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Epitaxial thick films by spray pyrolysis for coated conductors

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Abstract

Spray pyrolysis has been successfully used to synthesize many oxides, like transparent conducting films (SnO_2, ZnO and InO_3) or cuprate-based superconducting films. This technique has the great advantage of combining high deposition rates in a non-vacuum environment and cheap raw materials. In our work, spray pyrolysis has been used to grow superconducting epitaxial thick films of $YBa_2Cu_3O_{7-\delta}$ on textured substrates. A precursor nitrate solution is atomized and carried towards a substrate, which is heated at 850 °C. After growth, oxygenation is carried out by cooling under oxygen flow. YBCO films deposited on a single-crystal ($SrTiO_3$) exhibit a very good *c*-axis orientation ($\Delta\omega = 0.4°$) as well as an in-plane texture ($\Delta\varphi = 0.6°$). Transport measurement gives an I_c value close to 10 A (77 K, sf) on a 5-mm wide substrate. First YBCO depositions on metallic substrates display a reasonable out-of-plane texture ($\Delta\omega = 7°$) and a $T_{c_{onset}}$ of 90 K. Furthermore, a prospective work on buffer layers (Y_2O_3, CeO_2 and CuO) synthesis has been carried out. It has been evidenced a narrow relationship between the decomposition route of the precursors and the properties of the deposition. In certain cases NO_2 outgassing can be problematic as it can induce cracks or foam morphology.

Keywords: Films; Microstructure-final; Oxide superconductors; Spray pyrolysis

1. Introduction

In the past few years, intensive efforts have been orientated towards the preparation of long flexible high-temperature-superconductors (HTS) mainly for transformers, magnets, transmission cables, generators and fault current limiter applications. Coated conductor technology, based on the deposition of $YBa_2Cu_3O_{7-\delta}$ (YBCO) films on long flexible substrates, has produced conductors with critical current densities $J_c > 1$ MA/cm^2 (77 K, sf). But it has not yet been established which technique is the most appropriate for industrial applications and it is of a great importance to extend the investigations. In this paper, we focus on ultrasonic spray pyrolysis. The technique has the great advantage of combining high deposition rates in a non-vacuum environment and low cost raw materials (nitrates). Results on buffer layers deposited by spray pyrolysis are first reported. Then the performances of YBCO films on single-crystal and metallic substrates are presented.

2. Experimental

Y, Ba and Cu nitrate solutions are made by dissolving separately Y_2O_3 (Reacton 99.9%), $BaCO_3$ (Acros 99%) and CuO (Acros 98%) in an aqueous solution of nitric acid. The final precursor solution is prepared by mixing the individual solutions with the appropriate cation ratio. The concentration of the overall solution is 0.3 mol/L. The solution of cerium nitrate is obtained by dissolving $Ce(NO_3)_3$ in deionised water. The nitrate solution is sprayed into a mist using an ultrasonic generator that produces droplets of 15–20 μm in size. The mist is carried by argon onto the substrate, which is heated

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at around 850 °C. The spray is generated for 10 min. After growth, oxygenation is carried out by a controlled cooling to room temperature under oxygen flow. The films are characterized by scanning electronic microscopy (SEM), X-ray diffraction (XRD), AC susceptibility (χ_{ac}) and four probe resistive method.

3. Results and discussions

3.1. Buffer layers

3.1.1. Y_2O_3 and CeO_2

Prospective work on the synthesis of buffer layers by nitrate spray pyrolysis has been started. First Y_2O_3 and CeO_2 depositions have been performed at 700 °C under a flow of argon. In both cases we do not obtain continuous and dense films but sparse foams, made of hollow and cracked spheres. To determine the cause of this morphology we have investigated the decomposition of nitrate powder. In a previous work[1] we had shown that yttrium nitrate powder placed in a crucible and heated up to 850 °C in a furnace under an argon flow led to Y_2O_3 foam because of a NO_2 outgassing out of a very viscous liquid. The important result is to stress that the morphology of the film depends, at least partly, on the mechanisms of nitrate decomposition. The morphology could probably be improved if di-aggregation of the foam is performed, for example by an increase in temperature or in nozzle–substrate distance.

3.1.2. CuO

CuO films have been obtained at 400 °C under argon flow on MgO (1 0 0). Fig. 1 shows XRD patterns ($\theta/2\theta$) of a CuO film. The film exhibits a (1 1 1) texture and a smooth surface with a thickness of 400 nm. The decomposition of copper nitrate powder leads to the formation of a fine powder of CuO above 300 °C. Such morphology is propitious to epitaxial film formation and could be useful for YBCO growth, provided cube texture growth of CuO could be selected.

