Role of the oxygen plasma during in situ growth of $YBa_2Cu_3O_{6+x}$ thin films by pulsed laser deposition

J. García López [a,*], D.H.A. Blank [a], H. Rogalla [a], J. Siejka [b]

[a] *Low Temperature Division, Department of Applied Physics, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*
[b] *Groupe de Physique des Solides, Université Paris 7, 2 Place Jussieu, 75251 Paris Cedex 05, France*

Abstract

The incorporation of oxygen into $YBa_2Cu_3O_{6+x}$ (YBaCuO) thin films during in situ growth by pulsed laser deposition (PLD) has been investigated as a function of the ablation conditions. A quenching technique has been used immediately after termination of growth to avoid any oxygen in or out-diffusion during the cooling down step. It is shown that superconducting YBaCuO thin films can be formed without any post-oxygenation procedure, contrary to what is expected from the (P_{O_2}, T) thermodynamic diagram. Moreover, it is found that there is an optimal target–substrate distance, D, for each O_2 deposition pressure, P_{O_2}, that leads to the higher critical temperature (i.e., higher oxygenation) as well as to the best structural and morphological properties of quenched films. The results are discussed considering the formation of reactive oxygen in the laser-induced plasma during film growth. © 1998 Published by Elsevier Science B.V. All rights reserved.

Keywords: YBaCuO; Laser ablation; Atomic oxygen; Thin film

1. Introduction

Pulsed laser deposition (PLD) has become a powerful method for the fabrication of high-T_c superconducting thin films. Much work has been done to optimize the deposition process by changing the ablation conditions as ambient gas pressure, substrate temperature, target density, laser fluence, etc. (see for example, Ref. [1]). Nowadays, high quality $YBa_2Cu_3O_{6+x}$ (YBaCuO) thin films with $T_c \approx 90$ K and smooth surfaces are routinely produced by PLD.

However, the series of chemical reactions resulting in growth and oxygenation of YBaCuO phase are undoubtedly complex and presently not well understood. It is generally believed that at temperatures around 750°C and oxygen partial pressures, P_{O_2}, in the range 0.1–1 mbar, normally used for in situ growth of YBaCuO films by sputtering or PLD, a semiconducting tetragonal phase ($x = 0$, 0.2) is formed, according to the YBaCuO thermodynamic (P_{O_2}, T) diagram [2]. Thus, the superconducting phase ($0.4 \leq x \leq 1$) can only take place with additional oxygen indiffusion during the cooling down cycle after deposition [3]. However, this model of YBaCuO film growth neglect completely the presence of atomic and ionic oxygen in the plasma formed by sputtering or laser ablation, which could

* Corresponding author. Present address: National Accelerator Center, Parque Tecnologico 'Cartuja 93', Av. Thomas A. Edison, Isla de la Cartuja, 41092 Seville, Spain. Tel.: +34-95-4460344; Fax: +34-95-4460145; E-mail: fjgl@cica.es

significantly increase the oxygen potential and, therefore, the oxidation state of the films during deposition. Indeed, it has been recently shown that the sputtered YBaCuO films cooled down after deposition in pure Ar or N_2 atmosphere (without post-oxygenation) are superconducting with $T_c \approx 88$ K [4–6]. Moreover, YBaCuO films deposited by laser ablation and subsequently cooled down to room temperature in Ar atmosphere or using a quenching technique were superconducting with $T_c \approx 61$–86 K [7,8]. These results clearly indicate that the oxygen content of the films during the high temperature growth can be much higher than that expected from the thermodynamic diagram. However, a systematic study of the oxygen incorporation in laser ablated YBaCuO films as a function of the deposition conditions has not been reported so far. In this work, the oxygenation of YBaCuO films during deposition by PLD has been investigated as a function of the target/substrate distance at different oxygen pressures. 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 active oxygen present in laser-induced plasma on the superconducting 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 1–10 Hz and a fluence of ~ 1.1 J/cm^2 at the rotating target. The films were deposited on $SrTiO_3$ substrates, which were glued with silver paint to the stainless steel heater block to ensure good thermal contact. The heater temperature was set at 765°C and is henceforth referred to as the deposition temperature. A high density (99%) $YBa_2Cu_3O_6$ tetragonal target was used for ablation. Films prepared using high density targets shows significantly lower density of particles as compared with lower dense targets [9]. The length of the visible luminous plume, L, generated with the YBaCuO target is a function of the oxygen pressure, P_{O_2}. This length was estimated experimentally to be $L = 65$, 63, 61 and 57 mm for $P_{O_2} = 0.2$, 0.3, 0.4 and 0.5 mbar, respectively. For each oxygen pressure P_{O_2}, a

