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Physics Procedia 36 (2012) 514 – 519

Physics Procedia

Superconductivity Centennial Conference

Combinatorial synthesis of $(Y_xGd_{1-x})Ba_2Cu_3O_x$ superconducting thin films

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Abstract

Environmentally friendly water-based $YBa_2Cu_3O_x$ (YBCO) and $GdBa_2Cu_3O_x$ (GdBCO) precursor solutions were synthesized to realize thin films by chemical solution deposition. Pure YBCO and GdBCO precursor solutions were used for ink plotting on $SrTiO_3$ substrates and subsequent thermal treatment at the corresponding crystallization temperature. Phase formation of Gd123 requires a higher crystallization temperature of 840 °C compared to the Y123 phase. The critical temperature of YBCO films is about 92 K with a sharp transition into the superconducting state. Micro liter sized ink volumes of YBCO and GdBCO were successfully mixed for two-dimensional ink plotting of a $(Y_xGd_{1-x})Ba_2Cu_3O_x$ film library. A homogeneous surface and no indication of a-axis growth were found in all mixed films.

water-based solutions; YBCO films; GdBCO films; ink plotting

1. Introduction

$YBa_2Cu_3O_{7-x}$ (YBCO) coated conductors is the current favourable superconducting design due to the excellent properties including sufficient high J_c-performance. Chemical Solution Deposition (CSD) is a promising process for industrial long length production of high temperature superconducting tapes thanks

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 doi:10.1016/j.phpro.2012.06.076

to its high-speed production and good scalability. In particular, ink plotting is a promising process for a low cost fabrication of complicated and high end decorated patterns as for example required for ac-losses. Metal-organic deposition based on trifluoroacetate (TFA) chemistry is the most common and well established synthesis route. The use of TFA salts avoids the formation of $BaCO_3$ as the stability of barium fluoride is greater than that of barium carbonate. The main disadvantage of this process is the formation of toxic hydrofluoric acid. Therefore, recent efforts have concentrated on environmentally-friendly fluorine-free water-based routes [1, 2, 3, 4, 5]. One of the most important reasons for the change of YBCO to GdBCO, is that the Gd-based thin films reveal a higher T_c and higher J_c in the magnetic field as compared with YBCO films [6].

In this paper we present the results on the application of fluorine-free water-based YBCO and GdBCO precursor solutions, which were used to realize superconducting thin films by CSD. Additionally, micro liter sized ink volumes of YBCO and GdBCO were successfully mixed for two-dimensional ink plotting of a $(Y_xGd_{1-x})Ba_2Cu_3O_x$ film library on single crystal $SrTiO_3$ substrates.

2. Experimental

The aqueous precursor solutions were prepared starting from $Y_2(CO_3)_3$ $1.9H_2O$ (99.9 %, Sigma Aldrich) or $Gd_2(CO_3)_3$ $3.1H_2O$ (99.9 %, Sigma Aldrich), $Ba(OH)_2$ $8H_2O$ (98 %, Janssen) and $Cu(NO_3)_2$ $2.5H_2O$ (98 %, Alfa Aesar) salts dissolved in water and nitrilo-triacetic acid (NTA, 99 %, Alfa Aesar) in a 0.55 : 1 ratio for NTA : total metal concentration. The addition of triethanolamine (99+ %, Acros Organics) increases the pH and the viscosity to the desired values of 6 to 8 and 5.0 mPa s at 25 °C respectively. The viscosity of the solutions was determined using a Physica Rheolab MC 100 viscometer. The total metal concentration of the precursor solution was 0.94 mol/L (0.156 mol/L YBCO), as verified by ICP-OES (Spectro, Genesis).

