Physica C 485 (2013) 39–46

Contents lists available at SciVerse ScienceDirect

Physica C

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

Yttrium-enriched $YBa_2Cu_3O_x$ thin films for coated conductors fabricated by pulsed laser deposition

Alexey V. Khoryushin [a,*], Peter B. Mozhaev [a,1], Julia E. Mozhaeva [a,1], Niels H. Andersen [a], Jean-Claude Grivel [b], Jørn Bindslev Hansen [a], Claus S. Jacobsen [a]

[a] *Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*
[b] *Department of Energy Conversion and Storage, Technical University of Denmark, DK-4000 Roskilde, Denmark*

ARTICLE INFO

Article history:
Received 30 August 2012
Accepted 19 October 2012
Available online 30 October 2012

Keywords:
Coated conductors
Artificial pinning centers
$YBa_2Cu_3O_x$
Yttria nanoparticles

ABSTRACT

The effects of excess yttria on the structural and electrical properties of the $YBa_2Cu_3O_x$ (YBCO) thin films are studied. The films were deposited on $(LaAlO_3)_{0.3}$–$(Sr_2AlTaO_8)_{0.7}$ substrates by pulsed laser ablation from targets with different elemental composition. An increase of yttrium content of the target leads to formation of porous films with significantly improved current-carrying capabilities. Structural studies of these films reveal presence of yttria nanoparticles embedded into the YBCO matrix. The highest obtained critical current density in an external magnetic field of 5 T was 2.6 MA/cm^2 at 50 K and 9.4 MA/cm^2 at 20 K. The fabricated Y-enriched YBCO films remain *c*-oriented at least up to 600 nm thickness with no significant suppression of the critical current density.

1. Introduction

The successful implementation of coated conductors in power applications, like motors or generators, requires high current-carrying capabilities in magnetic fields of 3–5 T. Natural pinning centers in high-temperature superconducting (HTSC) thin films, like dislocations, grain boundaries, or point defects, cannot provide sufficient pinning, thus the introduction of artificial pinning centers (APCs) is needed [1]. The technology of APCs formation should meet the following requirements: (1) the APCs should be sufficiently dense ($>10^{11}$ cm^{-2}) to provide efficient pinning at high magnetic field; (2) the pinning force of an APC should be high enough, usually provided by the size of APC exceeding the coherence length (typically 3 nm for $YBa_2Cu_3O_x$, YBCO) and (3) the APC material should not compromise the adjacent HTSC area. Utilization of "foreign" phases – i.e., APCs composed of elements other than that of the HTSC – always results in suppression of superconductivity in the neighboring area, and starting from some certain volume percentage (2–5% for different APC materials, see, e.g., [2,3]) the overall superconducting properties of the composite are suppressed. This makes the "natural" particulates present in HTSC thin films, consisting of the same elements as the superconductor, more favorable as APCs. Among the "natural" oxides the Y_2BaCuO_5 and Y_2O_3 (yttria) have attracted the main attention because they are not expelled from the YBCO matrix and can form nanosize inclusions in the superconductor layer. The Y_2BaCuO_5 nanoparticles are relatively big and their introduction may result in cracks in the neighboring superconductor [4,5]. Y_2O_3 inclusions are smaller and form a coherent interface with the YBCO matrix due to matching lattice constants [6–8], leading to minimal reduction of the critical temperature of the superconductor. This set of features have resulted in extensive studies of yttria nanoparticles as possible APCs [3,9–17].

