NUCLEATION MECHANISM OF YBa$_2$Cu$_3$O$_7$ BY CSD USING TFA PRECURSORS

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Abstract. The heteroepitaxial growth of YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) films prepared by the trifluoracetate TFA route was characterized by TEM/EELS, μ-Raman spectroscopy and X-Ray diffraction of specimens quenched from various temperatures. We find that after the pyrolysis, the film consists of a homogeneous, partly amorphous, nanocrystalline matrix of Ba$_{1-x}$Y$_x$F$_{2+x}$ and CuO. Upon heating, such a precursor undergoes a strong phase segregation on a length scale of 100 nm. Simultaneously, the Ba$_{1-x}$Y$_x$F$_{2+x}$ solid solution is decomposed into BaF$_2$ and Y$_2$O$_3$, and part of this Y$_2$O$_3$ eventually reacts with the CuO to give Y$_2$Cu$_2$O$_5$. Our results make evident that the nucleation of YBCO takes place exclusively at the interface with the substrate, within the fluoride phase. The fluoride phase appears highly textured from the early stages of phase evolution, above 600 ºC, and determines the orientation of the YBCO. The microstructural heterogeneity of the precursor film prior to the nucleation of YBCO strongly suggests that more than one reaction path may operate simultaneously.

1. Introduction

Second-generation HTS wires are based on epitaxial YBCO films deposited on a biaxially textured template. Metalorganic decomposition (MOD) is a promising approach due to its reduced cost and easy scaling. Nowadays, the phase evolution yielding YBCO still constitutes an open issue. Early work by McIntyre et al [1] showed that the intermediate film consists of BaF$_2$, CuO and Y$_2$O$_3$ prior to the formation of BaCuO$_2$ and Y$_2$Cu$_2$O$_5$ (Y225) and YBCO. More recently, Smith et al [2] has identified intermediate phases BaF$_2$, CuO and Y225, thus supporting earlier reports. Moreover, Wu et al [3] suggested the intermediate phases Cu$_2$O and Y-Ba-O-F (oxyfluoride). In addition, Venkataraman et al [4] stated the same intermediate phases as Smith et al but followed by a series of plausible individual steps producing Y$_2$O$_3$, Ba(OH)F and BaCuO$_2$ on their samples prepared onto Ni-3% RABITS substrates by the TFA process. Further insights into the phase evolution prior to the growth of YBCO were provided by Yoshizumi et al [5], signaling that at 400°C the [F]/[Ba] ratio is 2.7 and decreases with temperature, thus indicating a fluoride phase with variable composition.

In the present work we further explore the phase evolution yielding YBCO epitaxial films grown by the MOD-TFA route.
2. Synthesis and characterisation

TFA solutions were prepared following a modified procedure, as reported elsewhere [6]. A solution with an ion metal concentration of 1.5 mol/l was spun onto 5x5 mm (00l)-oriented LaAlO3 (LAO) single-crystal substrates.

First, the films are calcinated at 300 °C under a wet oxygen atmosphere, in order to burn out the organic content of the precursor. Secondly, a high temperature (795 °C) crystallization step is performed in an atmosphere of N2/O2 and P(O2) = 200 ppm and P(H2O) = 0.6 kPa under a gas flow of 0.61 l/min to form the YBa2Cu3O7-x phase [7]. Finally, the films are oxygenated at 450 °C in flowing O2, during 3.5h.

Films where quenched from 600 °C, 700 °C and 795 °C, and characterized by X-Ray diffraction, μ-Raman spectroscopy and cross sectional transmission electron microscopy (XTEM) equipped with an EELS spectrometer. Thin foils for XTEM observation were prepared by the conventional cutting, gluing and grinding procedures, followed by a final milling step with Ar ions down to perforation.

3. Results and discussion

Fig. 1 shows a series of /2 scans of precursor films quenched at different temperatures. After the pyrolysis, the patterns exhibit only broad features, consistent with the nanocrystalline nature of the film, which were identified as Ba1-xYxF2+x (BYF) and CuO. Fig. 2(a) and (b) show a low magnification image and a high-resolution XTEM image, respectively, corresponding to a pyrolyzed film observed from the [100]LAO direction. The precursor forms a homogeneous, 800 nm-thick, film composed of nanoparticles with a size of 10-20 nm embedded in an amorphous matrix. Fig. 2(c) shows the corresponding selected-area electron diffraction pattern, which can be indexed with the BYF and CuO phases, in agreement with XRD patterns. No signatures of Y2O3 were found in the pyrolyzed films, neither by XRD nor by μ-Raman spectroscopy, thus suggesting that after the pyrolysis, at least a large fraction of the Y content in the precursor film is integrated in the BYF solid solution. Further insights into the distribution of Y can be obtained from the dependence of the lattice parameter on the composition of the solid solution, x [8]. From several pyrolysis we have estimated the BYF lattice parameter as 6.04 Å, giving x = 0.28, with an uncertainty of ± 7%. This value corresponds to a Y/Ba ratio of 0.38. Thus, although most of the Y present in the pyrolyzed film is contained in the BYF solid solution, some amount of free Y2O3 may be present, which cannot be detected by XRD and μ-Raman due to its nanocrystalline or even amorphous nature.