Deposition of YBCO and GdBCO inks was carried out on single crystalline $SrTiO_3$ (100) substrates by ink plotting using a “Sonoplot GIX Microplotter”. The Sonoplot ink plotter is capable of applying picoliters of fluid continuously, creating features onto a surface. Ink is loaded by capillary forces into a hollow glass needle, which is attached to a piezoelectric element. At the resonant frequency of the loaded dispenser the fluid is sprayed out of a 10 μm diameter opening at the end of the needle. First, YBCO as well as GdBCO single layers were plotted separately on STO substrates. In a next step, micro liter sized ink volumes of YBCO and GdBCO were mixed for two-dimensional ink plotting of a $(Y_xGd_{1-x})Ba_2Cu_3O_x$ film library. The wet films were dried and annealed in a tube furnace from “Ströhlein Instruments”. YBCO films were pyrolized at temperatures between 200 and 400 °C in air and crystallized at 790 °C for 1 h in a dry nitrogen atmosphere mixed with 100 ppm oxygen. After heat treatment, oxygenation was performed at 450 °C for 2 h in oxygen atmosphere. GdBCO films were crystallized at temperatures between 800 °C and 840 °C. The superconducting properties were measured in a commercial physical property measurement system (PPMS) (Quantum Design) by a standard four-probe method. The crystalline quality and phase purity of the thin film were examined by X-ray diffraction (XRD) using θ / 2θ-scans and 102 ϕ-scans. Topography and film thickness were studied by atomic force microscopy (AFM) in a DI 3100. The surface morphology was additionally investigated using a scanning electron microscope (SEM).

3. Results and discussion

Figure 1 (a) shows the results for GdBCO films prepared on STO single crystals, which were annealed at different crystallization temperatures. The main diffraction peaks in all patterns are related to the (00*l*) planes of the $GdBa_2Cu_3O_{7-x}$ crystal structure indicating a (00*l*) preferred growth direction. The intensity of the (00*l*) GdBCO peaks is increasing with higher crystallization temperature of T = 840 °C pointing to a higher crystalline quality and improved phase formation. A minor diffraction peak appears at about 38°, which is correlated to the (103) plane of GdBCO suggesting a small non-textured fraction in the film. The standard diffraction patterns of YBCO films are very similar to the patterns of the GdBCO films, pointing out a high quality of crystalline Y123 phase and a strong c-axis orientation. X-ray diffraction patterns indicate a complete dissolution of $BaCO_3$ phase, which is known to destroy the superconducting properties of GdBCO- and YBCO films. The measurement of the YBCO (102) pole figure shown in figure 1 (b) confirmed a strong in-plane texture exhibiting a four-fold symmetry and a FWHM of 1°.

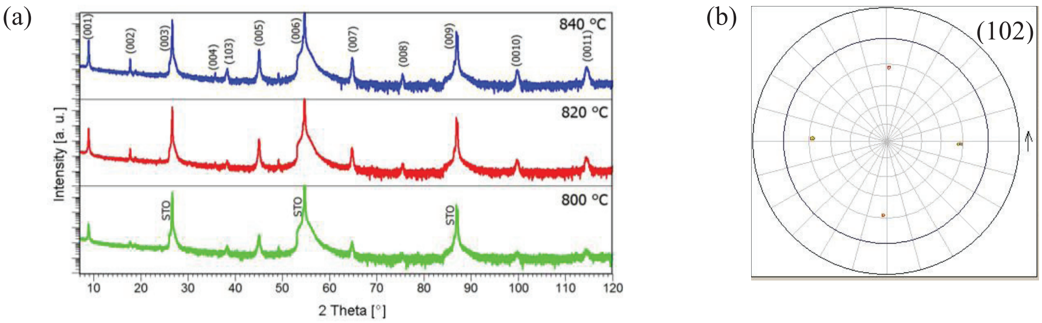

Fig. 1. (a) X-ray diffraction pattern (using Co-K_α radiation) of GdBCO films deposited on $SrTiO_3$ prepared from water-based precursor solution annealed at different crystallization temperatures; (b) YBCO (102) pole figure of a film annealed at a crystallization temperature of 800 °C.

The superconducting transition temperature of YBCO films annealed at a crystallization temperature of 790° and 820°C were measured by a standard four-probe method. The results evidence a high critical temperature $T_{c(50)} \geq 92$ K and a sharp transition into the superconducting phase for both films, see figure 2 (a). In particular, the sharp transition of the film crystallized at 790 °C originates from a high crystalline quality of the $YBa_2Cu_3O_{7-x}$ phase. The superconducting transitions of GdBCO films crystallized at different temperatures are shown in figure 2 (b). The formation of the superconducting Gd123 phase is promoted by higher crystallization temperatures, which leads to sharper transitions from the superconducting into the normal state.

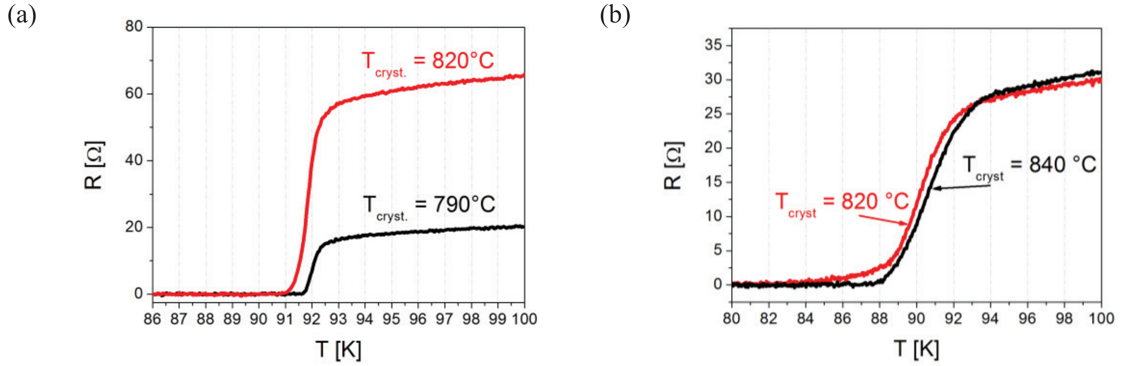

Fig. 2. (a) Measurement of the critical temperature (T_c) of (a) YBCO films and (b) GdBCO films, crystallized at different temperatures.

Micro-liter sized ink volumes were mixed with different ratios of YBCO- and GdBCO- precursor solutions and plotted on STO substrates. A two dimensional film library of at least 9 different solution compositions was plotted on the same substrate with a size of 1 by 1 cm. The joint thermal treatment of the combinatorial library $(Y_xGd_{1-x})Ba_2Cu_3O_x$ was carried out at a crystallization temperature of 820 °C as the $GdBa_2Cu_3O_x$ phase requires a higher crystallization temperature compared to the formation of the pure YBCO phase. Representative surface morphologies of the $(Y_xGd_{1-x})Ba_2Cu_3O_x$ film library are shown in figure 3 [7]. Pure YBCO films are characterised by smaller grains. With increasing amount of the GdBCO- phase the grains get larger. The average roughness was measured to be 14 nm for YBCO films which is similar to the GdBCO based films with 10 nm for a measured area of 5 μm^2. The layer thickness of all films is in the range of 40 to 50 nm.