number of YBaCuO films were formed at various target/substrate distances, D. At the end of the deposition process, after 1200 laser pulses, the films were quenched at growth pressure. This was accomplished by removing the substrates from the heater using a mechanical arrangement. Due to the small thermal mass of the substrates, their temperature drops quickly after contact with the chamber walls ($T_{chamber} \approx 40°C$), making, both, oxygen out-diffusion and in-diffusion negligible during the cooling down step. For comparison, also films were cooled down using standard conditions. Typically, after deposition the chamber was filled with 1 bar of O_2 and the films were cooled slowly to room temperature, with annealing steps of 5 min at 600°C and 530°C.

The samples were characterized by four-probe resistivity $R(T)$ measurements, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The composition and thickness of the films were determined by Rutherford Backscattering Spectrometry (RBS) using a 2.2 MeV $^4He^+$ beam in random geometry. The crystal quality of the samples was estimated from the minimum yield in the Ba region of the spectrum, χ_{min}, which is the ratio of the backscattered yield along the (001) direction to that of random incidence.

3. Results

To demonstrate the effectiveness of the quenching process the following experiment was performed: a series of 100 nm thick YBaCuO films were annealed during 5 min at $T = 750°C$ and $P_{O_2} = 0.1$, 1, 10 and 100 mbar, respectively. This time is long enough to equilibrate the oxygen content of the films with the surrounding atmosphere [4], which corresponds from the (P_{O_2}, T) diagram to $x \approx 0.15$, 0.2, 0.3 and 0.4, respectively [2]. The samples were subsequently quenched to room temperature at the annealing pressure.

The $R(T)$ curves of the films with $x = 0.15$ to 0.4 are plotted in Fig. 1. It is interesting to note that even for the films with $x = 0.15$ and 0.2, a positive temperature coefficient is disclosed between 300 and 175 K or 50 K, respectively, indicating that hole doping occurs at x slightly above 0. At lower temperatures the carriers are localized and both films
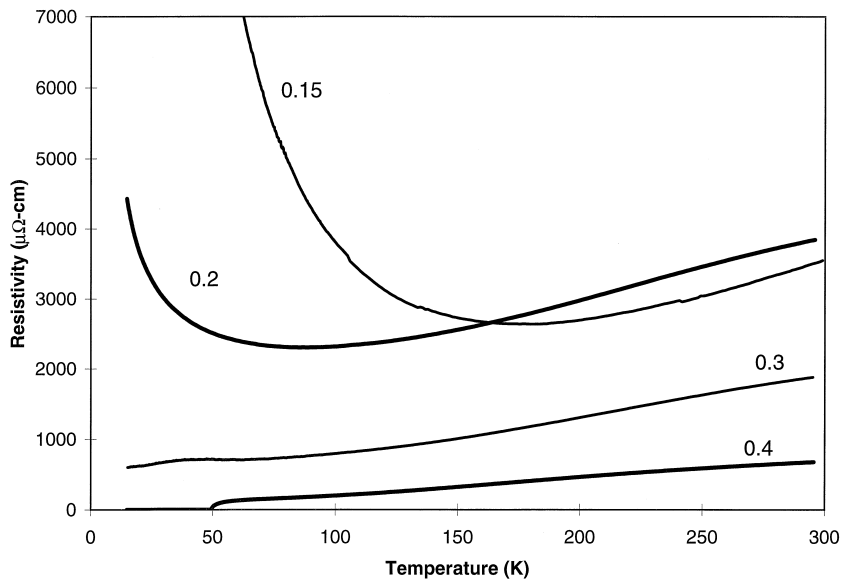
Fig. 1. Resistivity as a function of temperature for quenched films. The numbers for the curves indicate oxygen contents, x, of $YBa_2Cu_3O_{6+x}$ films after annealing at $T = 750°C$ in O_2.