In agreement with phase diagram studies [8], Fig. 1 shows that increasing the temperature the peaks of this solid solution are shifted to lower 2θ values, indicating a decrease of the Y content. At 700 °C the value corresponding to pure BaF2 is reached. Simultaneously, the intensity corresponding to BaF2 and Y2O3 increases, and part of that Y2O3 reacts with CuO giving Y225. Thus, the data shown in Fig. 1 suggests that several reactions take place prior to the nucleation of YBCO.

At 700 °C we first observe the (00l) peaks of YBCO. Samples quenched from 795 °C exhibit sharp (00l) YBCO reflections, as well as unreacted BaF2, BYF, Y225, Y2O3 and CuO (Fig. 1).
Fig. 3 shows a low-magnification XTEM image of the film quenched from 795 °C, viewed along the [100]LAO direction. EELS analyses performed at several points of the cross section revealed a strong phase segregation, which builds up within a length scale of 100 nm. Results are indicated in the image. It is also found that YBCO islands have nucleated on the substrate surface and grown preferentially with their c-axis perpendicular to the film. Such islands present a homogeneous thickness of 80 – 90 nm, thus suggesting that their growth rate is similar throughout the film. An a-axis-oriented YBCO grain reaching the film surface, nucleated on top of a c-oriented island, can also be observed. The film exhibits at this stage of the growth process, approximately half of the precursor film thickness, i.e. 450 nm. Therefore, the a-axis grains will outcrop above the flat c-axis oriented surface [9].

YBCO islands are surrounded by a nanocrystalline or quasi-amorphous matrix with composition Ba – F – O and very tiny amounts (<2 at %) of Cu and Y. To date, there has not been a unique proposal for the chemical composition of the F-containing phases. Hence, other authors have proposed the presence of an yttrium oxy-fluoride or yttrium hydroxide [10] and even a barium-yttrium oxy-fluoride [3]. CuO and Y225 particles appear typically far from the interface.

Fig. 4 is a high resolution XTEM image of the LAO interface. The substrate is partly covered by (001) oriented YBCO and partly covered by the Ba – F – O quasicrystalline matrix. Careful analysis of FFT spectra taken on different regions of the image shows BaO nanoparticles embedded in the BaF2.
quasicrystalline matrix. The BaF₂ matrix displays a patched-like contrast but exhibits crystallographic alignment throughout the image. The orientation of this oxy-fluoride matrix (indicated by arrows) is such that (111) BaF₂ // (001) YBCO // (001) LAO, and [011] BaF₂ // [100] YBCO // [100] LAO.

![Figure 4](image_url)

**Figure 4.** High resolution XTEM image of the LAO interface. The substrate is partly covered by (001) oriented YBCO and partly covered by a Ba – F – O quasicrystalline matrix. Analysis of FFT spectra taken on different regions of the image showing BaO nanoparticles embedded in a BaF₂ quasicrystalline matrix.

4. Conclusion

A XTEM investigation of the growth mechanism of MOD-TFA YBCO reveals that the precursor film, after the pyrolysis, consists of a partly amorphous nanocrystalline BYF and CuO mixture. The BYF composition evolves with temperature, previous to YBCO nucleation at T ∼ 650 ºC, to a BaF₂+Y₂O₃ mixture. The first YBCO nuclei appear, in a strongly segregated matrix, on the LAO interface, within the (111) oriented fluoride phase, which determines their orientation.

5. Acknowledgments

This work has been financed by the EU within the scope of the Solset project, contract No. G5RD-CT2001-00550, by the Spanish CICYT (MAT02-02642 and MAT2003-01584) and by the Generalitat de Catalunya (2001-SGR-00336 and CERMAE). JG, MC and AP acknowledge financial support to the Spanish Ministry of Educación y Ciencia through FPI, FPU and Ramón y Cajal programs, respectively. We acknowledge Serveis Científico-Tècnics de la Universitat de Barcelona, Grupo de Física del Estado Sólido de la Universidad Carlos III and CNRS/CEMES, Toulouse, for the use of TEM-EELS facilities.

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