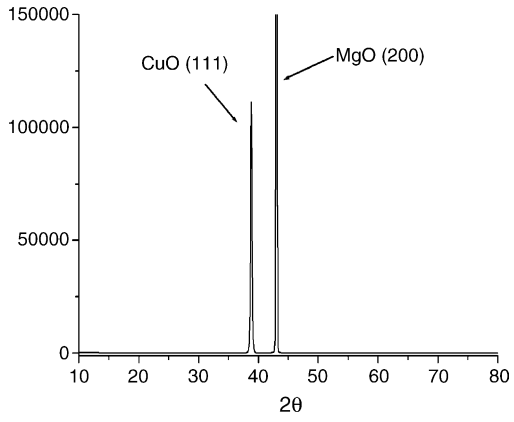

Fig. 1. XRD pattern ($\theta/2\theta$) of a CuO film deposited on a MgO single-crystal.

Table 1
Microstructures (grains size, in-plane and out-of-plane textures, *c*-axis/*ab*-plane growth proportion, T_c) of YBCO films deposited respectively at 840, 850 and 860 °C on $SrTiO_3$ single-crystals

	M1	M2	M3
Grain size (μm)	<1	~1–2	10
Texture			
(1 0 3)	$\Delta\varphi$=1.0°	$\Delta\varphi$ = 0.6°	$\Delta\varphi$ = 0.6°
(0 0 5)	$\Delta\omega$=0.6°	$\Delta\omega$ = 0.6°	$\Delta\omega$ = 0.8°
c-Axis growth proportion (%)	66	75	92
T_c (AC susceptibility) (K)	82	90	No screening
	ΔT_c = 3 K	ΔT_c = 1 K	

3.2. YBCO films on single-crystal

3.2.1. Composition

The composition of the precursor solution is not conserved in spray pyrolysis. For this reason the first step to process is an adjustment of the stoichiometry in the starting solution. We have found the optimal value of the cationic ratio to be Y:Ba:Cu = 1:2:1. It is interesting to note that most authors use a stoichiometry close to 1:2:*x*.[2–4] Therefore, the ratio Y:Ba is independent from experimental conditions and moreover it is equal to the initial ratio. Copper is deposited at a higher rate. We can explain the preferential deposition of copper by the fact that copper nitrate is already decomposed in oxide when it hits the substrate ($T_{CuO\ formation} \approx 300$ °C) while barium and yttrium are pushed back from the substrate by NO_2 outgassing which occurs during precursors decomposition on the substrate ($T_{Y_2O_3\ formation} \approx 550$ °C et $T_{BaO\ formation} \approx 700$ °C).

3.2.2. Microstructure

The films microstructures vary drastically in a narrow temperature range and have important effects on the superconducting properties. Three different microstructures M1, M2 and M3 have been obtained for films deposited on $SrTiO_3$ (STO) substrates, which have been heated respectively at 840, 850 and 860 °C. The microstructural and superconducting properties (grains size, φ-scan, ω-scan, proportion *c*-axis/*ab*-plane growth, critical temperature T_c) are reported in the Table 1. Fig. 2 shows SEM photographs of the films cross sections. First statement is that grains size increases strongly with temperature: it is less than 1 μm for a deposition temperature of 840 °C and more than 10 μm at 860 °C. Moreover the proportion of *c*-axis growth compared with *ab*-plane growth is larger at 860 °C (92%) than at 840 °C (66%). We note that the φ-scan and ω-scan full-width-half-maximum = $\Delta\varphi$ (FWHM) values are not significantly changed. Nevertheless, no χ_{ac} transition has been detected for M3, and M1 exhibits a broad transition. Only M2 displays a narrow transition at 90 K. At 840 °C some porosities are observed (Fig. 2a) inside the film, which are caused by the crossing of *c*-axis and *ab*-plane grains. Moreover the diffusion of the cations is not very active as shown by the small grains size and impurities are probably trapped in the film. These defects generate

Fig. 2. SEM photographs of cross sections of YBCO films deposited on $SrTiO_3$ single-crystals. The corresponding microstructural characterizations are reported in the Table 1. (a) M1, (b) M2 and (c) M3.

a broad χ_{ac} superconducting transition. At 860 °C a larger diffusion enables the growth of large grains and an efficient mixture of the species. But a XRD peak at $2\theta = 36.6°$ reveals the presence of a non-identified phase, which is probably a reaction phase with the substrate, that precludes the χ_{ac} superconducting transition. Therefore, the best microstructure is a compromise between a maximum of *c*-axis growth and an absence of parasite phase. It was found for a temperature of 850 ± 3 °C.