become semiconducting. The film with $x = 0.3$ exhibits metallic behavior in the whole temperature range but it does not become superconductor above 12 K. Only the film with $x = 0.4$ is superconductor, with $T_c = 48$ K. These $R(T)$ curves correspond very well with those reported in literature for YBaCuO thin films [10] and bulk material [11] with well-known oxygen content. Two main conclusions can be drawn from this result. Firstly, at equilibrium conditions (without the oxygen plasma), the (P_{O_2}, T) diagram is a good guide for the oxygen content of the YBaCuO films. Secondly, our quenching technique preserves the initial oxygenation of the samples.

3.1. Superconducting properties

It is known that, for the growth of superconducting films by pulsed laser ablation, there exists an optimal target/substrate distance for each deposition pressure, which leads to the best film's quality. So far, this has been related to the velocity distribution of the various species in the plume [12,13]. However, others parameters such as the oxygenation kinetics play 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-sample spacing, we have measured the $R(T)$ curves of samples quenched immediately after end of growth. Fig. 2 shows the critical temperature of these films, $T_c(R = 0)$, as a function of the target/substrate distance for different oxygen pressures. The first important observation is that superconducting YBaCuO films can indeed be formed without any post-oxygenation procedure. This is contrary to that expected from the (P_{O_2}, T) thermodynamic diagram, from which quenched films should be semiconducting ($x = 0, 0.2$). Moreover, a strong dependence of T_c on both the target/substrate distance, D, and the oxygen pressure is observed. For $P_{O_2} = 0.2$ and 0.3 mbar, T_c increases with D, reaches a maximum value when the substrate is placed several mm beyond the plume boundary and decreases slightly at longer target/substrate distances. It is interesting to note that films produced well within the YBaCuO plasma were found to be semiconducting. Similar T_c–D correlation was observed for the films deposited at $P_{O_2} = 0.4$ and 0.5 mbar, although in that case T_c does not decrease at long target/substrate separation. It is also shown from Fig. 2 that, for a fixed target/substrate distance, T_c presents a sharp maximum at $P_{O_2} \approx 0.3$ mbar and decreases considerably at lower or higher
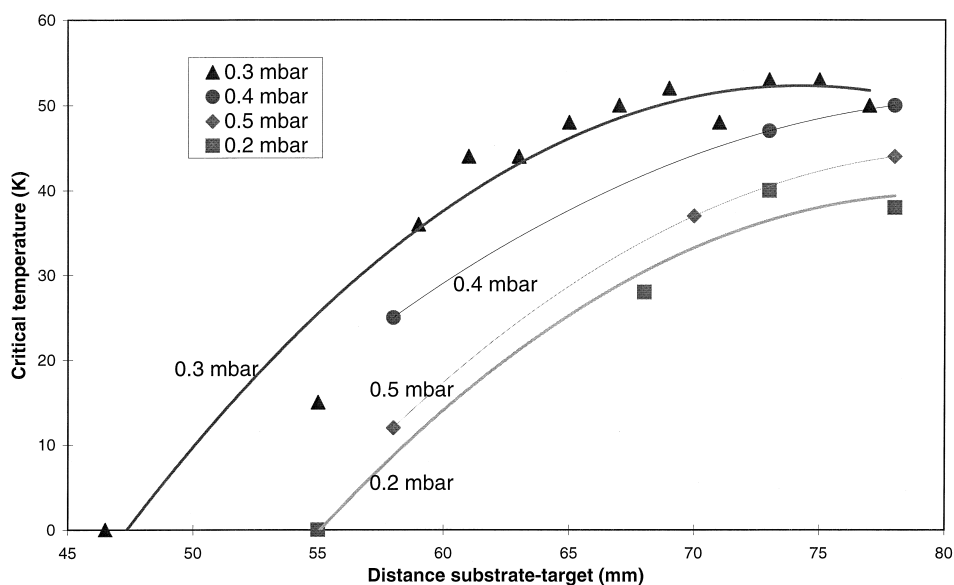
Fig. 2. Critical temperature of quenched films as a function of the target/substrate distance for different oxygen pressures.

