Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1831–1835
www.elsevier.com/locate/jeurceramsoc

Chemical solution techniques for epitaxial growth of oxide buffer and $YBa_2Cu_3O_7$ films

A. Cavallaro, O. Castaño, A. Palau, J.C. González, M.D. Rossell, T. Puig, F. Sandiumenge*, N. Mestres, S. Piñol, X. Obradors

Institut de Ciència de Materials de Barcelona, CSIC, 08193 Bellaterra, Catalonia, Spain

Abstract

Chemical solution techniques have been investigated for the growth of both, oxide buffer layers suitable for coated conductors and $YBa_2Cu_3O_7$ thin films, on single crystal substrates. Growth conditions have been optimised for CeO_2 and $BaZrO_3$ buffer layers, leading to high quality epitaxial films (misorientation spread typically below 1°). $YBa_2Cu_3O_7$ films (thickness: 250 nm) have been grown from trifluoroacetate precursors. The kinetic hindrances for the formation of single phases have been investigated by means of Raman spectroscopy and fluorine analysis. After optimisation of the deposition and growth conditions very high critical currents have been achieved ($J_c^{ab} = 3.2\times10^6$ A/cm^2 at 77 K and 2.7×10^7A/cm^2 at 5 K).

Keywords: Coated conductors; Films; Oxide superconductors; Sol-gel processes

1. Introduction

Chemical solution growth of thin films has arisen as a new very exciting opportunity for the development of advanced functional ceramic materials. It has been particularly shown that epitaxial thin films can be grown on single crystalline substrates thus rising new opportunities for many applications where the material anisotropy or the granular character needs to be controlled. This includes ferroelectric-based devices, magnetoelectronic oxides, superconducting materials, etc.[1]

A very outstanding challenge, from the materials preparation point of view, is the preparation of superconducting coated conductors where a biaxial texture of the superconducting oxide needs to be reached on metallic substrates. These metallic substrates can be either textured themselves through metallurgical processes, such as the RABiT technique,[2] or they can have an oxide buffer template textured by the IBAD technique,[3] or the so-called inclined substrate deposition (ISD) method where the substrate is directed at a certain angle of the deposition beam generated by pulsed laser deposition (PLD). Over the past years many experimental techniques have been investigated to obtain $YBa_2Cu_3O_7$ thin films, with a thickness as high as possible, on metallic substrates. This includes PLD, sputtering, thermal co-evaporation, CVD, Liquid Phase Epitaxy, etc. Among these techniques, those based on a chemical solution growth process appear as very promising in view of the preparation of low cost conductors.[4,5] It is however a complex issue to reach a full control of all the microstructural factors which may influence the superconducting properties of these conductors. It appears then very appealing to investigate first the influence of the processing parameters on the growth mechanisms and the microstructural development on single crystalline substrates. In this work we present a study of the growth of oxide buffer layers, particularly $BaZrO_3$ and CeO_2, which have a good crystallographic and chemical compatibility with the high T_c oxide superconducting materials, and the growth of $YBa_2Cu_3O_7$ by means of the so called trifluoroacetate (TFA) route.[4–7]

2. Experimental details

CeO_2 and $BaZrO_3$ buffer layers have been grown on (100)Y-stabilised ZrO_2 (YSZ) and (100)$LaAlO_3$ (LAO)

* Corresponding author. Tel.: +34-93-580-18-53; fax: +34-93-580-57-29.
E-mail address: felip@icmab.es (F. Sandiumenge).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00448-5

single crystal substrates, respectively. The precursor solutions were 2,4-pentadionate dissolved in glacial acetic acid for Ce and Zr and Barium acetate for Ba. The concentration of the precursor solutions was modified in order to obtain a suitable solution and films of the desired thickness. The solutions were then spinned under constant acceleration at a speed within the range 3000–6000 rpm. After a drying process carried out at 150–200 °C for 30–60 min, a high temperature treatment (650–900 °C) under an Ar/5%H_2 atmosphere promotes the growth of single phase layers.

