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Fluorine-free sol gel deposition of epitaxial YBCO thin films for coated conductors

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Abstract

The current trend of coated conductor development has motivated an increasing need for a novel synthesis route by which a highly epitaxial YBCO film can be readily deposited on buffered substrates. It has been demonstrated that the fluorine-based sol gel approach can produce high quality, epitaxial YBCO thin films that exhibit a superconducting J_c of over 3–5 MA/cm^2 in self-field, 77 K. In this study we have developed a new fluorine-free sol gel approach (FFSG) as an effective alternative. The advantages of this new approach is three-fold: (1) no HF during the processing that is detrimental to the film; (2) the FFSG solution is much less reactive to the buffer layer, and (3) the microstructure of the YBCO thin film is more uniform and denser than achieved by the fluorine-based method. Using the new FFSG method, the YBCO thin films have been deposited on the LAO substrates. A high J_c on the order of 5×10^5 A/cm^2 at 77 K and self-field has been reported. Experimental results on film synthesis, and superconducting properties are presented.

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Keywords: Coated conductor; Sol gel; Superconducting films

1. Introduction

To improve the transport properties of high temperature superconducting coated conductor, extensive experimental investigations have been carried out in developing highly textured thin films on a variety of substrates [1,2]. The fabrication of $YBa_2Cu_3O_x$ (YBCO) films by epitaxial deposition on rolling assisted biaxially textured substrates (RABiTS) has proved to be successful in the conductor development for large-scale applications [1–3]. The RABiTS technique uses well-established, industrially scalable, thermomechanical processes to impart a high degree of grain texture to a base metal. Buffer layers are then deposited to yield

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chemically and structurally compatible surfaces. Epitaxial YBCO films are grown on such a surface, resulting in a critical current density at 77 K on the order of 10^6 A/cm^2 [1–3]. This approach has shown a promise for developing long conductors for industrial applications.

Trifluoroacetate (TFA) MOD is well established as a promising method for the fabrication of high J_c (over 1 MA/cm^2) YBCO films and has been applied on biaxially textured metal substrates like RABiTS [3]. The interest in fluorine-containing precursors for YBCO arises because it is believed that non-fluorine precursors might result in the formation of stable $BaCO_3$ at the grain boundaries [4]. The use of TFA salts appears to avoid the formation of $BaCO_3$ because the stability of barium fluoride is greater than that of barium carbonate and fluorine can be removed during the high temperature anneal (>700 °C) in a humid, low oxygen partial pressure environment.

Nonetheless several factors maintain interest in a fluorine-free precursor MOD approach. The most important being that removal of fluorine at high temperatures is a non-trivial process [4,5]. There appear to be many issues related to fluid-flow and complicated reactor designs may be required for scale-up. Based on our knowledge and experiment data from the deposition of YBCO thick films on metallic substrates [6], we developed one new fluorine-free sol gel approach (FFSG). According our experiments, we find that by selecting proper ingredients of precursor solution and adopting appropriate heat-treatment procedure, we can also effectively remove the carbon element in the YBCO films without the involvement of fluorine. In this work, high quality YBCO films were made by using FFSG approach, the transport critical current density of these films is over 0.5 MA/cm^2 at 77 K and self-field, a value rarely reached by other chemical solution deposition except TFA [7].

2. Experimental

The sol gel YBCO solutions were developed in house. For the precursor solution, stoichiometric (1:2:3) yttrium trimethylacetate, barium hydroxide, and copper trimethylacetate powders were dissolved in a mixed propionic acid/amine solvent with an oxide concentration between 0.1 and 0.5 mol/l. The addition of amine was important since it greatly improved the solubility of the precursor powders in propionic acid. Xylenes of alcohols were used for dilution and for controlling solution viscosity at 10–100 cp. The films were deposited by spin coating at 3000–3500 rpm and were then dried at 200–250 °C for several minutes. This process was repeated to build up the desired film thickness (0.5–0.6 μm). The films were heated at 750–810 °C under controlled atmosphere and O_2 annealed at 450 °C for 1 h. The substrates used in this experiment were commercial LAO single crystals with the (0 0 1) orientation. The LAO single crystals had dimensions of $12 \times 12 \times 1$ mm^3. One side of the single crystal was polished as-purchased.

Philips X'Pert MPD X-ray diffractometer was used to determine the texture of the YBCO film. The surface morphology were characterized by using the LEO 1530 scanning electron microscope (SEM). The superconducting transition temperature, T_c, was measured by both using an ac susceptometer and a four-probe method.