oxygen pressures. It should be noted, however, that when the films were cooled down at high oxygen pressure, in standard conditions, their critical temperature was comparable, $T_c = 88 \pm 2$ K, independently of the target/substrate distance and P_{O_2} in the window of parameters explored.

3.2. Composition, structure and morphology

Several characteristics of quenched films deposited at $P_{O_2} = 0.3$ mbar are listed in Table 1. The most striking feature is the deviation from the proper stoichiometry for films placed within the plasma plume, whereas those prepared at distances longer

that the plume range, L, were found to have a composition closer to 1–2–3, specially for the film grown at 77 mm (1.2 L). Despite the non-stoichiometric composition of some films, X-Ray Diffraction studies using the standard Bragg–Brentano geometry revealed no traces of parasite phases. Only the peaks corresponding to the $YBa_2Cu_3O_{6+x}$ phase oriented with the c-axis perpendicular to the substrate were detected in the XRD pattern. Similar results have been found for Y- and Cu-enriched YBaCuO films grown by sputtering [14]. In that case, CuO precipitates on the YBaCuO matrix were detected by TEM [15]. Besides, the XRD studies show that the relationship between the value of the c-axis parameter

Table 1
Composition and structural and electrical properties of quenched films grown at different target/substrate distances

Target/substrate distance (mm)	Relative composition Y–Ba–Cu	Thickness (Å)	Average growth rate (Å/pulse)	χ_{min} (%)	T_c (K)	c-axis value (Å)
46.5	1–1.4–2.3	3000	2.5	33	semi-conductor	11.82
61	1–1.5–2.6	1250	1	7.5	44	
69	1–1.8–3.2	930	0.8	5.8	53	11.74
77	1–1.9–3.1	500	0.4	21	50	

and T_c, establish for YBaCuO bulk material [16], also holds for our laser ablated films. Samples cooled down at high P_{O_2} ($T_c \approx 88$ K) have $c = 11.70$ Å, whereas quenched films formed at $D = 46.5$ mm (semiconducting) and $D = 69$ mm ($T_c = 53$ K) have $c = 11.82$ Å and 11.74 Å, respectively.

Important information about the crystallographic perfection of the samples was obtained from the χ_{min} values of the Ba-sublattice. The best minimum yield of 5.8% is only slightly worse than that observed for YBaCuO single crystals [17] and thin films [18], which indicates that films with excellent crystalline quality are formed near the tip of the plume, despite the deviation from the proper stoichiometry. On the contrary, films located well within or beyond the plume present an important disorder, as revealed by the high χ_{min} values, varying from 33% ($D = 46.5$ mm) to 21% ($D = 77$ mm).

Table 1 also reveals that T_c (thus, the degree of oxygenation during deposition) and χ_{min} are correlated, the higher T_c leading to the lower χ_{min}. This correlation does not hold for the film grown at 77 mm. In that case, however, the deterioration of the χ_{min} value was mainly due the presence of a-axis inclusions into the c-axis matrix (see below), which are known to introduce strong disorder into the films [18].

