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Oxygenation mechanism of $YBa_2Cu_3O_{6+x}$ thin films during growth by pulsed laser deposition.

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Abstract. We have studied the incorporation of oxygen in $YBa_2Cu_3O_{6+x}$ (YBaCuO) thin films during the growth at high temperature by laser ablation. Using a quenching technique, we have demonstrated that it is possible to obtain superconducting films without the need of any oxygen intercalation during the cooling down step. This result reveals that the oxygenation of YBaCuO films during growth is strongly enhanced in comparison to the previsions of the (P_{O2}, T) thermodynamic diagram, due the high reactivity of atomic and ionic oxygen present in the laser plasma.
The dependence of the critical temperature of quenched films on the target-to-substrate distance suggests that the concentration of reactive oxygen is not homogeneously distributed within the plume. Furthermore, we have experimentally demonstrated that atomic oxygen plays an important role in the process which governs the reaction kinetics of the YBaCuO phase formation, enhancing the mobility of species incident on the substrate, which leads to an important improvement of the morphological and structural properties of the films.
In conclusion, we show that the presence of reactive oxygen in the laser plasma is important to understand the mechanism of growth of YBaCuO films and probably has to be taken into consideration for the growth of new oxide materials by PLD and sputtering.

1. Introduction

In the last ten years the formation of epitaxial $YBa_2Cu_3O_{6+x}$ (YBaCuO) thin films by the pulsed laser deposition (PLD) technique has been extensively studied. Although much is known about the mechanism of target ablation and the evolution of species ablated from the target, the series of gas-phase and surface reactions leading to the growth and oxygenation of the YBaCuO phase are complex and not fully understood. It is generally believed that at temperatures around 750° C and oxygen partial pressures, P_{O2}, in the range of 0.1-1 mbar, normally used for in situ growth of YBaCuO films by PLD, a semiconducting tetragonal phase ($x = 0, 0.2$) is formed, according to the YBaCuO thermodynamic (P_{O2}, T) diagram [1], whereas the superconducting phase ($0.4 < x < 1$) only takes place with additional oxygen intercalation during the cooling down cycle after deposition [2]. However, this model of YBaCuO film growth neglect completely the presence of reactive oxygen in the plasma formed by laser ablation, which could significantly increase the oxidation state of the films during deposition, as recently suggested by several studies [3, 4].

The aim of this work is to give some insight about the role of the oxygen plasma during the growth of YBaCuO films by PLD. In particular, two important questions have been studied: What is the actual oxygen content of YBaCuO films during deposition by

PLD? In which way the oxygenation state of YBaCuO films during growth affects their physical properties? Such a study helps to understand the interaction of the expanding cationic species in the plume with the background gas and the influence of the reactive oxygen present in laser-induced plasma on the morphological and structural properties of YBaCuO films.

2. Experimental

The experiments were carried out using a 248 nm KrF excimer laser with pulse energy of 300 mJ, repetition rate of 10 Hz and a fluence of 1.1 J/cm^2 at the rotating $YBa_2Cu_3O_6$ target. The films were deposited on $SrTiO_3$ substrates at 765° C and oxygen pressure P_{O2} = 0.3 mbar. In order to avoid any oxygen out or in-diffusion during the cooling down step, the films were quenched at growth pressure at the end of the deposition process, after 1200 laser pulses. The validity of the quenching procedure to preserve the oxygenation of the as-grown films is demonstrated in ref. 4. The oxygen content of the films, x, was determined at room temperature from the value of the c-axis parameter measured by X-ray Diffraction (XRD). The samples were also characterised by four-probe resistivity R(T) measurements, Scanning Electron Microscopy (SEM) and Rutherford Backscattering Spectrometry (RBS)/channelling.

3. Results and discussion

In pulsed laser ablation, there is an optimal target-substrate distance for each deposition pressure which leads to the best properties of the films. So far, this has been related to the velocity distribution of the various species in the plume [5]. However, the oxygenation kinetics also plays an important role in the growth of good quality superconducting films. To investigate if the degree of oxygenation of the films during deposition depends on the target-to-substrate spacing, D, we have studied the physical properties of a series of quenched samples grown at different target-substrate distances. Figure 1 shows the R(T) measurements of these films for different values of D/L, where L is the length of the visible luminous

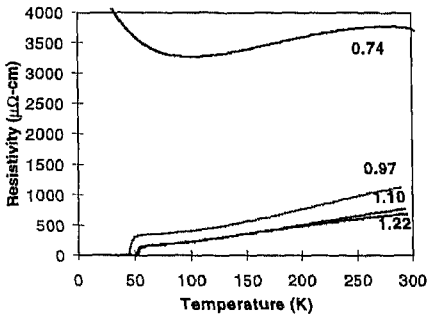

Figure 1. Resistivity versus temperature for YBaCuO quenched films. The numbers of the curves indicate the normalised distance D/L.

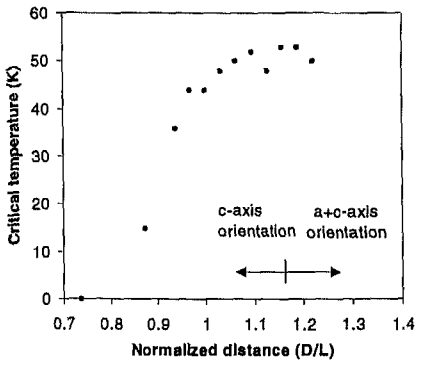

Figure 2. Tc (R = 0) for quenched films versus normalised target-to-substrate distance D/L. The orientation of the films is also indicated.

plume generated with the YBaCuO target. The most important observation is that superconducting YBaCuO films can indeed be formed without any post-oxygenation procedure, in opposition to that expected from the (P_{O2}, T) thermodynamic diagram, from which the quenched films should be semiconducting (x = 0, 0.2). This result shows that the oxygen content of the films during growth can be enhanced (x > 0.2) due to the presence of activated oxygen species in the laser-induced plasma. Indeed, spectroscopic studies indicate that the plume generated with YBaCuO targets contains atomic oxygen, generated by dissociation of O_2 gas during collisions with electrons, ions and neutrals in the plasma [6].