3.2.3. Superconducting properties

The best YBCO films deposited on STO single-crystals display a $T_c = 90$ K with $\Delta T = 1$ K. J_c measured by χ_{ac} are regularly larger than 1 MA/cm^2 (77 K, sf) for a thickness of 1 μm, showing a good homogeneity of the film volume. Fig. 3 shows transport measurement on a 5-mm wide tape. The critical current value is equal to $I_c = 9.7$ A (77 K, sf).

3.3. YBCO films on substrates prepared by ion beam assisted deposition (IBAD) method

YBCO films have been deposited on YSZ (ZrO_2 doped with 10% of Y_2O_3)-IBAD substrates covered with a homo-epitaxial YSZ layer deposited by metal organic chemical vapour deposition (MOCVD).[5] Fig. 4 displays the $\theta/2\theta$ scan

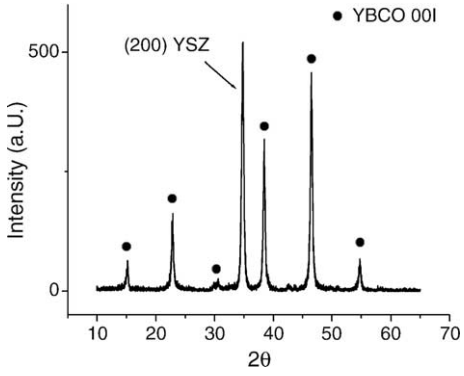

Fig. 4. XRD pattern ($\theta/2\theta$) of a YBCO film deposited on a YSZ-IBAD substrate.

of this film: YBCO-film is *c*-axis textured as revealed from the enhanced 0 0 ℓ peaks. The out-of-plane texture (0 0 5) is rather good ($\Delta\omega = 7°$) but the in-plane texture (1 0 3) ($\Delta\omega > 35°$) needs to be improved. Probably the rather large mismatch of YBCO with YSZ (~6%) accounts for the absence of in-plane texture. Fig. 5 shows a χ_{ac} transition of such an YBCO film with a T_c onset of 90 K and a T_c endpoint of 75 K. The broad transition is probably due to the presence of porosities in the film as well as secondary phases caused by a small deviation of the composition.

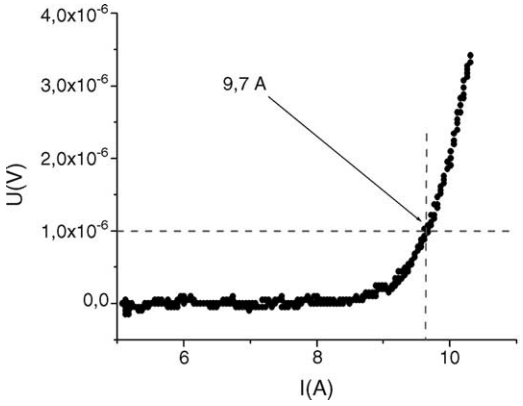

Fig. 3. I_c (77 K, sf) transport measurement of a 5-mm wide YBCO film deposited on a $SrTiO_3$ single crystal.

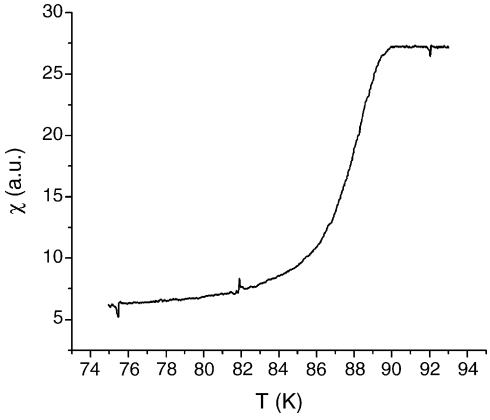

Fig. 5. χ_{ac} measurement of an YBCO film deposited on a YSZ-IBAD substrate.

4. Conclusion

Nitrate spray pyrolysis is an efficient method for YBCO films synthesis. A suitable microstructure requires the absence of *ab*-plane growth and parasite phases, and has been obtained at around 850 °C in a temperature range of 3 °C. It has been not yet elucidated if the critical evolution of the microstructure versus temperature is caused by kinetic or thermodynamic factors. The synthesis of simple oxides (buffer layers) strongly depends on the characteristics of the precursors. Y_2O_3 and CeO_2 morphologies are not propitious due to foam formation while CuO fine powders is more favourable for the growth of epitaxial films.

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