Fig. 3 shows scanning electron micrographs of the films characterized in Table 1. Samples grown well within the plume, at $D = 46.5$ mm (Fig. 3a), were found to have a rough surface containing holes and small spherical-shaped particles with typical size between 0.2 and 0.4 μm and number density of several $10^8 / \mathrm{cm}^2$. Much better surface morphology was found for films deposited at the plume boundary (Fig. 3b), which present a smooth texture with out-

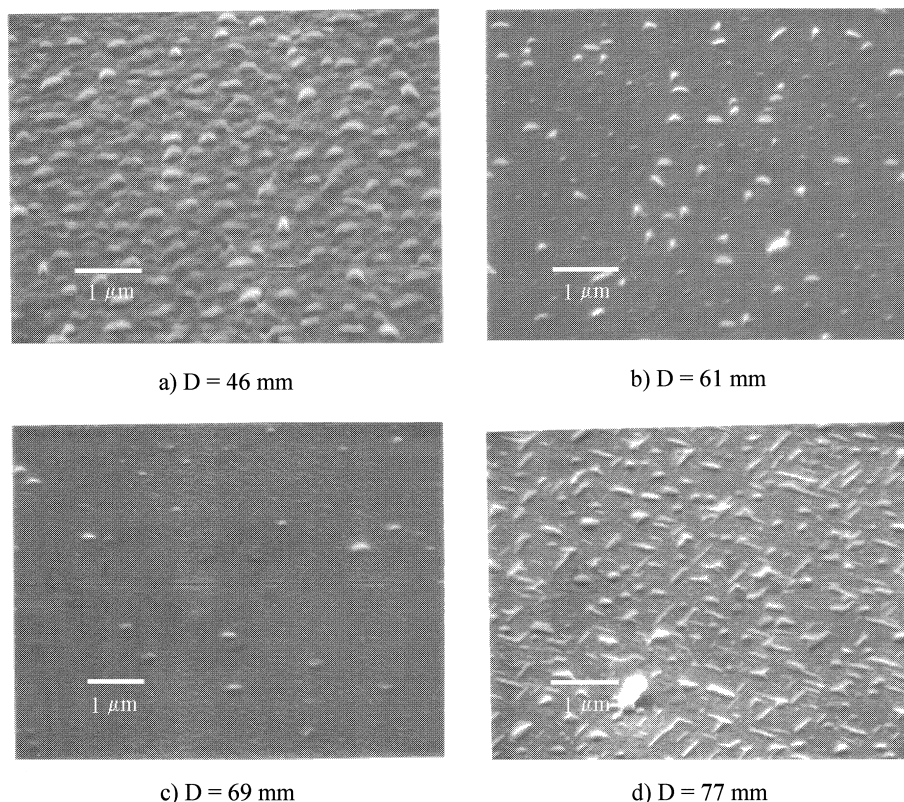a) D = 46 mm

b) D = 61 mm

c) D = 69 mm

d) D = 77 mm

Fig. 3. Surface morphology of films deposited at $P_{O_2} = 0.3$ mbar vs. the target/substrate distance, D. The length of the plume was 63 mm. (a) $D = 46$ mm; (b) $D = 61$ mm; (c) $D = 69$ mm and (d) $D = 77$ mm.
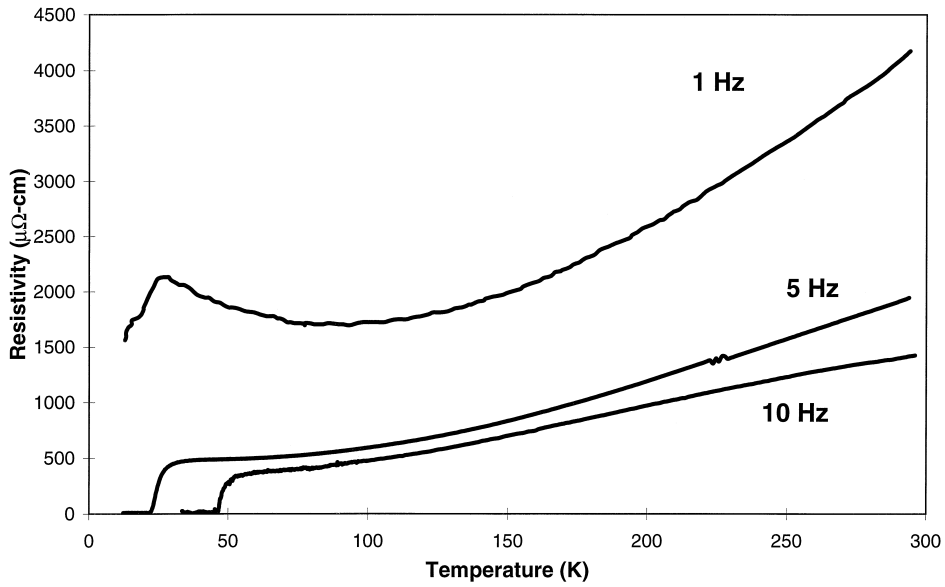
Fig. 4. Effect of laser repetition rate on the $R(T)$ curves for quenched $YBa_2Cu_3O_{6+x}$ films.

