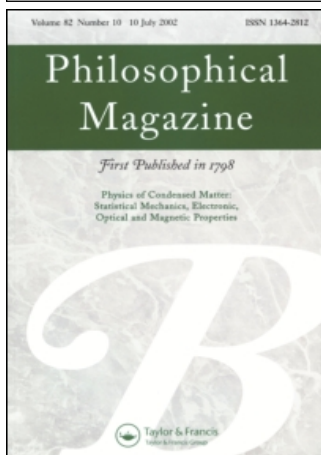


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### A study of $\text{YBa}_2\text{Cu}_3\text{O}_x$ films grown by metal-organic deposition on different substrates

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## A study of $\text{YBa}_2\text{Cu}_3\text{O}_x$ films grown by metal–organic deposition on different substrates

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### ABSTRACT

In this work we describe the microstructural features of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (YBCO) superconducting films, obtained by metal–organic deposition produced on different substrates: metallic (Ag and Cu), polycrystalline ( $\text{Al}_2\text{O}_3$  and  $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{1.93}$ ) and single crystals ( $\text{MgO}(001)$ ,  $\text{SrTiO}_3(001)$ ,  $\text{LaAlO}_3(001)$ ,  $\text{NdGaO}_3(001)$  and  $\text{CaNdAlO}_4(001)$ ). The samples were characterized by X-ray diffraction and scanning electron microscopy analyses. We observed that the YBCO film orientation is influenced by the substrate nature: on single-crystal substrates, YBCO films show a preferential (001) orientation. The alkaline-earth–rare-earth aluminates have proven an excellent choice for deposition.

### §1. INTRODUCTION

As many of the most important and advantageous applications (Nakahara 1993) of superconductivity refer to the remarkable possibilities of superconducting materials in electronic fields, the preparation method of thick films is of important practical interest. Thick films of high-temperature superconductors have potential applications in high-current transmission lines, magnetic shields, resonators for microwave filters, Josephson junction devices, etc. (Alford *et al.* 1997). Several deposition methods (Stoessel *et al.* 1993) have been developed since 1987, and they can be devised in *in-situ* and *ex-situ* methods; in the first the crystal film is directly obtained in a cell under vacuum and in the second the film is obtained as amorphous and, successive annealing leads to the desired crystal form. Most of the preparation techniques (Vase *et al.* 1990, Catana and Locquet 1993) such as laser ablation deposition and molecular-beam epitaxy need sophisticated instruments and give good-quality films, which are not versatile in form and size. It is difficult to state which is the best method, giving more advantages than the others. The deposition method should be simple, low cost, fast and with a good control of the film composition. Moreover, it must include a good mixing of precursors and be useful to cover large areas of different forms and shapes.

One of the very simple chemical methods used to prepare thick, polycrystalline films is metal–organic deposition (MOD) (Teng and Wu 1989, Sathyamurthy and Salana 1998) of the precursor materials. The MOD technique consists of several steps. The solution is prepared with suitable amounts of metal–organic salts in order to obtain the desired stoichiometric ratios, and then it is sprayed on to a substrate. Subsequently, the samples are pyrolysed and annealed under

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appropriate temperature and atmosphere conditions to obtain the final superconducting material.

The superconducting properties of the resulting material are very sensitive to the heat treatment conditions, which are crucial for the quality of the samples. Therefore, an improvement in the annealing cycle results in a long-standing problem (Zandbergen *et al.* 1993, Scheel 1994). The preparation of a good film is substantially affected by the kind of compound used as the substrate. For the electronic component used in the technological applications, the ideal substrates would be Si, sapphire and GaAs (Blank *et al.* 1989).

Unfortunately, besides the high value of lattice mismatch, the high chemical interaction between substrate and film spoils the superconducting properties. Therefore, it is necessary to deposit a buffer (Kim *et al.* 1992) layer, a few nanometres thick, to prevent contact between the substrate and the film.

For a few years a modified MOD technique has been used in our laboratory to prepare both  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (YBCO) and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  films (Manfredotti *et al.* 1994). In this study we deposited YBCO films by the modified MOD method on several substrates having different crystalline and dielectric properties without changing the YBCO film deposition parameters.