Trifluoroacetate (TFA) precursors for the growth of $YBa_2Cu_3O_7$ were prepared by dissolving stoichiometric mixtures of Y, Ba and Cu acetates in an aqueous solution of 25% of trifluoroacetic acid. After drying, the resulting blue glassy residue was dissolved in methanol to obtain a solution of suitable viscosity, in the range 0.8–1.2 cp, allowing a uniform coverage of the substrate during the spin coating process performed at 6000 rpm. The concentration of the precursor solution was adjusted to obtain a film thickness $t \approx 250$ nm. The wet films were calcined in three stages. First, the organic material was pyrolysed at 400 °C and a slow rate (20 h) in an O_2 atmosphere, then crystallised at high temperatures (750–830 °C) in a humid atmosphere ($PH_2O = 7.3\%$) and $PO_2 = 20$ ppmO_2. It is important to stress that a humid atmosphere is needed in both steps: (1) In the pyrolysis step it prevents from Ba–TFA evaporation by the formation of copper hydroxyltrifluoracetate which decomposes to CuO before evaporating, thus preserving the initial stoichiometry; and (2) In the crystallisation step, when the Ba–TFA has transformed to BaF, a humid atmosphere allows the transformation to BaO through the reaction: $BaF_2 + H_2O \rightarrow BaO + 2HF$. Typically 3 h allowed to complete the reaction for films of 250 nm. In the last stage the films were oxidised at 450 °C in a dry oxygen atmosphere during 1 h to obtain the superconducting phase.

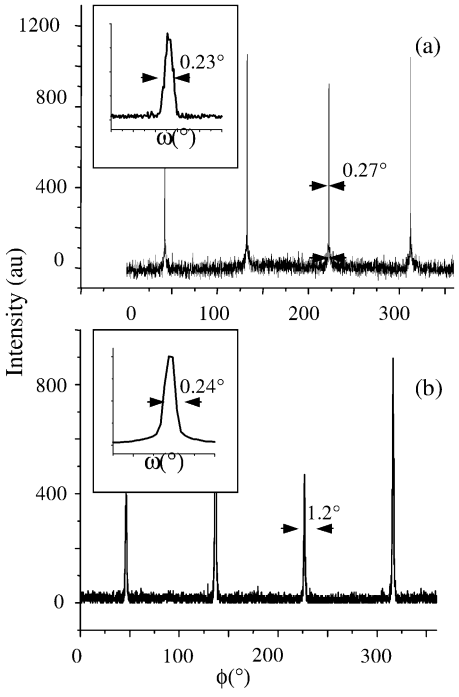

Fig. 1. (a) (111)-reflection ϕ-scan of a CeO_2 buffer layer grown on YSZ, inset shows the (400)-reflection rocking curve; (b) (111)-reflection ϕ-scan of a $BaZrO_3$ buffer layer grown on $LaAlO_3$, inset shows the (200) rocking curve.

X-ray diffraction ($\theta/2\theta$, ω-scan, ϕ-scan and pole figures) was used to determine the phase purity and the crystallographic texture of the films. μ-Raman spectroscopy was used to detect the misoriented grains, as well as impurity phases hardly detected by X-ray diffraction. Fluorine analysis of the exhaust gases in the furnace was performed using a selective electrode in order to monitor the reaction transforming BaF_2 to $YBa_2Cu_3O_7$ through the formation of HF. SEM and AFM were used to study the microstructure and the surface roughness, respectively. Finally, the superconducting properties were studied through four-points electrical resistivity measurements and low field dc susceptibility. Inductive critical currents were measured with a SQUID magnetometer. The critical currents were calculated from the irreversible magnetization using the critical state model which states that $J_c^{ab} = 30\ \Delta M/2R$, where ΔM is the irreversible magnetization and R the radius of the sample.

3. Results and discussion

3.1. Growth of buffer layers

After optimisation of growth conditions, careful inspection of $\theta/2\theta$ scans only reveal (00l) type reflections both in CeO_2 on (001)YSZ and $BaZrO_3$ on (001)LAO. Fig. 1(a) shows the (111) ϕ-scan corresponding to CeO_2 on (100)YSZ. The inset corresponds to the (400) rocking curve (ω-scan). Very small FWHM values were typically obtained in both cases, $\Delta\phi = 0.27°$ and $\Delta\omega = 0.23°$, indicating an excellent epitaxy. The uniqueness of the cube on cube texture was verified by pole-figure measurements. Similar values are obtained in films having a thickness in the range 20–100 nm. $BaZrO_3$ films grown on LAO also displayed excellent epitaxial features [Fig. 1(b), $\Delta\phi = 1.2°$, $\Delta\omega = 0.24°$].