The variation of Tc (R=0) and the orientation of the films as a function of D/L is shown in Figure 2. Films grown well within the YBaCuO plume (D/L = 0.74) were found to be semiconducting, whereas those samples formed at D/L ≥ 0.87 were superconducting. For pure c-axis oriented films, the critical temperature increases with D/L, reaches a maximum value (Tc = 52 K) at D/L ≈ 1.1 and decreases slightly at a longer target/substrate distance. For D/L ≥ 1.15 the growth direction alters gradually from c- to a-axis orientation, as observed by SEM [4]. These a + c-oriented films were also superconducting, with Tc ≈ 53 - 50 K within the range of D/L values explored. However, it is important to note that in this case Tc could in part be due to oxygen uptake during the quenching procedure, because of the much faster oxygen diffusion along the a-axis direction of YBaCuO. Thus, we will only discuss the results corresponding to c-oriented films.

The increase of Tc with distance is presumably due to a non-homogeneous spatial distribution of the atomic oxygen produced during collision of O_2 with atoms. Indeed, for the highly exothermic reactions of Ba and Y the total scattering cross section would be expected to decrease with increasing collision energy [6]. It is known that the velocities of ejected species from the target are fast (~ 10^6 cm/s) and slow down with the distance due to collisions with the background gas. Therefore, the cross sections and, in consequence, the quantity of atomic oxygen available in the proximity of the substrate, would increase with distance. This effect and the fact that the flux of Ba, Y and Cu species decreases with target-to-substrate distance (see Table 1) results in a low oxygenation (x = 0, 0.2) of films grown well inside the plume (D/L ~ 0.75), whose oxygen content agrees with the previsions of the (P_{O2}, T) thermodynamic diagram. On the contrary, at D ~ 1-1.1 L, the concentration of atomic oxygen is high enough to increase the oxygenation of the as-grown films up to x ≈ 0.6 (see Table 1). In other words, at optimal D/L ratio, the chemical potential of the oxygen plasma increases by nearly four orders of magnitude in comparison with the chemical potential of O_2 at P_{O2} = 0.3 mbar. This higher oxygenation has a strong effect on the structural properties of the films, as observed in Table 1.

Table 1. Characteristics of YBaCuO quenched films as a function of the normalised distance D/L.

D/L	Thickness (Å)	Average growth rate (Å/pulse)	Xmin (%)	Tc (K)	c-axis value (Å)	Oxygen content x (from XRD)
0.74	3000	2.5	33	semiconductor	11.82	0.1
0.97	1250	1	7.5	44		
1.1	930	0.8	5.8	52	11.74	0.6
1.22	500	0.4	21	50	a+c oriented	

The XRD studies show that the relationship between the value of the c-axis parameter and Tc, establish for YBaCuO bulk material, also holds for our laser ablated films. The semiconducting sample has c = 11.82 Å, whereas the film with Tc = 52 K has c = 11.74 Å. The oxygen content deduced from the c-axis length is x = 0.1 and 0.6, respectively.

Information about the crystallographic perfection of the samples was obtained from the χ_{min} values of the Ba-sublattice. The low minimum yield of 5.8 % indicates that films with excellent crystalline quality are formed near the tip of the plume. Conversely, films located well within the plume present an important disorder, as revealed by the high χ_{min} value. The deterioration of χ_{min} for the film grown at D/L = 1.22 is mainly due to the simultaneous presence of c and a-oriented grains, which introduces strong disorder into the films [7]. For pure c-oriented films, Table 1 shows that the degree of oxygenation during deposition and χ_{min} are correlated, the higher oxygen content leading to the lower χ_{min}. Similar correlation was found between the quality of the surface morphology of the films and their oxygen content. Films deposited near the plume boundary (high oxygenation) present smoother texture and lower number of outgrows compared to low oxygenated semiconducting films [4]. These results make clear that to obtain good quality films by PLD, where the instantaneous deposition rate can be as high as 10^{19} species/cm^{2}s [2], it is not sufficient to satisfy the thermodynamic stability criteria. In addition, it is necessary to meet the high kinetic requirement during growth. In that respect, the presence of abundant reactive oxygen near the substrate plays an important role in the kinetics of the YBaCuO phase formation, due to the mobility enhancement of species incident on the substrate, which results in an important improvement of the morphological and structural properties of the films.

5. Conclusions

In this paper, we have studied the oxygenation mechanisms of YBaCuO thin films during *in situ* growth by PLD. It was found that oxygen incorporation during the cooling down procedure is not necessary to form superconducting films, contrary to the predictions of the (P_{O2}, T) thermodynamic diagram. This has been related to the presence of reactive oxygen in the laser-induced plasma, which increases considerably the oxidation state of the films during deposition at high temperature. The dependence of the oxygen content of the films on the target-to-substrate distance supports the mechanism by which atomic oxygen produced during collisions of atoms ejected from the target with O_2 is responsible for the enhanced oxygenation of the films. Moreover, the presence of atomic oxygen increases the surface reaction kinetics of YBaCuO formation, improving the structural and morphological properties of the films. In consequence, our experimental results suggest that the origin of an optimal target-substrate distance for YBaCuO growth is related to the spatial dependence of the density of atomic oxygen. As stated before, this is correlated to the velocity distribution of the various species through the energy-dependent cross section of the dissociation reaction.

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