## §2. EXPERIMENTAL DETAILS

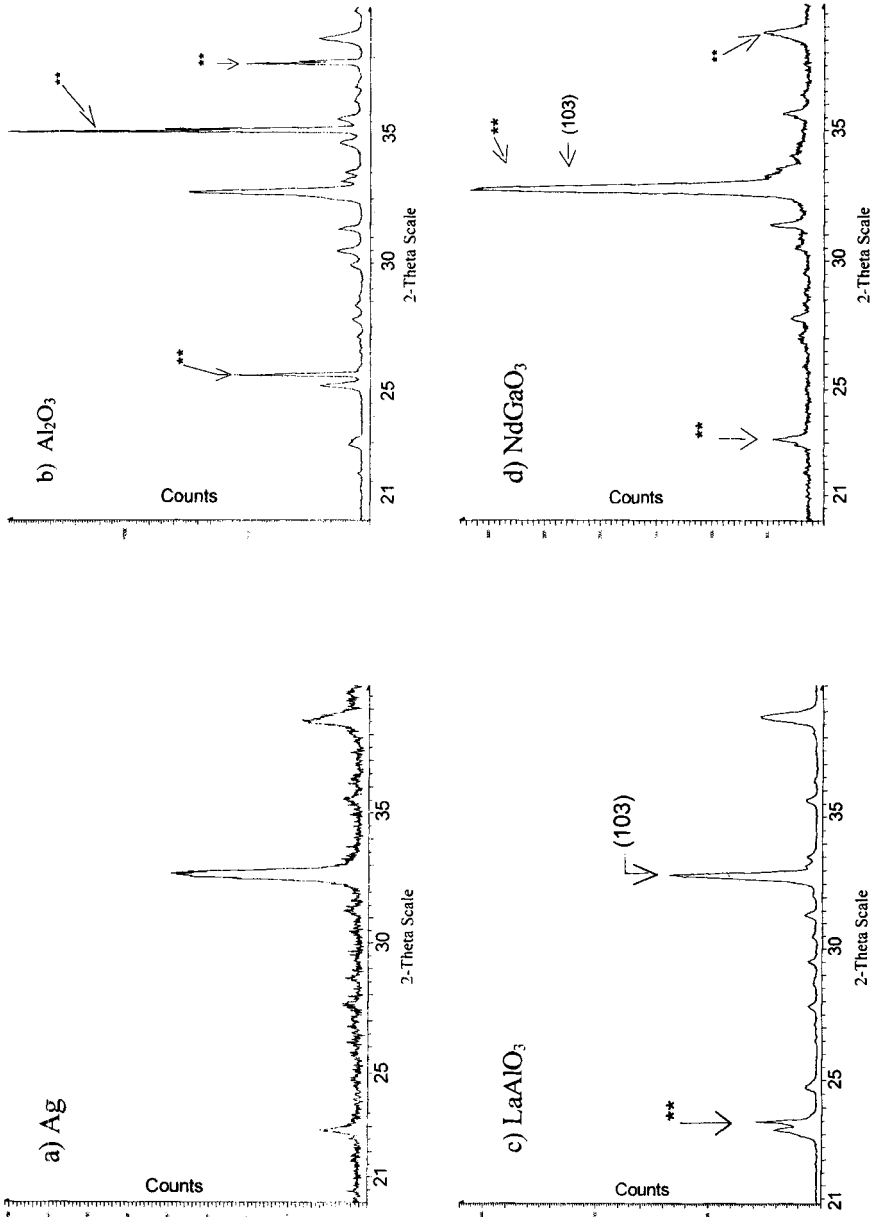
The MOD method is generally applied using spinning, while deposition by spray pyrolysis (Conde-Gallardo *et al.* 1996) is used for aerosols of aqueous solutions of nitrates. Considering that the use of MOD solution provides an optimal mixing of precursors and that spray pyrolysis is a simple deposition technique, we performed spray deposition of superconducting films using organic solutions of precursors salts, with an air brush.

