Physica C 482 (2012) 58–67

Contents lists available at SciVerse ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Nucleation and mesostrain influence on percolating critical currents of solution derived $YBa_2Cu_3O_7$ superconducting thin films

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ARTICLE INFO

Article history:
Accepted 21 April 2012
Available online 15 May 2012

Keywords:
$YBa_2Cu_3O_7$
Critical currents
Chemical solution deposition
Thin film growth
Mesostrain
Trifluoroacetate precursors

ABSTRACT

After briefly reviewing the present understanding of the nucleation process of YBCO films, a new approach is presented to enhance the stability of *c*-axis nucleation in epitaxial chemical solution deposited YBCO thin films derived from TFA precursors. We show that with silver addition to the TFA precursor *c*-axis nucleation can be reached in a wide range of temperature thus keeping high percolating J_c. We argue that silver reduces supersaturation and makes more stable the *c*-axis nuclei without modifying T_c. Additional advantages of silver addition are an enhanced surface smootheness and a reduced porosity of the YBCO films. The second reported topic relates to the discovery of an adverse relationship between percolating J_c and YBCO films mesostrain, as determined through X-ray diffraction line broadening. We show that mesostrain is enhanced in processes leading to inefficient strain healing at grain boundaries, for instance annealing times too short or growth temperatures too low. It is suggested that the strained regions at the low angle grain boundaries lead to a weak link behavior which can be microscopically understood on the basis of pair formation prevention, as proposed by the bond contraction pairing model.

1. Introduction

Achieving high critical current in high temperature superconducting (HTS) wires has been a very significant objective of research during recent years. High quality biaxially textured conductors (coated conductors, CC's) has been developed which helped to overcome the main factor limiting the performance of CC'— grain boundaries.

In the last years considerable effort has been devoted to understand the mechanisms controlling epitaxial growth and grain boundary structure of superconducting thin films based either on vacuum-deposited or low-cost chemical solution deposition (CSD) methods in order to boost their use in coated conductors technology [1–3]. The so-called trifluoroacetate (TFA) route has been up to now the most successful CSD approach [4–6]. Briefly, a precursor solution of Y, Ba and Cu trifluoroacetates or other metallorganic salts is deposited on the substrate by an adequate technique such as spin, dip or web coating, ink jet deposition) [2,3,7] leading to uniform and controlled thickness. Then, the precursor solution is heat treated to from YBCO thin films previous formation of solid nanocrystalline intermediate phases, one of them being BaF_2. This CSD ex situ growth process bears many similarities, and some discrepancies, to physical vapor deposition (PVD) techniques of Y and Cu metals together with BaF_2 [1–3,8,9]. This is because the intermediate process steps in CSD films, i.e., solution deposition, metallorganic pyrolysis and solid precursors phase transformations have a complex interplay into the final YBCO film microstructure and superconducting performances which still remain controversial in many aspects [2,3,5,10–12]. More precisely, the knowledge of the influence of the different reaction parameters (temperature, gas flow, partial water pressure, oxygen pressure, etc.) on the film epitaxial quality and superconducting properties remain still poor [5,10,12]. One essential issue has been proven to be avoiding the undesired formation of randomly oriented or *a*/*b*-axis grains which introduce high angle grain boundaries and very often enhance the film porosity. Hence understanding how the nucleation process proceeds has a top priority [13–21].

It is now understood that ex situ growth process is characterized by a Volmer–Weber heterogeneous nucleation mechanism where islands are formed at the interface with the substrate, and then the grains grow until coalescence forming finally a continuous film. Stringent efforts have been made to understand the grain boundary (GB) structure resulting from this ex situ process in order to achieve high percolating critical current densities J_c [22–25], however many details relating the GB structure with the critical currents remain elusive [26,27]. A new view of this problem has been recently proposed: It has been suggested that the tensile

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http://dx.doi.org/10.1016/j.physc.2012.04.020

strain associated with the dislocations located along GB's lies at the origin of the universal weak link behavior observed in HTS and pnictides and keeping some parallelism to the modified mesoscale magnetism at grain boundaries in colossal magnetoresistive films [28,29].

In this work we will first review the nucleation process of YBCO films and then we will report about two new contributions for achieving an enhanced control of microstructure and self-field critical currents in YBCO films grown by CSD. First, we will show that by adding silver to the YBCO-TFA solution we can enhance the *c*-axis nucleation and hence extend the temperature window where epitaxial films can be obtained. A second advancement reported in this work arises from an experimental analysis of the inhomogeneous strain at grain boundaries (mesostrain) which influences adversely the percolating critical currents. We will show that during the zipping process, following the island coalescence, the mesostrain accumulated at the GB is healed out and this increases the percolating critical current density of the films.

2. Experimental

The YBCO films used in this work were prepared by the trifluoroacetates route as described in detail previously [2] by using anhydrous precursor solutions with 1.5 M concentration [30]. Silver trifluoroacetate in molar proportions ranging from 2.5 mol% to 20 mol% were added when indicated. Gel films formed after dip or spin coating followed a fast pyrolysis (∼30 min) process at 310 °C in oxygen atmosphere while growth was performed with different annealing times at temperatures between 720 °C and 810 °C. Normal pressure conditions (P_t = 1 bar), PO_2 = 0.2 mbar and $P_{H_2O} = 23$ mbar were used; linear gas flow velocity of 26×10^{-3} m/s. The heating ramp to reach the reaction temperature was of 1500 °C/h. The substrates were YSZ single crystals buffered with PVD-CeO_2 (100 nm) supplied by THEVA GmbH or with CSD-$Ce_{0.9}Zr_{0.1}O_2$ (CZO/YSZ) or $LaAlO_3$ (LAO) single crystals. The YBCO film thickness was 250 ± 20 nm, as determined by profilometry.