The evolution of the microstructural modifications induced by changes in the growth temperature was followed through AFM observations. Fig. 2 displays a typical image corresponding to CeO_2 on (100)YSZ, showing a nanometric grain size ($\Phi \approx 30$ nm), a very low porosity and a surface roughness of rms≈1 nm. Similar values were achieved in the case of $BaZrO_3$ layers.

3.2. Growth of $YBa_2Cu_3O_7$ films

The conversion of the TFA salts into $YBa_2Cu_3O_7$ thin films is a complex process which involves, first, a pyrolysis step where the metalorganic precursors are decomposed at low temperature into nanometric CuO, Y_2O_3 and BaF_2.[4,5] The pyrolysis conditions must be optimised in order to avoid compositional inhomogeneities, as well as the generation of cracks during the thermal shrinkage. The second reaction step occurs at high temperatures where the decomposition of BaF_2 and its reaction with the oxides leads to the formation of the $YBa_2Cu_3O_7$ phase. The kinetics of this reaction is mainly governed by the diffusion of the atomic species and the elimination of HF.

Fluorine analysis indicated that the reaction time was doubled when the temperature was reduced from 830 to 700 °C, when the remaining parameters were kept fixed. μ-Raman spectroscopy appeared to be a powerful tool to clearly detect small amounts of unreacted phases,[8] even when they were hardly detected in the X-ray diffraction pattern. This is particularly the case of $BaCuO_2$, which is an impurity that probably appears as a result of a kinetic hindrance promoted by metal macrosegregation effects generated during the deposition or the pyrolysis steps. We have found that the formation of this impurity is avoided when the reaction is performed at high temperature.

A typical X-ray diffraction pattern of an optimised sample is shown in Fig. 3(a). No impurity phases are detected, while the $YBa_2Cu_3O_7$ film only exhibits (00*l*) type reflections. Fig. 3(b) is a ϕ-scan corresponding to the (113) reflection. The in-plane misorientation spread of the film is 0.6°, as revealed by the FWHM of the peaks. The inset corresponds to the (005)-reflection

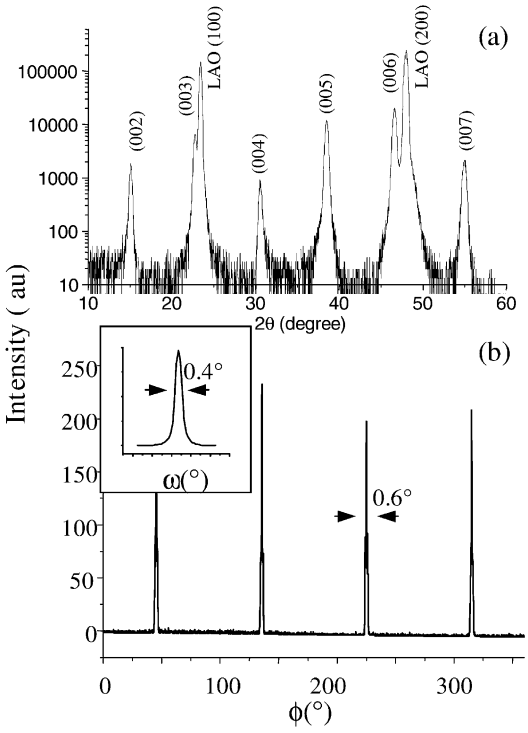

Fig. 3. (a) $\theta/2\theta$ X-ray diffraction pattern of a $YBa_2Cu_3O_7$ film deposited on a $LaAlO_3$ substrate; (b) (113)-reflection ϕ-scan. Inset shows the (005)-reflection rocking curve.