Samples were prepared starting from a solution of neodecanoate of Y, Ba and Cu in the correct stoichiometry proportions (1:2:3) in pyridine and xylene (5:5). The solution was atomized using an air brush; during the pyrolysis the drops were dried and transformed into oxides or carbonates. The film deposition was obtained by a series of deposition–pyrolysis cycles at 500°C in air, which affects both the final thickness and the surface smoothing of the obtained film. The annealing took place under oxygen at 940°C for 10 min, followed by oxygenation at 450°C for 24 h.

The X-ray diffraction (XRD) analyses were performed with a Siemens D5000 (Cu  $K\alpha$ ) diffractometer. The measurements was performed in the  $2\theta$  range between 20° and 40° with a 0.02 step during one night. The unit cell of the sample was obtained by means of least-squares software. The sample morphology was investigated by scanning electron microscopy (SEM) with a Leika instrument. The critical temperature was measured by magnetic susceptibility investigations with a Lakeshore 7000 instrument.

## §3. RESULTS

Metallic (Ag and Cu), polycrystalline ( $\text{Al}_2\text{O}_3$  and  $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{1.93}$  (YSZ)), and single-crystal (MgO(001),  $\text{SrTiO}_3$ (001),  $\text{LaAlO}_3$ (001),  $\text{NdGaO}_3$ (001) and  $\text{CaNdAlO}_4$ (001)) (10 mm × 10 mm × 1 mm) substrates were tested for the growth of YBCO films. Films of YBCO, with thicknesses ranging from 6 to 8  $\mu\text{m}$ , were obtained on all the substrates. The critical temperatures, obtained from susceptibility



Note: the substrate peaks falling between  $2\theta = 20^\circ$  and  $2\theta = 40^\circ$  are marked by \*\*. The (103) reflection of YBCO is labelled.

Figure 1. XRD patterns for YBCO films on (a) Ag, (b) Al<sub>2</sub>O<sub>3</sub>, (c) LaAlO<sub>3</sub> and (d) NdGaO<sub>3</sub> substrates.

measurements, are around 85 K with the exception of sample on  $\text{LaAlO}_3$  which exhibits a  $T_c$  of 90 K.

Some of the XRD patterns of a number of YBCO films obtained on different substrates are reported in figure 1. Figure 1 (*a*) shows the spectrum of a YBCO film on metallic substrate (Yin *et al.* 1992), particularly Ag; characteristic peaks of the superconductive phase are clearly visible at  $2\theta = 22.8, 32.8$  and  $38.5^\circ$  attributable to (030), (103) and (050) reflections respectively; the spectrum does not differ from that of the bulk sample (Joint Committee for Powder Diffraction Standards 38-1433).

Analogous patterns are obtained using the Cu substrate; nevertheless the film surface does not appear smooth, because a rough CuO layer is formed during the first cycle of pyrolysis.

The XRD pattern for a film on a polycrystalline substrate (Shaw 1992) ( $\text{Al}_2\text{O}_3$ ) is shown in figure 1 (*b*); in this case, the film structure is also randomly oriented; some peaks are evident between  $2\theta = 29.5$  and  $31.5^\circ$ , which can be assigned to  $\text{Y}_2\text{BaCuO}_5$ . A similar spectrum is obtained for the YBCO film on YSZ; some cracks are present, indicating that the thickness exceeds 50 nm. Cracking is caused by a mismatch between the coefficients of thermal expansion for the film and the substrate.