Two main routes of yttria nanoparticle incorporation into the YBCO film were suggested: decoration of the substrate surface, resulting in seeding of yttria nanoparticles [9–11], and addition of yttria to the growing film [11–18]. The first technique provides excess yttria only in the very beginning of the thin film growth, and the effect on the critical current density is mainly due to formation of extended linear defects in the YBCO film overgrowing the yttria nanoparticle. The second route has been implemented by direct addition of yttria into the film composition by sputtering [12] or ablation [13,14], or by using targets with excess rare-earth element [15,16], and by sequential deposition of YBCO layers and intermediate quasi-layers of yttria [3,17,18]. In [11] the excess yttrium in the film resulted from the features of the deposition technology. In these studies the yttria nanoparticles were formed during the growth of the superconducting layer, and were overgrown by the YBCO matrix resulting in a 3D-net of pinning centers, embedded in the superconductor. No suppression of superconductivity, or just a minor effect on the transition temperature, T_c [17], was observed

---

* Corresponding author. Address: Physics Department, Technical University of Denmark, DTU Building 309, Kgs. Lyngby 2800, Denmark.
E-mail address: khoryushin@ya.ru (A.V. Khoryushin).

[1] Institute of Physics and Technology RAS, Nakhimovsky Ave. 34, 117218 Moscow, Russian Federation.

0921-4534/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physc.2012.10.010

in such composites. The coherent interfaces between the yttria particles and neighboring YBCO result in absence of strained/distorted areas around the APCs [18]. The 3D-distributed yttria particles provide better pinning of an arbitrarily oriented external magnetic field compared with columnar 1D-pinning centers ($BaZrO_3$, $BaSnO_3$ nanorods or dislocations in YBCO), even though they provide somewhat smaller pinning forces [1].

In this paper we present results of our studies of yttria enrichment of the YBCO films deposited by PLD by changing the target elemental composition. The structural and electrical properties of the obtained films are reported.

2. Experimental

All films were deposited by pulsed laser deposition (KrF excimer laser, $\lambda = 248$ nm). The details of the deposition technique can be found elsewhere [19]. The deposition of superconducting layers was done in conditions optimized for formation of high crystal quality and high critical temperature thin YBCO films on $LaAlO_3/SrTiO_3$ perovskite substrates (stoichiometric target $YBa_2Cu_3O_7$, substrate temperature 770 °C, 0.8 mbar total pressure, Ar/O_2 flow ratio 8/2 sccm, laser energy density on target 1.5 J/cm^2, repetition rate 2 Hz, deposition rate 0.165 nm/s, post-deposition oxygenation in 500 mbar O_2 at 450 °C for 1 h). Changes of the elemental composition of the deposited films usually result in changing optimal deposition conditions; as this study was not performed, we believe that the superconducting properties of all films except the ones deposited from a stoichiometric $YBa_2Cu_3O_{7-x}$ target are inferior to the best achievable.

The yttria-enriched YBCO layers were deposited from commercially available high-density targets with nominal compositions $Y_{1.25}Ba_2Cu_3O_7$ and $Y_{1.5}Ba_2Cu_3O_7$, the films from these targets will be referred to as 25%- and 50%-yttrium enriched. The elemental composition of the films from the 50%-yttrium enriched target was determined by inductively coupled plasma (ICP) analysis based on quantitative optical emission spectroscopy to be $Y_{1.70}Ba_{2.15}Cu_{3.00}O_x$. The increase of Y and Ba contents in the film compared with the target composition is due to stronger scattering of the light Cu atoms on the way from target to substrate. The measured amount of excess material corresponds to 12 wt% or 15 vol% addition of yttria, assuming all excess yttrium forms yttria particles. The actual amount of Y_2O_3 particles formed is probably smaller, due to yttrium incorporation into YBCO lattice, segregation of yttrium on interfaces and formation of complex oxide particles like $CuYO_2$ or Y_2BaCuO_5.

Most of the films were grown on (1 0 0) $(LaAlO_3)_{0.3}$–$(Sr_2AlTaO_8)_{0.7}$ (LSAT) perovskite substrates, providing fine conditions for YBCO formation: good lattice match (3.867 Å, less than 0.3% mismatch with the (*ab*) plane of YBCO), small difference of thermal expansion coefficients, no twinning or lattice phase transitions in the deposition temperature range. The substrates were glued to the surface of a sample holder with silver paint to obtain good thermal contact. The difference of temperature between the sample holder and the growing film, measured with a pyrometer, was less than 5 °C. Other perovskite substrates, (0 0 1) $SrTiO_3$ (STO) and (1 1 0) $NdGaO_3$ (NGO), were used for fabrication of reference samples. We note that the temperature of the film growing on NGO substrate is 20–25 °C lower than that on LSAT or STO due to the IR transparency of the NGO substrate, so when deposition on these substrates was done simultaneously, the film on NGO grew in non-optimal conditions, especially during the early stages of growth.