3. Results

Using the film syntheses and heat-treatment procedures described in the experimental details, we obtained well-textured YBCO thin films on LAO single crystal. The XRD analysis of the YBCO film on LAO substrate is shown in Fig. 1. As can be seen in this figure, all the (0 0 l) peaks exhibit strong intensities indicating a well textured, *c*-axis oriented grain structure. This is a quite typical XRD pattern observed from most of the sol gel derived films on LAO in our experiments. This textured structure was confirmed by high resolution TEM (HRTEM) as shown in Fig. 2, the growth of YBCO film is clearly epitaxial at the interface.

Fig. 3 shows the SEM images of YBCO film surface microstructure, which exhibit rather smooth morphology with a significant surface density. The *a–b* plane of the YBCO grains is well aligned parallel with the substrate surface showing a good

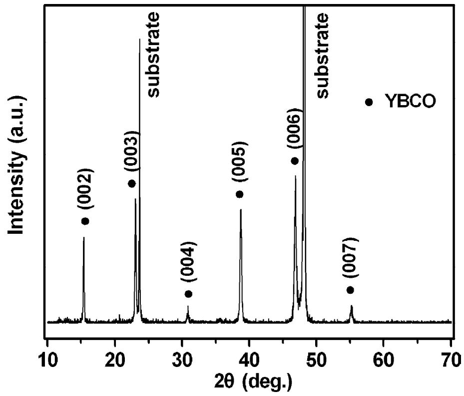

Fig. 1. XRD spectra of YBCO film on LAO substrate.

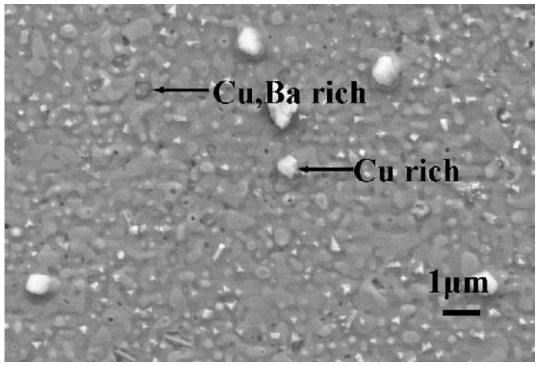

Fig. 3. SEM image showing the surface of the film on LAO.

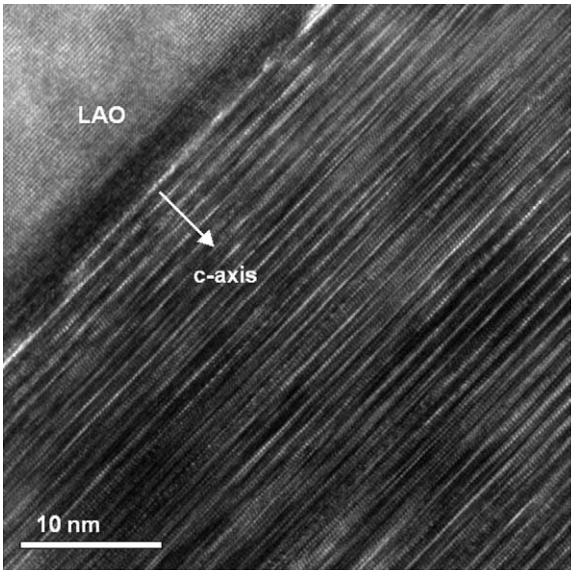

Fig. 2. HRTEM image of the interface between YBCO film and LAO substrate.

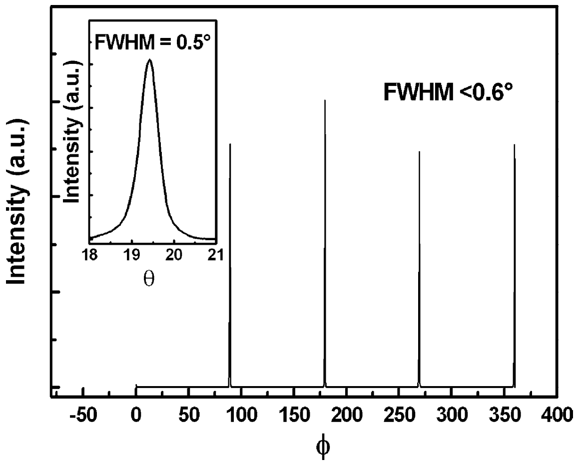

Fig. 4. (1 0 3) phi-scan of the YBCO film on LAO substrate. The inset shows the (0 0 5) omega-scan of the film.

c-axis texture. No needlelike *a*-axis oriented grains were observed. Such microstructural characteristics indicate an epitaxial growth of the YBCO film. Only a few large Cu- and Ba-rich particles on the surface can be seen from these SEM photographs. The composition of the particles was determined by using EDX.