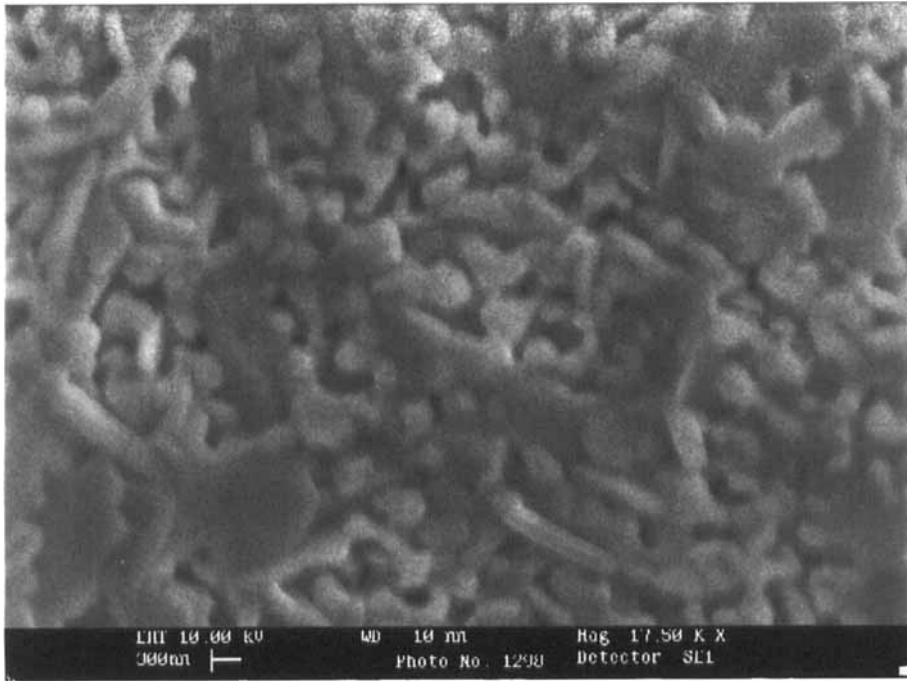
In figures 1 (*c*) and (*d*) the spectra of YBCO films on the single-crystal substrates  $\text{LaAlO}_3$  and  $\text{NdGaO}_3$  are shown respectively (Phillips *et al.* 1992). YBCO films on the other single-crystal substrates exhibit similar XRD spectra. The figure shows that these films are strongly oriented with the *c* axis perpendicular to the substrate surface (Jeschke *et al.* 1995). In fact the XRD patterns show strong (001) peaks. Moreover a peak at around  $2\theta = 32^\circ$  (labelled (103) in figures 1 (*c*) and (*d*)) assigned to the (103) reflection is present. This line (which is the strongest in a powder diffraction pattern) indicates that, even if a preferential orientation with the *c* axis is observable, YBCO grains having different orientations are present. From the XRD patterns the unit-cell parameters for YBCO samples on the different substrates are obtained and the results are reported in table 1.

Figure 2 (*a*) is a micrograph of a YBCO film on a  $\text{LaAlO}_3$  substrate; the image confirms the X-ray spectrum data indicating a strong orientation, but the alignment of the grains is not perfect, as some grains form different angles with respect to the

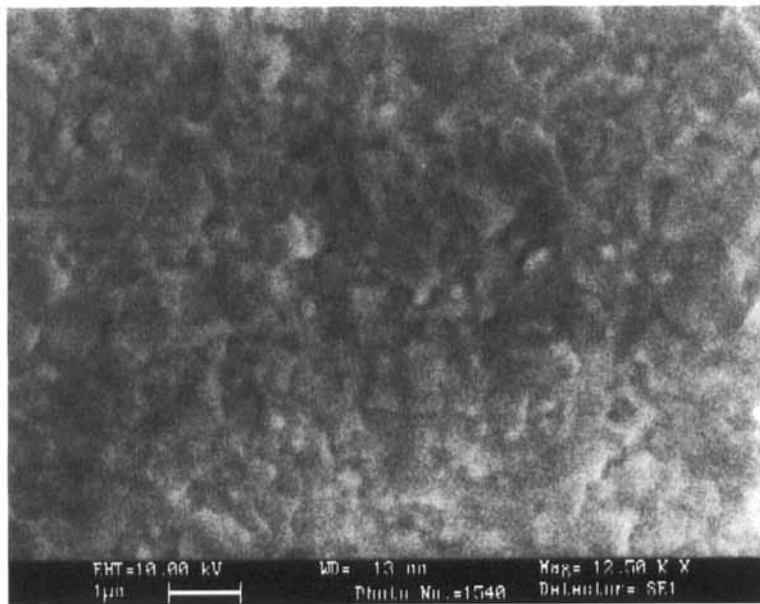
Table 1. Parameters of unit cells of YBCO films on different substrates.