Structural characterization of films fully processed (additionally annealed for 2 h in 100% O_2 at 450–500 °C) or just quenched after annealing at 770 °C was made using X-ray diffractometer equipped with a 2D detector (GADDS-Bruker). Conventional θ–2θ patterns were recorded to determine the microstrain using the Williamson–Hall (WH) plot after correction for the instrumental width of Bragg peaks. Out-of-plane ($\Delta\omega$) and in-plane (Δ_ϕ) grain misorientation were those typical of single crystalline substrates (∼0.5° and ∼1°, respectively). FE-SEM and atomic force microscopy in the tapping mode (AFM) images were also obtained to visualize the surface morphology of the films which confirmed typical flat-like grain morphologies. Critical current densities of the YBCO films were measured inductively with a SQUID magnetometer up to applied fields of 7 T while T_c was found inductively to be in the range of 90–91 K. Both percolating J_c^{PERC} and intragrain J_c^G critical currents were determined simultaneously in some cases following a method recently proposed by Palau et al. [31,32]. For some samples, the YBCO film growth was monitored by in situ electrical resistance measurements using a DC 4-probe method following the procedure recently described by Chen et al. [13].

3. Nucleation in YBCO thin films

It was early discovered that YBCO thin films grown by whatever in situ or ex situ technique have specific regions of the PO_2-T phase diagram where *c*-axis nucleation and growth is optimal while at reduced temperatures and PO_2 values a coexistence of *c*-axis and *a*-axis orientations is observed [33]. The origin of such a behavior has been not yet clearly established and while early assessments attributed this to kinetic effects, more recent analysis suggest that it has a thermodynamic origin and classical nucleation theory can essentially cope with it.

Ex situ grown YBCO films have been shown to nucleate following a Volmer–Weber mode, i.e., single islands are first formed in random positions of the interface with the substrate and then grow along all directions, at different growth rates, and finally coalesce leading to a continuous film [9,34,35]. However, some systems display a complex growth behavior, such as REBCO (RE = Rare Earth) or CeO_2 [36–38], because diverse crystal orientations have close energies and so they can be formed simultaneously. A thermodynamic analysis of the parameters influencing the nucleating event is thus required to achieve a tight control of the final microstructure of the films [39].

YBCO oxide can nucleate with the *c*-axis either perpendicular to the substrate ((001) plane parallel to the substrate, *c*-axis nuclei) or parallel to it (i.e., (100) plane parallel to the substrate, *a*-axis nuclei), depending on several parameters such as temperature, $P(O_2)$, lattice misfit with the substrate, RE ion [38,40–46]. A crossover temperature exists where the most stable crystalline orientation during the nucleation process changes from one type to another. This may happen because the free energies of two crystalline orientations have a different dependence on the nuclei size. In this way, when the supersaturation conditions are modified the critical size of the first stable nuclei also change and, eventually, the most stable island orientation is controlled [38,44]. This issue has often been not taken into account and oversimplified scenarios were suggested. Classical nucleation theory states that the stability of the first nuclei is controlled by the Gibbs energy barrier ΔG^* to form islands and so the energy of an isolated interfacial island needs to be computed. In general the energy of an epitaxial island has a term determined by the surface and interface energy contributions E_{surf} and a second term E_{relax} arising from the relaxation of the elastic energy associated with the lattice misfit between the nucleus and the substrate [39,47]. At the nucleation stage, however, the second term can be neglected due to the small size of the first stable nuclei. Therefore we can compute the Gibbs energy barrier ΔG^*, if we assume a cylindrical shape for the interfacial epitaxial grains with height h and radius r [38,44]. The total Gibbs change during YBCO crystallization can be written as

$$\Delta G(r) = \frac{\pi h r^2}{v}\Delta\mu + 2\pi h r \gamma_{\mathrm{lat}} + \pi r^2(\gamma_{\mathrm{up}} + \gamma_{\mathrm{int}} - \gamma_{\mathrm{sub}}) \tag{1}$$

where v and γ represent the unit cell volume and surface free energy per unit area (lat = lateral surface, up = upper surface, int = interface, sub = substrate), $\Delta\mu$ (<0) is the chemical potential change per molecule between the epitaxial YBCO phase and the precursor random nanocrystalline state. The energy barrier for heterogeneous nucleation ΔG^*, corresponding to the critical nuclei radius $r^* \propto (-1/\Delta\mu)$, can be deduced by maximizing ΔG^* vs. r in Eq. (1), i.e., $(\partial\Delta G(r)/\partial r = 0)$, which leads to the following result,

$$\Delta G^* = \frac{\pi(h\gamma_{\mathrm{lat}})^2}{-(\frac{h}{v})\Delta\mu - (\gamma_{\mathrm{up}} + \gamma_{\mathrm{int}} - \gamma_{\mathrm{sub}})} \tag{2}$$

This energy barrier has been found to be different for YBCO nuclei with different orientations and so the dependence of ΔG^* on $\Delta\mu$ can be calculated for the corresponding combination of surface energies (Fig. 1). As can be seen from Fig. 1, it is predicted that *c*-axis grains nucleate under low supersaturation conditions (low $|\Delta\mu|$), while *a*-axis and *c*-axis nucleation can have similar rates under high supersaturation conditions (large $|\Delta\mu|$) because the corresponding energy barriers $\Delta G^*(001)$ and $\Delta G^*(100)$ are very similar [38,40–42].

In ex situ growth of TFA-YBCO films the proper chemical conversion reaction is the following [11,13]: