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Compositional Effects on Morphology, Structure and Superconducting Properties of $Y_xBa_yCu_zO_{7-\delta}$ Thin Films Prepared by Metalorganic Chemical Vapour Deposition

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Abstract. In this paper we report the preparation of quasi-stoichiometric layers (Ba-deficient and Ba-rich) by MOCVD. The compositional effects on the morphology, structure and superconducting properties were studied too.

1. INTRODUCTION

Many groups [1] have demonstrated that the morphology, microstructure and superconducting properties of $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films depend on the composition of Y, Ba, Cu and O. Zhao et al. [2] have proved that optimal j_c in YBCO layers, was obtained for compositions Ba/Y= 1.6 and Cu/Y= 5 which are very far from the "123" stoichiometry. In this case, the surface morphology was not flat. On the contrary, Hudner et al. [3] got flat surfaces in YBCO layers with a composition evaluated in Ba/Y= 1.5 and Cu/Ba= 1.9 (Ba deficient layers) and with a critical current density $j_c = 3.10^6$ A/cm². It should also be noted that films prepared by CVD demonstrated excellent behaviour in the presence of magnetic field. The pinning mechanisms which induce high critical current densities are poorly understood. However, some authors [4] suggested that Y_2O_3 nanoprecipitates act as active flux pinning centers when the applied field is perpendicular to CuO_2 planes.

From these antecedents, it should be concluded that the control of the morphology and composition of the deposits is a relevant fact which can be achieved in MOCVD, mainly, by the control of the composition of the gas phase and the deposition temperature. The evaporation temperature of the precursors and substrate temperature are two of the more important technological parameters which control the concentration of the precursors in the gas phase and the deposition yield of the Y, Ba and Cu, respectively.

This paper deals with the study of the variation of the morphology and superconducting properties in quasi-stoichiometric and off-stoichiometry layers prepared by MOCVD. It should be noted that in Ba deficient layers yttria nanoprecipitates, that could act as pinning center, are incorporated into the YBCO matrix [5].

In this context, it will be discussed as well, the best experimental conditions for preparing YBCO layers with smooth surfaces (indispensable for electronic applications) and the influence of the Ba concentration on the critical temperature (T_c) of the superconducting films.

2. EXPERIMENTAL

The films were grown by MOCVD on different substrates (SrTiO₃, YSZ, MgO) in a horizontal hot-wall reactor. The β -diketonates: Y(thd)₃, Cu(thd)₂ and Ba(thd)₂ were used as organometallic precursors. The study of the chemical composition of the deposits as the function of the deposition temperature (T_{sub}) was performed by means of the layers prepared at T_{sub} ranged between 700°C and 825°C.

The total pressure in the reactor was 10 Torr. The thickness of the layers was ranged between 200 and 500 nm.

The off-stoichiometric films were obtained at standard experimental conditions [6] although the evaporation temperature of the Ba-precursor changes from 210 to 214°C. These layers show different Ba-content, varying from Ba/Y = 1.5 (Ba-deficient) to Ba/Y = 2.5 (Ba-rich). The Cu/Y ratio was held in a quasi-stoichiometric range of 3 ± 0.2 .

The chemical composition and structure of the layers were obtained by electron microprobe analysis and X-ray diffraction, respectively. Superconducting properties of the films were measured by AC-susceptometer and SQUID.

3. RESULTS AND DISCUSSION

3.1 Dependence of the composition on T_{sub}

Deposition temperature is a relevant technological parameter in the control of the stoichiometry of the deposited layers because the deposition yield of the Cu, Ba and Y depends on this temperature. Figure 1 shows the evolution of the ratio between the deposited and evaporated molar fraction of Cu/Y and Ba/Y as a function of the substrate temperature. These dependences have been obtained from layers grown on different substrates (SrTiO₃, MgO, NdGaO₃ and YSZ).

As a general trend, it can be concluded that in our experimental set up the Cu efficiency in the deposition is higher than the Y while the Ba yield is less than the Y one. It should be also observed that the efficiency in the deposition of the Ba/Y is held constant in the range of $T_{\text{sub}} = 700\text{--}820^\circ\text{C}$ while Cu/Y increases from 1.5 to 3. Consequently, at 820°C, the incorporation of the Cu into the layer is twice with respect to 700°C, providing the same Cu evaporated mass.

