxygenation annealing step. The pyrolysis process generates a homogeneous porous nanocrystalline film formed by CuO, Y$_2$O$_3$ and BaF$_2$ following a decomposition reaction which is still poorly known

$$\text{Cu (TFA)$_2$ + Ba(TFA)$_2$ + Y(TFA)$_3$ + H}_2\text{O + O}_2 \rightarrow \text{CuO + BaF}_2 + \text{Y}_2\text{O}_3 + \text{non identified volatile products} \quad (1)$$

This is an exothermic process which occurs at about 250-300$^\circ$C and the composition of the generated volatile products is still not known in details [5, 6]. The volatilization of organic solvents and/or the decomposition of the gel film may cause pores, and the strong film shrinkage generated during the pyrolysis step may lead to macroscopic inhomogeneities, such as cracks or film buckling [7, 8]. Obtaining homogeneous crack-free fluoride-containing solid film through the pyrolysis step is very important for fabricating high quality YBCO films. Consequently, a very slow pyrolysis process (8-20h) has been widely used in the past to control the decomposition [1-3], however, this process is not suitable for the fabrication of long length YBCO-coated conductor by continuous reel-to-reel method.
To solve this problem several authors have proposed to change the composition of the TFA precursors, either using diethanolamine additives [4], or reducing the F content of the metalorganic precursors using Cu-naphthenate [3].

In this work we will demonstrate for first time that high critical current YBa$_2$Cu$_3$O$_7$ thin films, i.e. $I_c=3\text{MA/cm}^2$, with film thickness of $\approx 300\ \text{nm}$ can be grown following a new fast calcinations process, lasting only 60 min. Our successful approach is achieved using purified TFA precursors by controlling the key parameters of the pyrolysis process- time, temperature, heating ramp and gas flow velocity.

2. Experimental details

Two types of purified solutions are presented. The first one is prepared from YBCO commercial powders dissolving in a stoichiometric quantity of trifluoroacetic acid, following [9]. The other one is obtained following alternative method which has been detailed elsewhere [10]. Film deposition was performed by spin coating at typical rotation speed of 6000 rpm and acceleration of 3000 rpm s$^{-1}$ on LaAlO$_3$ single crystal substrates. The first calcinations process was carried out following the heat profile in fig.1. Then the samples were heated with a temperature ramp of 1500°C/h up to 795°C with a high temperature hold of 180 min under a humid nitrogen/oxygen atmosphere, and later oxygenated at 450°C for 5h. The film thickness was controlled with a profilometer, and for all samples after growth, it is around 300 nm. FT-IR spectra have been obtained to determine the TFA decomposition time at different temperatures. XRD was used to analyze the texture quality while AFM, TEM and SEM were used to analyze the film microstructure.

3. Results and discussion

Through identification of the absorption line in the FT-IR spectra due to the carboxyl group, the decomposition of the TFA precursors could be easily determined at different temperatures. It was found [10] that using a heating ramp of 300°C/h up to 310°C and a hold time of 30 min allowed to reach a full decomposition of the TFA precursor. We decided therefore to investigate a new heating profile, fig.1, where the dwell time is limited to 30 minutes at 310°C. This process would be extremely shortened as comparison with previously used (~20h) [2].

We further investigated the pyrolysis process through a study of quench samples from 200°C, 250°C, and 310°C after a constant heating ramp of 300°C/h and a constant gas flow 4.4 mm s$^{-1}$. These experiments allowed to determine the temperature window, where big stresses are generated. The thickness dependence of the films on the annealing temperature, fig.2, shows three different temperature domains in the large interval from room temperature to 795°C. In the first one (1), from room temperature to 250°C, the thickness is reduced by 11%, so, we relate it to solvent evaporation and/or a slight decomposition of the precursors. The second range, marked by (2) in fig.2, extends between 250°C and 310°C and presents clear evidence of a strong film shrinkage (66%) due to the TFA decomposition. At this stage the film pyrolysis has been completed. Finally, the film thickness changes by 9% in the last interval (3) (fig.2.), extending from 310°C to 795°C where the crystallization of the YBa$_2$Cu$_3$O$_7$ phase occurs [11, 12].

