Physica C: Superconductivity and its applications 519 (2015) 47–52

Contents lists available at ScienceDirect

Physica C: Superconductivity and its applications

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

Co-doping effects of Gd and Ag on YBCO films derived by metalorganic deposition

Meijuan Sun, Zhiyong Liu, Chuanyi Bai, Yanqun Guo, Yuming Lu, Feng Fan, Chuanbing Cai*

Shanghai Key Laboratory of High Temperature Superconductors, Physics Department, 99 Shangda Road, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 13 June 2015
Revised 22 August 2015
Accepted 24 August 2015
Available online 8 September 2015

Keywords:
MOD
Superconducting thin film
Gd doping
Ag addition

ABSTRACT

$Y_{1-x}Gd_xBa_2Cu_3O_{7-\delta}$-Ag ($x = 0, 0.25, 0.5, 0.75, 1$) thin films were prepared on oxide buffered Hastelloy substrates by low fluorine metalorganic depostion (MOD) process. The effects of co-doping of Ag and Gd on the microstructures and superconducting properties of YBCO thin films are investigated with respect to improvement on texture and superconducting performance in case of optimized doping content. It is found that optimum addition of Ag and Gd may lead to better *c*-axis orientation, superior surface microstructure and finally give rise to much improvement of superconducting performance.

1. Introduction

Second generation high temperature superconducting wires based on the $REBa_2Cu_3O_{7-\delta}$ (REBCO, Re=Y, Gd, Sm, Dy etc.) coated conductors (CCs) have emerged as hot topics due to power transport and device applications in high magnetic fields [1–3]. Among various approaches making superconducting layer, the metalorganic deposition (MOD) is an attractive technique for low cost, high rate deposition of REBCO CCs, applicable in atomosphere ambient pressure, in comparison with other methods including PLD [4–11].

For the commercialization of CCs, there exist two critical issues i.e., the achievement of high production rate and the improvement of J_c properties. It is reported that critical current density (J_c) values and flux pinning force density can be improved by adding elements to YBCO samples [4,5]. In particular, it is worthwhile to notice that RE doping can result in a significant enhancement of J_c for REBCO superconductors [12,13]. In MOD process, RE doping can be easily realized, as the composition of the films can be easily changed through chemical modification in the MOD precursor solution.

Silver addition is believed to decrease the poor connectivity between grains of ceramics, while it is hard to destroy the YBCO lattice generally, and thus appears to be a promising route to increase the J_c of REBCO thin films [14]. In reality, it has been reported that the J_c can be enhanced for the Ag-doped YBCO thin films prepared by the PLD technique. Also, there are a number of reports on the Ag doping effects for the YBCO bulks prepared from solid state reaction [15,16]. In contrast, the synthesis and performance of YBCO-Ag thin films prepared by MOD methods are still limited [8,17]. Possible reasons could be attributed to the bad adaptability of silver salts to the YBCO precursor solution [18] as well as the easy evaporation of silver, leading to no obvious doping effects observed.

In our previous work, it is observed that optimum addition with about 5 mol% Ag leads to better *c*-axis orientation and improved surface microstructure of GdBCO thin films [19]. In the present work, a series of thin films namely Gd-doped $Y_{1-x}Gd_xBa_2Cu_3O_{7-\delta}$ ($x = 0, 0.25, 0.5, 0.75, 1$) together with 5 mol% Ag addition are prepared by low fluorine MOD technique. For reference, pure $Y_{1-x}Gd_xBa_2Cu_3O_{7-\delta}$ ($x = 0, 0.25, 0.5, 0.75, 1$) samples without Ag doping are prepared by traditional low fluorine route as well.

By studying the crystalline orientation, morphology and surface quality, critical current density, we attempt to understand the co-doping effects of Gd and Ag on YBCO in low fluorine MOD process.

2. Experimental

Stoichiometric quantities of Y, Gd and Ba acetates were dissolved in de-ionized water with an excess stoichiometric quantity of trifluoroacetic acid, Cu (Y:Gd:Ba:Cu = 1–*x*:*x*:2:3, $x = 0, 0.25, 0.5, 0.75, 1$) acetate was dissolved in de-ionized water with an excess of propionic acid to get the coating solution. The next step in solution preparation was refining the solution by drying, and redissolving in methanol several times. This process removed the excess acetic acid, water and other impurities from the solution. Finally, the Y, Gd, Ba and Cu solutions were mixed, evaporated, and diluted in propionic acid to

* Corresponding author. Tel.: +86 21 66132926.
E-mail address: cbcai@t.shu.edu.cn (C. Cai).

http://dx.doi.org/10.1016/j.physc.2015.08.011
0921-4534/

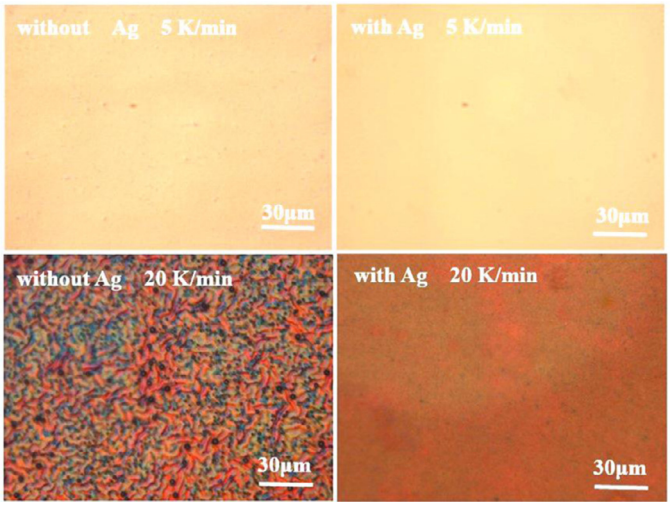

Fig. 1. Optical images of the pyrolyzed films quenched at 500 °C during temperature ramping using conventional low fluorine metalorganic solution or 5 mol% Ag doped low fluorine metalorganic solution with the heating rate of 5 K/min and 20 K/min.

control the viscosity. The coating solution's total cation concentration was 1.5 mol/L. In the meanwhile, the 5 mol% silver trifluoroacetate was added as well. Finally, a small amount of diethanol amine was added to the precursor solution to increase its stability. The resultant solutions are deposited on Hastelloy/Al_2O_3/Y_2O_3/MgO/$LaMnO_3$ substrates by dip-coating. Gel films are followed by a fast pyrolysis (20 K/min) process up to 500 °C in wet oxygen atmosphere, while the further thin film growth is performed at 780 °C in a humid mixed N_2/O_2 gas. Normal pressure conditions ($P_T = 1$ bar, $P(O_2) = 0.15$ mbar and $P(H_2O) = 42$ mbar) are applied during the crystallization stage. Finally, the films were anealed at 450 °C for 1 h in dry oxygen atmosphere.

The film thickness was measured with a step profiler and a typical thickness for all present films is around 400 nm. The surface morphology of the YBCO film is observed by field emission scanning electron microscopy, and the critical current density is measured by an inductive method at 77 K.

3. Results and discussion

3.1. Surface morphology and texture analysis

To explore the Ag effect on the surface of pyrolyzed REBCO, four precursor GdBCO film samples by normal low fluorine solution with and without 5 mol% Ag doping were pyrolyzed using heating rate of 5 K/min and 20 K/min, respectively. Fig. 1 shows the typical metallographic optical microscope (OM) images of GdBCO precursor films with and without Ag dopants, quenched from 500 °C during temperature ramping for the prolyzed rate at 5 K/min and 20 K/min, respectively. Obviously, the surface of samples pyrolyzed at lower heating rate is smooth without cracking, bucking or pores. However, as a higher heating rate was applied, the typical wrinkles are observed on the pyrolyzed sample in case of without Ag doping, as shown in Fig. 1. The precursor film with 5 mol% Ag doping exhibits a smooth and crack-free microstructure. Stress relief is the driving force leading to smooth or structurally inhomogeneous films, displaying buckling or macrocracks, depending on the rate of film transformation [20]. It is suggested that the Ag doped low fluorine solution makes the beneficial effects on the stress relief and then minimizing the surface degradation of pyrolyzed films. The addition of Ag can even remedy microcracks in YBCO bulks [21].

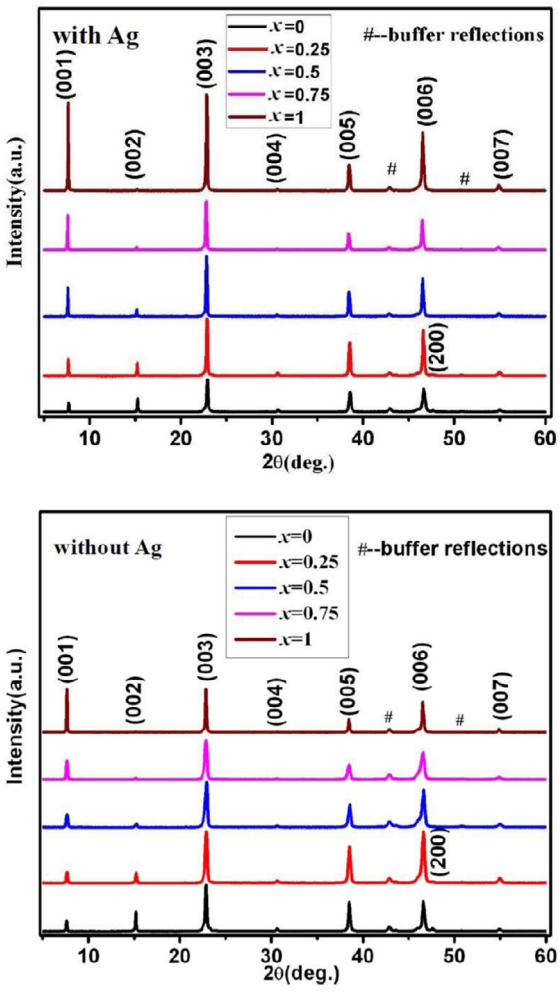

Fig. 2. X-ray diffraction patterns of the studied YGBCO thin films with and without Ag.

The XRD patterns of YGdBCO with and without Ag fired at 780 °C are shown in Fig. 2. It is seen that all thin films are pure without undesirable phases, but Ag hardly detected. It is believed that Ag does not occupy the space in YGdBCO lattice, it plays role on the suppression of *a*-axis nucleation of YGdBCO films [8]. The intensity of (00l) peaks of YGdBCO films with Ag is higher than YGdBCO films without Ag, indicating the crystallization of YGdBCO films with Ag is better than YGdBCO films without Ag. The YGdBCO-Ag films are *c*-axis oriented. However, when Gd to Y molar ratio is less than 50 percent the YGdBCO has a diffraction peak corresponding to (200), which is confirmed by SEM morphologies. A similar trend is observed in YGdBCO films without Ag, except that the (200) reflections are higher, which is contrary to reference [10]. The role of Gd in the improvement of surface morphology and *c*-axis nucleation is complicated. According to reference [8], the REBCO nucleation depends on parameters such as firing temperature, oxygen partial pressure, and lattice misfit with the substrate. We propose that the current processing parameters such as firing temperature, oxygen partial pressure are optimal for GdBCO.

To further understand the co-doping effect of Gd and Ag on grain texture, the ratio of YGdBCO (005) to (004) peak intensity was calculated to evaluate the oxygen content of the derived films [22]. The peak intensity ratio of (005) to (004) and FWHM of YGdBCO (005) is shown in Fig. 3. It is found that the peak intensity ratio of I(005) to I(004) increases almost linearly, which may be due to the lattice