Figure 1: Evolution of the deposition yield $(M/Y)_{\text{dep}} / (M/Y)_{\text{ev}}$ [$M = \text{Cu, Ba}$] with the substrate temperature

3.2 Structure of quasi-stoichiometric layers

Figure 2 shows the X-ray diffractogram of YBCO layers deposited on SrTiO_3 (100) at three different temperatures. At lower $T_{\text{sub}} = 650^\circ\text{C}$, the film exhibits a majority preferential orientation along the a-axis which is perpendicular to the surface of the substrate. When T_{sub} increases, the preferential orientation changes gradually from a-axis to c-axis orientation. The morphology exhibited by the layers was discussed elsewhere [7]. Layers prepared at 800°C exhibit a high c-axis orientation with a mean value in the FWHM (005) rocking curve of 0.5° . Their texture was studied by means of the (104)-YBCO pole figure. This reflection was chosen because is off-plane and it does not overlap with someone coming from the substrate. The pole figure shows four spots indicating a four fold-symmetry with respect the c-axis. The domains are aligned with the principal directions of the substrate and they appear rotated 90° around the c-axis [001]. The critical temperature of these films was $T_c(\text{onset}) = 91.5\text{K}$ and the critical current density $j_c = 10^6 \text{ A/cm}^2$ (77K,0T).

figure2: X-ray diffractograms of YBCO layers deposited at (a) $T_{\text{sub}} = 650^\circ\text{C}$, (b) $T_{\text{sub}} = 725^\circ\text{C}$, (c) $T_{\text{sub}} = 800^\circ\text{C}$

3.3 Morphology and superconducting properties of off-stoichiometry layers

Off-stoichiometric layers deposited on SrTiO_3 (100) were obtained at $T_{\text{sub}} = 800^\circ\text{C}$ in order to induce a preferential orientation along the c-axis

3.3.1 Morphology of off-stoichiometric layers

Figure 3 collects the evolution of the surface morphology of the layers with the concentration of Ba. The density, shape and size of the microprecipitates change when the layers reach the zone of stoichiometry "123". For Ba-concentration below the stoichiometry, Y_2O_3 and $\text{Y}_2\text{Cu}_2\text{O}_5$ precipitates were identified in the layers. The yttria precipitates were detected by X-ray diffraction ($2\theta = 34^\circ$ identified as the (004) reflection of cubic Y_2O_3). These precipitates did not appear in the surface suggesting that the excess of Y is incorporated into the layers. On the contrary, for Ba-concentration above the stoichiometric concentration, barium carbonate and BaCuO_5 precipitates were obtained.

Figure 4a shows the surface morphology of the layer obtained at $T_{\text{sub}} = 800^\circ\text{C}$ with a composition $\text{Cu}/\text{Y} = 3.7$ and $\text{Ba}/\text{Y} = 1.8$ (Ba deficient layer). The evaporation temperature of Y, Ba and Cu precursors were: $T_{\text{Y}} = 117^\circ\text{C}$, $T_{\text{Ba}} = 212^\circ\text{C}$ and $T_{\text{Cu}} = 103^\circ\text{C}$. The substrate was SrTiO_3 (100). It should be noted that the surface was rough with the presence of precipitates identified mostly as $\text{Y}_2\text{Cu}_2\text{O}_5$. The critical temperature measured by an AC susceptometer was $T_{\text{c}}(\text{onset}) = 83\text{ K}$.

The result showed at figure 1 suggested that Cu and Y excess in the layers could be reduced by decreasing the deposition temperature. These reasons induced to carry out deposits at 700°C without any change in the composition of the gas phase. Figure 4b displays the surface morphology of a layer obtained at these conditions. The films were quasi-stoichiometric ($\text{Cu}/\text{Y} = 2.8$, $\text{Ba}/\text{Y} = 1.85$) and the density of microprecipitates was very small leading to almost flat surfaces. The Cu excess was eliminated because the different efficiency in the incorporation of this cation to the layer, besides Ba/Y ratio is maintained when the deposition temperature decreases, as predicted in figure 1. XRD analysis permitted to evaluate in 70 the percentage of volume which correspond to the c-axis domains in the deposit. The critical temperature of th film was $T_{\text{c}} = 88\text{K}$.

Figure 3: SEM micrographs showing the morphology of the layers prepared at $\text{Cu}/\text{Y} = 3 \pm 0.2$. Ba concentration varies from $\text{Ba}/\text{Y} = 1.8$ (a) to 2.3 (b).

Figure 4: SEM micrographs corresponding to (a) off-stoichiometric layer: rough surface, (b) quasi-stoichiometric deposit: flat surface.

3.3.2 Superconducting properties of off stoichiometric layers

Figure 5 indicates the variation of T_c as a function of the ratio Ba/Y when Cu/Y ratio is held at 3 ± 0.2 . The evolution essentially agrees with the results published by Zhao et al. which correspond to films prepared by PEMOCVD [2]. The highest critical temperature was obtained at Ba/Y ratio of 1.9 which does correspond with the stoichiometric one.

figure 5: Dependence of the critical temperature with the ratio Ba/Y in highly c-axis oriented YBCO.

The evolution of the critical temperature (up to $Ba/Y = 1.9$) cannot be correlated with variations in the oxygen concentration of the layers. Figure 6 shows the dependence of c -lattice parameter with the ratio of Ba/Y . The value of c is close to $11.67 \pm 0.01 \text{ \AA}$ indicating that the films are fully oxygenated. It should be pointed out that quasi-stoichiometric layers ($Ba/Y=2$) were further annealed in pure oxygen at temperature of 480°C , no variations in the values of c parameter and consequently, in its T_c were detected. These facts suggest that our value of the c parameter correspond to layers fully oxygenated and thus, the evolution of T_c versus Ba/Y is not related with the oxygen content of the films. Above $Ba/Y = 1.9$, the value of c increases while T_c decreases strongly. An explanation of this fact have been proposed by Matijasevic et al.[8]. The enlargement of the c parameter is due to the substitution, in the unit cell, of Y by Ba with increasing Ba content in the deposit.

The determination of the mechanism of the c enlargement and the reasons of the evolution of the T_c on the Ba/Y ratio requires an accurated study of off-stoichiometric samples which is underway.

Figure 6: Dependence of the c parameter with the ratio Ba/Y in c -axis oriented YBCO layers.

Figure 7 shows the dependence at 5 K of j_c with a magnetic field, applied perpendicular to the CuO_2 planes (in our case, these planes are parallel to the substrate). Sample **a** corresponds to quasi-stoichiometric layer while sample **b** is off-stoichiometric film with Ba/Y ratio of 1.8 and Cu/Y of 2.8. The critical current densities decrease from $4 \cdot 10^6$ to $5 \cdot 10^5 \text{ A/cm}^2$ at 5 T (sample **a**) and from $1.2 \cdot 10^7$ to $5 \cdot 10^5 \text{ A/cm}^2$ at 5 T (sample **b**). The yttria precipitates detected in Ba -deficient layers seem to act, below 1T, as pinning centers [9] enhancing the critical current density from $4 \cdot 10^6$ (quasi-stoichiometric layers) to $1.2 \cdot 10^7 \text{ A/cm}^2$ at $B = 0 \text{ T}$. At high magnetic field the dependence of j_c is similar for both layers, indicating that the mechanism of pinning is independent of the concentration of yttria precipitates and second phases and probably depends on the intrinsic quality of the material (density of dislocations...).

It must be remembered that both samples have similar orientation, essentially the same density of twins and a -oriented domains but different densities of Y_2O_3 and second phases. At this moment is difficult to elucidate exactly the mechanism of pinning but there is a correlation between the non-stoichiometry in the layers and the behaviour of j_c with respect to the magnetic field. Accurated texture, microstructure and transport characterizations must be carried out in order to elucidate univocally the pinning mechanisms at low and high magnetic field.

Figure 7: Dependence of j_c with an external magnetic field, parallel to YBCO c-axis, measured in two samples, (a) quasi-stoichiometric, (b) Ba-deficient.

3.CONCLUSIONS

1.- The efficiency of the deposition of Cu, Ba and Y depends on the deposition temperature. This fact can be used for elimination of Cu and Y-rich microprecipitates in Ba-deficient layers by decreasing the deposition temperature. Flat surface, precipitates free and quasi-stoichiometric c-oriented layers can be prepared for technological applications.

2.- The influence of Ba content on properties such as morphology, structure and superconducting properties was studied by means of off-stoichiometric layers prepared by varying the evaporation temperature of the Ba precursor between 210°C and 214°C. The critical temperature shows a dependence with the Ba/Y ratio. This evolution is not correlated with a change in the oxygen content in the films (for Ba/Y < 1.9) because in all this range the c parameter correspond to a fully oxygenated layer. The enlargement of the c parameter above the quasi stoichiometric composition (Ba/Y > 1.9) could be attributed to a substitution of Y by Ba with increasing Ba content.

3.- Ba deficient layers show precipitates that seem to act as pinning centers at low magnetic field (1T). At higher values, mechanisms related with the intrinsic quality of the material seem to control the mechanism of pinning.

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