grows incorporated at the surface. The outgrows (several $10^8/cm^2$) have irregular shapes and their size ranges between 50 and 200 nm. The number of outgrows can be reduced by 1 order of magnitude (several $10^7/cm^2$) by increasing the distance target/substrate (Fig. 3c, $D = 69$ mm). Further increase of D (Fig. 3d) leads to films exhibiting outgrows and a lattice of small needles aligned along the (100) and (010) directions of the substrate (Fig. 4d). These needles indicate the presence of a-axis oriented grains which, as stated above, are responsible of the strong deterioration of the crystalline quality of this film.

3.3. Influence of the laser repetition rate

All the results presented so far were obtained by using a laser repetition rate of 10 Hz. In this section we show some preliminary experiments describing the relationship between the laser repetition rate, v, and the electrical properties of films quenched after growth. The films were deposited at $P_{O_2} = 0.4$ mbar during 600 laser pulses and optimal target/substrate distance. The only difference was on the laser repetition rate. Fig. 4 shows the $R(T)$ curves for films deposited at $v = 10$, 5 and 1 Hz, respectively. It is observed that T_c increases and the resistivity value

decreases with increasing laser repetition rate. Films grown at $v = 10$ Hz have $T_c \approx 48$ K, whereas those films grown at $v = 5$ Hz only have $T_c \approx 22$ K. Further decreasing of v to 1 Hz leads to not superconducting films above 10 K. As shown in the discussion, the influence of the repetition rate on the electrical characteristics of quenched films provides important information about the mechanism of oxygen incorporation and losses on YBaCuO films during PLD.

4. Discussion

4.1. Oxygenation during film growth

It is demonstrated in Fig. 2 that superconducting films can be formed without any supplementary oxygen indiffusion during the cooling down step. Although the oxygen content of our films was not directly measured, two experimental results strongly suggest that the T_c observed is due to an enhanced oxygenation during film growth and not to other kind of doping, as cation vacancies [6]. Firstly, films cooled in 1 bar of O_2 have $T_c \approx 89$ K, as expected for fully oxygenated samples, *independently of the ratio between cations*. That means that overdoping of

holes, seen by Thesima et al. in their sputtered films [6] is not observed in our films. Secondly, the correlation found in YBaCuO bulk material between the c-axis value and T_c also holds for our films. Thus, the c-axis parameter of the films must be associated with their oxygen content, x, in the same way that for bulk YBaCuO. Using a relation of $c = 11.835 - 0.1501 x$ determined by a linear least-square fitting for the data of polycrystalline samples [19], we found $x = 0.9$, 0.6 and 0.1 for films with $c = 11.70$, 11.74 and 11.82 Å, respectively.