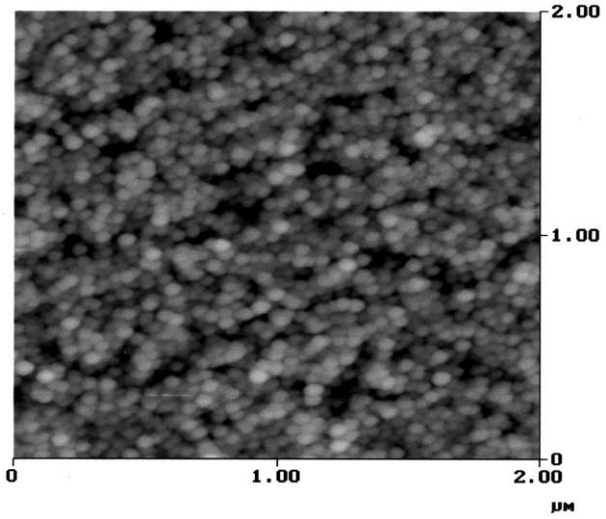

Fig. 2. AFM image of the surface of a CeO_2 buffer layer grown on YSZ.

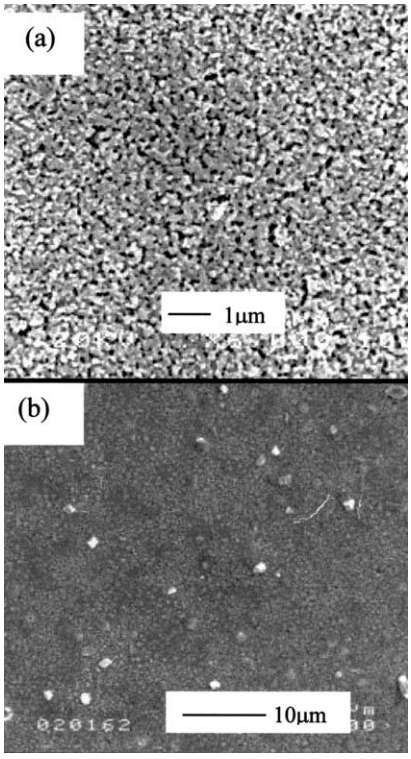

Fig. 4. SEM images of the surface of two $YBa_2Cu_3O_7$ films grown at 700 °C (a) and 830 °C (b). Note that in (b) no residual porosity is observed.

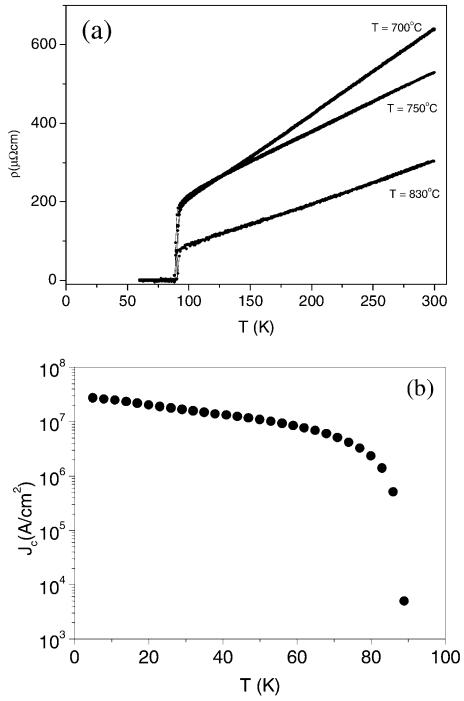

Fig. 5. (a) Temperature dependence of the electrical resistivity in $YBa_2Cu_3O_7$ thin films grown at different temperatures displaying different concentrations of pososity; (b) Temperature dependence of the critical currents $J_c^{ab}(T)$ in a high quality $YBa_2Cu_3O_7$ thin film.

rocking curve, indicating an out of plane misorientation spread as small as 0.4°. These results indeed demonstrate that an excellent degree of epitaxy can be achieved by the TFA process.