The surface morphology of the films was observed with atomic force microscopy (AFM) using a Nanosurf EasyScan microscope, and a Philips scanning electron microscope (SEM). The structural parameters were determined by X-ray diffraction (XRD) measurements in a Bragg geometry using an X'Pert PRO two-axis diffractometer with a Cu Kα radiation source. The lattice constants *a*, *c* and the variations $\delta d/d$ along the substrate normal were determined using all available diffraction peaks of $\theta/2\theta$-scans (see, e.g., [20]). The crystallite size was also evaluated, but the results were not very reliable, as compared to direct thickness measurements, due to the complicated nature of reflections from the YBCO lattice.

The Energy Dispersive X-ray Spectroscopy (EDS) technique was used to study the local composition of the Y-enriched films. The films grown on $NdGaO_3$ (1 1 0) substrates were used for EDS measurements to avoid overlapping of the (Y,Sr) and (Ba,La) X-ray characteristic peaks that occurred when the LSAT substrate was used. The EDS spectra for calibration were acquired from a large area of 80×125 μm^2 to average over local variations of stoichiometry of the film. The correlation between the ICP results and the EDS spectra intensities was established using the least-squares method. All films had the same thickness of ~480 nm, so the obtained calibration made it possible to evaluate the elemental contents of YBCO films of thickness around 0.5 μm.

The superconducting properties of the samples were examined by magnetic, non-destructive methods: AC-susceptibility measurements and magnetization measurements by a vibrating sample magnetometer (VSM). The accuracy of the T_c determination is expected to be better than 0.1 K. The magnetization measurements were done using a Cryogenic Ltd. VSM instrument. Hysteresis loops *m* vs. *B* were recorded at 77, 50, 20 and 5 K (*m* is magnetic moment of the sample, *B* is applied magnetic field). For estimation of the critical current density j_c the critical state Bean model was employed for a geometry of thin films of rectangular shape: $j_c(B) = \frac{6 \cdot 2m(B)}{t \cdot a^3(3b/a-1)}$, where *t* is the film thickness, and *a* and *b* denote the dimensions of the film. At a given field the gap of the hysteresis loop (2*m*) was utilized in order to minimize the effect of any possible paramagnetic background signal, specific for the setup and the sample holder.

3. Results and discussion

The surface morphology of the YBCO films deposited from targets of different composition is shown in Fig. 1. The films deposited from the stoichiometric target (Fig. 1a) have relatively smooth surfaces with rare pores and outgrowths. An increase of yttrium content of the target results in the formation of deep and wide pores, and growth of particles on the film surface (Fig. 1b). The density of pores is almost the same, $\sim 10^8$ cm^{-2}, for all thin films with excess yttrium, but with increasing film thickness the density of pores decreases (Fig. 1c and d). The depth of the pores decreases, but the average diameter of the pores increases with an increase of the yttrium content. All the observed morphological features may be explained by seeding of some Y-containing particles in the very beginning of the film growth. The seeding requires only the presence of excess yttrium, so the density of particles depends weakly on the amount of excess yttrium and is determined by thermodynamic conditions on the film surface. The resulting particles are not wetted by the YBCO grains, so pores are formed over the particles. The overall amount of excess yttrium during deposition is insufficient to provide the same growth rate of the particle as that of the surrounding YBCO film, so the pore in a film with lower yttrium enrichment is deeper and narrower than in a film with a higher concentration of yttrium. At some threshold thickness the YBCO grains close over the particle, so the density of pores decreases with increasing film thickness.

The EDS measurements of the composition of the Y-enriched films show only excess yttrium when positioned on an YBCO grain, with barium and copper in stoichiometric ratio 2:3. The amount of excess yttria in the YBCO grains of the film grown from the target