Figure 1. The temperature heating profile of our decomposition process.  
Figure 2. Film thickness evolution with the temperature, when a heating ramp of 300°C/h is used during the pyrolysis step.
In Fig. 3 we show the AFM and optical microscope images of the quenched samples from 250°C and 310°C, respectively. It is clear by observing the smoothness of the films that a heating ramp of 300°C/h up to 250°C does not destroy the integrity of the film while it causes macro scale inhomogeneities when the films are heated up to 310°C. The stress, produced by the shrinkage occurring during the solvent drying and the decomposition of the TFA precursor, can relax in three different ways that can lead to smooth films or to film displaying buckling or cracking [7, 8]. The last two are suggested to be unfavourable from the point of view of superconducting performances. So, we decided to keep the heating ramp of 300°C/h up to 250°C, where the decomposition reaction is only being initiated, while the heating ramp R2 in the range 250-310°C would be modified in parallel with the gas flow velocity. The existing relationship between temperature annealing ramp and gas flow rate arises from the fact that both parameters control the decomposition reaction (1) which involve an homogeneous generation of gas exhaust.

As a criterion, in our study we used optical microscope images to ascertain the film quality. We classified as “good” samples those exhibiting smooth and homogeneous surfaces while those classified as “bad” exhibited some kind of macroscopic inhomogeneity (buckling or macro-cracks). Actually these, last, films after the growth process display very poor superconducting properties. So, we modified the heating ramp from 3°C/h to 1200°C/h, between 250 and 310°C, while the gas flow rate was modified within the range 0 to 25 mm s⁻¹. This investigation allows us to define a range of processing parameters (heating ramp and gas flow rate) where the film integrity was preserved (fig. 4).

The study has been carried out for two types of TFA precursor solutions. For both of them the deposition conditions were the same. Also, the film thickness after growth was found to be independent from the water content. The hatched region in fig. 4 corresponds to the region where homogeneous films are obtained for both solutions. For the solution without water this homogeneous zone is more extended. We note that these purified solutions could be fully pyrolyzed in a process which lasted only about 60 minutes. This is certainly a very significant progress as compared to the previous very long process which lasted about 20h [2]. Finally, we have investigated the microstructure of the YBCO films after pyrolysis, prepared with conditions from the hatched zone on
fig. 4, preserving good nanoscale homogeneity as it can be seen in the AFM and TEM photos (fig. 5). Note that, as expected, more of the generated nanometric particles remain smaller than those previously observed with longer decomposition times [13]. X-ray diffraction θ-2θ and texture analysis of these films showed a quality similar to those previously prepared using long pyrolysis procedures [1-6]. The typical critical current density of fast-calcinated films is \( J_c \approx 3 \text{MA/cm}^2 \) at 77K, thus confirming its high quality.

Figure 5. AFM (a) and TEM (b) images of an YBCO film after pyrolysis, prepared following a fast calcination scheme, show good nanoscale homogeneity.

4. Conclusions
We have demonstrated that a control of the pyrolysis process is essential to achieve the high quality superconducting YBCO films. We have identified three highly relevant temperature intervals associating different processes—evaporation of the solvent and initiation of the pyrolysis, decomposition of TFA precursors and crystallization. We have studied the relationship between temperature annealing ramp and gas flow velocity to shorten the pyrolysis process while preserving high quality pyrolyzed films. Our work has demonstrated that high critical current \( Y_{Ba_2Cu_3O_7} \) thin films, i.e. \( J_c = 3 \text{MA/cm}^2 \), with thickness of \( \approx 300 \text{ nm} \) can be grown with a new fast calcination process lasting only 60 min. This fastened calcination process allows to enhance the coated conductor production rate when purified metal-organic TFA precursor solutions are used.

Acknowledgments
This work has been financed by 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). KZ and JG acknowledge financial support to the Spanish Ministry of Education and Science through the FPU program.

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