Interestingly, the increase of the reaction temperature during the growth process not only has beneficial effects avoiding the formation of impurities, but also has proved to have a tremendous influence on the final microstructure, in particular the porosity, and the superconducting properties of the samples. A typical example is presented in Fig. 4, where two SEM images of the surface of two samples annealed at 700 °C (a) and 830 °C (b) are shown. In both cases the annealing duration was adjusted such as to ensure the completion of the reaction. The differences in the pore concentration in both samples are evident.

A quantitative indirect determination of this effect was performed through measurements of the electrical resistivity in the normal state. As it may be observed in Fig. 5(a), the slope of the temperature dependence of the resistivity and the residual resistivity are enhanced in the samples with higher porosity, thus indicating that the percolative behaviour of current is hindered in such disordered films. The resistivity observed at 300 K in the samples having a low porosity, $\rho(300\ K) \approx 300\ \mu\Omega cm$, along with the high resistivity ratio $\rho(300\ K)/\rho(100\ K) \approx 3.3$ are typical features of high quality thin films. In this figure we can also observe that the transition temperature $T_c \approx 90$ K was not modified by the annealing temperature.

Finally, the critical currents of the $YBa_2Cu_3O_7$ thin films were measured inductively by using a SQUID magnetometer. The critical currents were found to be very sensitive to the residual porosity of the films. Very high J_c^{ab} values were measured, instead, in samples showing no residual porosity. As it can be seen in Fig. 5(b), at zero field these samples displayed very high critical currents ($J_c^{ab} = 3.2 \times 10^6$ A/cm^2 at 77 K and 2.7×10^7A/cm^2 at 5 K). It is worthy to mention that such high performances in $YBa_2Cu_3O_7$ thin films usually require the use of vacuum techniques. Therefore, the present work further supports that chemical solution growth techniques have the potential to become competitive, from the performance point of view, with those techniques. We also note that in the present work no special refinement process of the metalorganic precursors was applied, as it was described in other works.[6]

In conclusion, we have demonstrated that a careful understanding of the influence of the wide variety of process parameters involved, allows the deposition of high quality buffer layers and superconducting $YBa_2Cu_3O_7$ thin films from chemical solutions on single crystal substrates. More importantly, the present work strongly supports that further insights into the influence of the processing parameters on film quality will allow the extension of this low cost technique to chemically based coated conductors.

Acknowledgements

This work has been supported by the Spanish Science Ministry (MAT 2001-1698 and 2FD97-1628), by the Catalan Pla de Recerca (00206) and the EU-Marie Curie Program (HPMT-CT-2000-00106). A.P. and M.R. acknowledge to C.S.I.C. and J.C.G. to A.E.C.I. for a doctoral fellowship.

References

1. Lange, F. F., Chemical solution routes to single-crystal thin films. *Science*, 1996, **273**, 903.
2. Norton, D. P. et al., Epitaxial YBCO on biaxially textured Nickel (00l): an approach to superconducting tapes with high critical current density. *Science*, 1996, **274**, 755.
3. Ijima, Y. et al., In-plane aligned YBCO thin films deposited on polycrystalline metallic substrates. *Appl. Phys. Lett*., 1992, **60**, 769–771.
4. Mclntyre, P. C. and Cima, M. J., Heteroepitaxial growth of chemically derived ex situ $YBa_2Cu_3O_{7-x}$ thin films. *J. Mater. Res*., 1994, **9**, 2219–2230.
5. Smith, J. A. et al., High critical current density thick MOD-derived YBCO films. *IEEE Trans. Appl. Supercond*., 1999, **9**, 1531.

6. Araki, T. et al., Coating processes for $YBa_2Cu_3O_{7-x}$ superconductor by metaorganic deposition method using trifluoroacetates. *Supercond. Sci. Technol.*, 2001, **14**, 783–786.
7. Jee, Y-A. et al., Texture development and superconducting properties of $YBa_2Cu_3O_x$ thin films prepared by a solution process in low oxygen partial pressure. *Supercond. Sci. Technol.*, 2001, **14**, 285–291.
8. Puig, T. et al., Texture analysis of coated conductors by micro-Raman and synchrotron X-ray diffraction. *Mat. Res. Soc. Symp.II5.6.1.-6.6.*, 2001, **659**.