Substrate <sup>a</sup>	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
Cu	3.836	3.849	11.658
Ag	3.8549	3.8749	11.670
$\text{Al}_2\text{O}_3$	3.850	3.852	11.612
YSZ	3.857	3.867	11.606
$\text{SrTiO}_3$	3.862	3.884	11.667
$\text{LaAlO}_3$	3.856	3.862	11.561
$\text{NdGaO}_3$	3.857	3.861	11.579

<sup>a</sup> The value for the Mg substrate is not reported, because from the XRD pattern it is not possible to extract a sufficient number of independent reflections to obtain the cell parameters.



(a)



(b)

Figure 2. Scanning electron micrographs of YBCO films on (a)  $\text{LaAlO}_3$  and (b)  $\text{Al}_2\text{O}_3$  substrates.

Table 2. Lattice mismatch.

Substrate	Cell parameter (Å)	Lattice mismatch (%)
Cu	3.6150	5.5
Ag	4.0862	7
Al <sub>2</sub> O <sub>3</sub>	4.758	21.9
YSZ	3.6338	4.9 <sup>a</sup>
MgO	4.2112	9.8
SrTiO <sub>3</sub>	3.936	3
LaAlO <sub>3</sub>	3.7929	0.7 <sup>a</sup>
NdGaO <sub>3</sub>	3.8403	0.6 <sup>a</sup>
CaNdAlO <sub>4</sub>	3.688	3.5

<sup>a</sup> On the diagonal.

substrate surface. In figure 2(b) a micrograph of a YBCO film on an Al<sub>2</sub>O<sub>3</sub> substrate is reported; the image clearly shows that no alignment of YBCO grains is present.

#### § 4. DISCUSSION

The choice of the substrate depends on the compatibility of the coefficients of thermal expansion, on the compatibility of the constants of the lattice between the film and the substrate, on its chemical inertness (Koinuma *et al.* 1988), on its lack of defects and on the similarity of the dielectric properties of substrate and film (Sobolewski *et al.* 1991).

From the above considerations the best substrates to obtain YBCO films are the single-crystal substrates. The main problems of the single-crystal substrates are the high cost and the limited size (10 mm × 10 mm); for example LaAlO<sub>3</sub> is a good material for microwave applications but it is expensive. Moreover, the 'ideal' substrate should have low dielectric losses up to terahertz frequencies. The lowest loss at 77 K is from MgO. On the other hand the values of lattice mismatch must also be considered. Table 2 reports the calculated values of lattice mismatch for the different substrates examined.

In some cases the diagonal length of the square surface of the substrate unit cell has been chosen as the cell parameter rather than the *a* axis, as the diagonal length closely matches that of the cell parameter of YBCO. Therefore, the lattice mismatch is lower; that is for YSZ the mismatch along a direction would be 30%, whilst along the diagonal it decreases to 4.9% (Fork *et al.* 1992). As a consequence of this behaviour, the substrate symmetry allows two orientations of the film and the structure of the film obtained may consist of different domains with different orientations (figure 2(a)).

It is worth noting the remarkable mismatch between the lattice constants of the non-perovskite material and of YBCO, indicating that it is impossible to obtain an oriented growth on non-perovskite substrates (figure 2(b))

#### § 5. CONCLUSIONS

The results obtained show metal-organic spray-deposition is an attractive method for the preparation of thin superconducting films, since the characteristics of our YBCO films are comparable to those of films prepared by laser ablation or sputtering. Note that by MOD, YBCO films are obtained both on metallic and

single-crystal or polycrystalline substrates. As expected the best films are obtained on single-crystal substrates and the results presented demonstrate that single-crystal alkaline-rare earth aluminates represent an excellent choice for the epitaxial deposition of high- $T_c$  film for ultrahigh frequency applications. On the other hand, even on metallic substrates (particularly Ag) good films are obtained of interest for future electric or electronic applications.

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