Preparation of anhydrous TFA solution for deposition of YBa$_2$Cu$_3$O$_{7-x}$ thin films

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Abstract. The realisation of superconducting thin films by MOD is possible using different precursors; among them, the most promising approach is the use of trifluoroacetates (TFA-MOD). However, one of the major drawbacks of this approach is the generation of water when trifluoroacetic acid (TFAH) is used. In this case, a lengthy purification process of the solution is necessary. As an alternative, trifluoroacetic anhydride (TFAA) has been used affording anhydrous TFA solutions without any additional purification. Anhydrous TFA solutions have allowed YBa$_2$Cu$_3$O$_{7-x}$ films to be obtained with high critical currents ($J_c$ > 3-4 MA/cm$^2$ at 77K, thickness 300nm).

1. Introduction

Chemical solution deposition is a very promising methodology to prepare superconducting materials. The Metal Organic Decomposition (MOD) process [2-4,8,9] of YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) preparation using metal trifluoroacetate (TFA) precursors [1,5-7] is considered to be a strong candidate as a low cost process for coated conductor production, since the TFA-MOD process is basically a non vacuum process. Additionally, it has been well confirmed that this process is able to provide high performance superconductor films with critical currents in the range of $J_c$~3-4 MA/cm$^2$. However, to obtain high $J_c$ YBCO films by TFA-MOD, a purified coating solution is necessary, because the presence of other impurities in solution deteriorates the films quality and thus the superconducting properties. The generation of water is described of one of the major drawbacks in the trifluoroacetic acid (TFAH) approach [10]. That implies a lengthy purification process of the TFA solution to be able to prepare high quality YBCO films.

In the present work an alternative process, starting from trifluoroacetic anhydride (TFAA), to obtain pure TFA solution (< 1ppm of water) is proposed. In this way we are able to grow YBa$_2$Cu$_3$O$_{7-x}$ films starting from anhydrous TFA solutions (1-1.5M concentration in metals) without any additional purification.
2. Experimental
The preparation of YBCO solution (figure 1) started by dissolving commercial YBCO powder (Yttrium-Barium-Copper-oxide, SOLVAY) in TFAA (Aldrich 99%), using recently distilled dry acetone (Panreac) as a solvent at 50 °C for several hours in argon atmosphere and with acid catalysis. The solution was filtered and concentrated in a rotary vacuum evaporator. The mixture of TFA compounds (Ba(TFA)₂, Cu(TFA)₂ and Y(TFA)₃) was obtained. The mixture was dissolved in methyl alcohol (Aldrich 99.8%) or distilled dry acetone in a range between 1-1.5M and the resulting solution was stored in sealed vials. The viscosity and the water contents of the solution were controlled and the stoichiometry of metals was verified by ICP analysis. Single film deposition was performed by spin coating at a typical rotation speed of 6000 rpm or by dip coating that has a range of withdrawal speed between 1.27-25.4 cm min⁻¹, on 5mm x 5 mm LaAlO₃ (100) single crystal substrates. After deposition, the thermal treatment consisted of three steps; pyrolysis (figure 2), crystal growth and finally oxygenation annealing (figure 3). Optical microscopy (O.M.) was used to verify the homogeneity after pyrolysis. The pyrolysis process was studied by IR spectroscopy and thermal decomposition (DTA and TGA) of YBCO. SEM was used to analyze the films microstructure and XRD to ascertain the phase purity and to determine the texture quality. The film thickness after pyrolysis and growth were determined using an optical interferometric technique or through direct measurements with a profilometer. Electrical resistivity and SQUID measurements were used to investigate the superconducting properties.

3. Results and discussion
3.1 Solution characterization and pyrolysis. The stoichiometry of the metals in the solution was calculated by ICP analysis. There weren’t differences between the theoretical and experimental values. The measurements of the viscosity of the precursor solution showed its stability for, at least, six months (3.5mPa.s). The use of dip coating and spin coating gave excellent results.

In the first thermal treatment (pyrolysis) all the organic content was pyrolyzed. The whole process was carried out under a wet oxygen atmosphere. DTA and TGA data (figure 4) of the dried gel obtained from the precursor solution gave information concerning the thermal decomposition process. It took place between 125°C and 310°C and the total loss of mass was about 70%. These results were in accordance with those obtained by IR spectroscopy. The typical COO⁻ function is observed as a broad band in the range of 1650-1720 cm⁻¹ and disappeared after 30-45 min at 310°C (figure 5). This
The technique has demonstrated that, in principle, the pyrolysis time could be much shorter than that usually used (20 hours, [7]).

The quality of the calcinated films has been investigated by O.M. and it was possible to see the homogeneity of the samples after short pyrolysis (figure 2).

3.2 Growth and characterization of the YBCO films. After pyrolysis, the films were fired at 795°C in a humid N₂ atmosphere with 200ppm O₂ as indicated on figure 3. XRD (figure 6) θ-2θ patterns showed that YBCO films only have (00l) reflections and no impurities were present. The films display a sharp texture (Δω = 0.3° for the (005) reflection and Δφ = 1.1 for the (113) reflection). SEM micrographs (figure 7) showed a low porosity film.

Through spin coating deposition following the conditions described above the film thickness after pyrolysis was in the range of 500-600 nm when the solution concentration was 1.5M. After growth the thickness was reduced down to ~ 300nm. In the case of the dip coated films, the effect of withdrawal speed has been investigated and similar films thicknesses could be achieved. Finally, the temperature dependence of the zero field current density J_c and the electrical resistivity were recorded in samples with anhydrous solution as a precursor (figure 8).
These measurements confirmed the high performance of YBCO films ($T_c \sim 91K$, $J_c \ (77K) = 3-4 \ \text{MA/cm}^2$, 300nm) prepared from anhydrous TFA precursors.

4. Conclusions

The use of anhydrous TFA solutions allowed good and reproducible high $J_c$ superconducting YBCO films with calcinations times of 90 minutes. The anhydrous TFA solutions have been proved to be more stable than the non-anhydrous ones and to be easier to prepare. Spin coating and dip coating deposition techniques have given excellent results.

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