In Fig. 4, we show the (1 0 3) phi-scan and (0 0 5) omega-scan of the YBCO film on LAO. As shown in this inset figure, full width at half maximum (FWHM) value of the (0 0 5) rocking curve is only about 0.5°. The (1 0 3) phi-scan shows four-fold symmetry with FWHM about 0.6°, indicating a high degree of in-plane texture. In the (1 0 3) pole figures of the films (Fig. 5), only four small poles located on the correct positions confirming that the YBCO phase grows epitaxially on the LAO substrate.

Fig. 6 shows the transport T_c of the YBCO thin film on LAO substrate measured by ac susceptometer. A sharp superconducting transition was observed near 90 K indicating the good quality

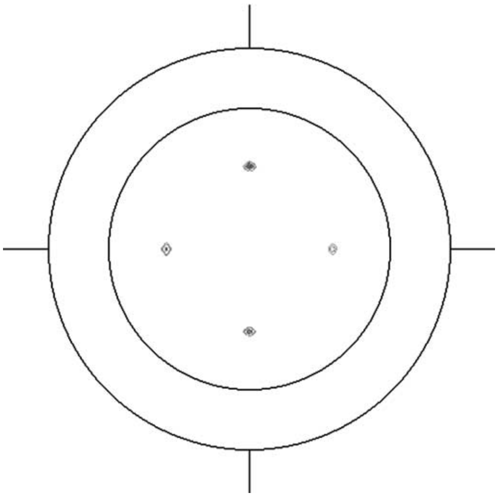

Fig. 5. (1 0 3) pole figure of the YBCO film on LAO.

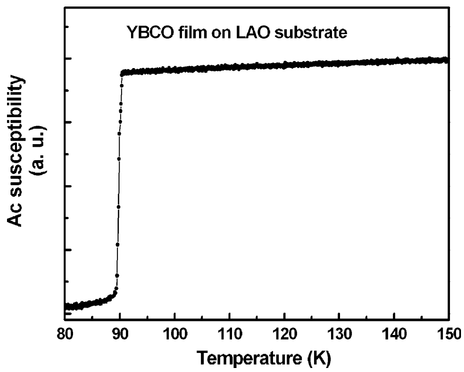

Fig. 6. Superconducting transport T_c of the YBCO thin film on LAO measured by ac susceptometer.

of the film. The transition width is only 1.0 K comparable to those of the best YBCO single crystals.

Fig. 7 shows the transport resistivity as a function of temperature for the sol gel YBCO thin film deposited on the LAO substrate. The sol gel derived YBCO film exhibits a sharp transition near 90 K. Transport critical current density has been measured for the YBCO film on LAO substrate. The measurements show a transport J_c of 0.5×10^6 A/cm^2 at 77 K and self-field, as can be seen in the inset of Fig. 7.

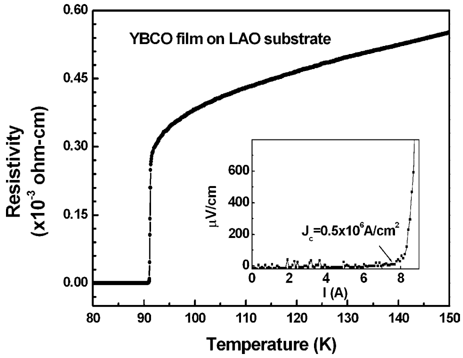

Fig. 7. Resistivity versus temperature for sol gel YBCO film on LAO substrate. The inset shows the *I–V* curve of this sample.

4. Discussion

The fluorine-free sol gel YBCO film deposited on LAO single crystal is reported quite recently. In the past, the major effort has been devoted to the TFA approach. However, we have found that, the TFA method inevitably generates HF, which is detrimental to the YBCO film, especially to the grains orientation in thick YBCO films [8]. Furthermore, in the coated conductor development, it will be critical to deposit the YBCO films on buffered substrate. And yet we have noticed a severe reaction with the buffer layer using TFA. However, this reaction is greatly reduced in the FFSG process, and we can effectively remove the carbon element by adopting appropriate heat-treatment procedure. For manufacture purposes, the stability of the precursor solution is of ultra importance because it will strongly influence the processing parameters. In FFSG method, the solution does not age during a storage life of at least six months. These are the important advantages in making long wires and tapes, especially in industrial manufacture.

5. Conclusion

Using FFSG we have deposited YBCO thin film on LAO single crystal. The YBCO film exhibits high degree of out-plane and in-plane texture. Transport measurements show sharp transitions with T_c near 90 K. A high transport J_c on the order of 0.5×10^6 A/cm^2 at 77 K and self-field has been reported.

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