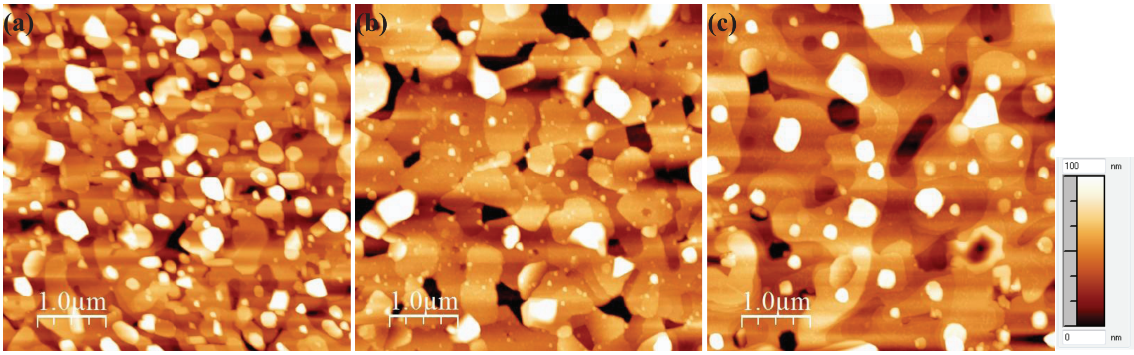

Fig. 3. AFM measurements of (a) $YBa_2Cu_3O_{7-x}$ (b) $(Y_{25}Gd_{75})Ba_2Cu_3O_{7-x}$ and (c) $GdBa_2Cu_3O_{7-x}$ films on a STO substrate crystallized at a temperature of 820 °C.

Investigations of the film library by SEM showed a homogeneous surface structure for YBCO-based as well as for GdBCO-based films, see figure 4. On all film surfaces some precipitates can bee seen which is consisted of a copper oxide phase. The surface of the films was observed to be flatter but less dense with increasing amount of Gd phase, which is consistent with the AFM results. Further studies are necessary to obtain a dense microstructure by a further optimization of the processing parameters such as the oxygen partial pressure or the crystallization temperature. No signs of an a-axis growth were found in all films.

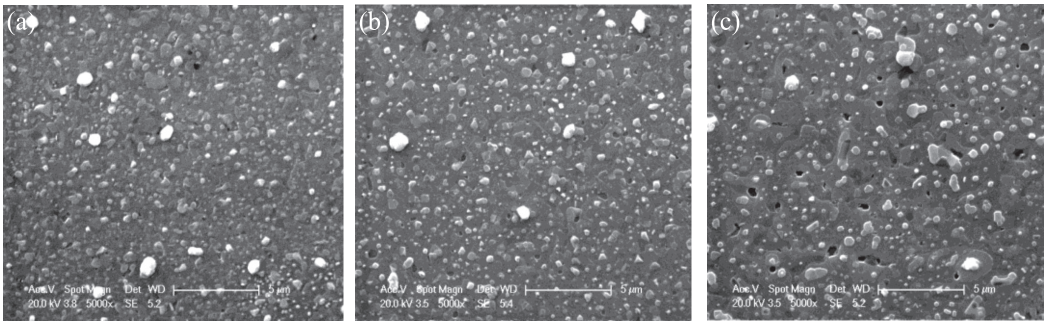

Fig. 4. SEM images of (a) $YBa_2Cu_3O_{7-x}$ (b) $(Y_{25}Gd_{75})Ba_2Cu_3O_{7-x}$ and (c) $GdBa_2Cu_3O_{7-x}$ films on a STO substrate crystallized at a temperature of 820 °C.

4. Conclusions

In this study we demonstrated the preparation of YBCO- and GdBCO- films by chemical solution deposition using environmentally-friendly water-based precursor solutions with Yttrium- and Gd-carbonate as starting salts. Two dimensional patterning of YBCO and GdBCO films was demonstrated by ink plotting and subsequent annealing. Phase formation of Gd123 requires a higher crystallization temperature of 840 °C compared to the Y123 phase formation at 790 °C. The critical temperature of YBCO films was measured to be about 92 K with a sharp transition into the superconducting state. The thermal treatment of GdBCO films need to be further optimized with regard to the transition temperature.

Micro liter sized ink volumes of YBCO and GdBCO were successfully mixed for two-dimensional ink plotting of a $(Y_xGd_{1-x})Ba_2Cu_3O_x$ film library. A homogeneous surface and no indication of a-axis growth was found in all mixed films. Pure YBCO films are characterised by smaller grains which get larger with increasing amount of GdBCO- phase.

Acknowledgements

This work was funded by the European Union within the collaborative project ‘EFECTS’ (FP7): FP7-NMP-2007-SMALL-1 grant n°205854.

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