As stated before, the oxygenation of the films during deposition can be higher than that anticipated from the (P_{O_2}, T) thermodynamic diagram due to the presence of active oxygen species in the laser-induced plasma, whose chemical reactivity with metals is much more important than that of molecular oxygen. Several types of active oxygen species, like atomic oxygen, ionic oxygen and excited molecular oxygen are usually present in oxygen plasmas with a concentration level on a few percent depending on plasma conditions [19]. Spectroscopic studies indicate that the plasma formed during laser ablation of YBaCuO targets in O_2 atmosphere contains atomic oxygen [1], which is generated by dissociation of O_2 gas during collisions with electrons, ions and neutrals [20]:

$$e + O_2 \rightarrow O + O + e$$
$$M + O_2 \rightarrow MO + O$$
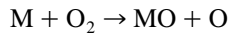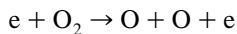
where M denotes an energetic ion or atom of Y, Ba and Cu ejected from the target. There is, however, very little information about the spatial distribution of the atomic oxygen density, its interaction with the expanding cationic species in the plume and how this affect the film growth.

It is logical to assume that the electron impact dissociation of O_2 takes place mainly close to the target region, where the electron density is the highest. The atomic oxygen flux created is attenuated during transport to the substrate because of reactive and elastic collisions with the background gas. This dependence of atomic oxygen density with distance is contrary to what we would expect from our experimental results, that is, T_c of quenched films *increases* with distance substrate/target. This suggests that atomic oxygen created near the target is not the

main factor for the enhanced oxygenation of the films during growth. It also could be argued that, in addition to surface reactions, gas phase oxidation accounts for the effectiveness of different oxidizing agents during laser ablation of YBaCuO, as indicated by Otis et al. [21]. This would favor the formation of diatomic oxides (YO, BaO and CuO), implying a further oxygenation of the YBaCuO phase during growth. However, although gas-phase reactions can be of importance, the presence of atomic oxygen in the vicinity of the substrate is necessary to prevent oxygen out-diffusion between laser pulses. Indeed, at growth temperature the oxygen diffusivity is high $(D \sim 10^{-12} \text{ cm}^2/\text{s})$ [4] and, once the ablated fragments reach the substrate and form the YBaCuO phase, the oxygen content of this layer (~ 1 Å/pulse) equilibrates with the surrounding atmosphere in a very short time ($\sim 10^{-4}$ s). Therefore, if the chemical potential of oxygen at the substrate surface were mainly determined by the concentration of molecular oxygen in the gas phase, the fast equilibrium would lead to low oxygenated ($x = 0$, 0.2) semiconducting films, according to the (P_{O_2}, T) thermodynamic diagram.

4.2. Dependence of T_c with substrate/target distance

While the reason for the increase of T_c with distance is still not clear, it is possible a result of the spatial distribution of the atomic oxygen produced during collision of O_2 with atoms. Although there is very little information available on the energy-dependent cross-sections of any of the reactions of interest, for the highly exothermic reactions of Ba and Y the total scattering cross-section would be expected to decrease with increasing collision energy [20]. As indicated by several studies, the velocities of ejected species from the target are fast ($\sim 10^6$ cm/s) and slow down with distance due to collisions with the background gas. Accordingly, the cross-sections and, therefore, the quantity of atomic oxygen available in the proximity of the substrate would increase with distance. Similar conclusion can be draw from the spectroscopic study on the laser plume of YBaCuO by Fukushima et al. [1], in which it is observed that the collisional reaction of the ejected

species with oxygen is enhanced by increasing the distance from the target surface. For substrates located well beyond the plume range, we could anticipate a decrease of T_c, because the deposition rate and kinetic energy of ablated species will fall into a very low value. It is important to note, however, that for films deposited at $D \geq 1.15L$, the growth direction alters gradually from c- to a-axis orientation, as observed by SEM. It is difficult to compare the results obtained for pure c-oriented, c- and a-mixed and pure a-axis oriented films. Firstly, the number and the energy of surface sites for oxygen adsorption could be different for the various crystallographic directions of YBaCuO and, therefore, the oxygen content of the films during growth is expected to be dependent on the film orientation. Secondly, because of the much faster oxygen diffusion along the a-axis direction of YBaCuO [22], we can not exclude that for a-axis oriented films some oxygen uptake occurs during the quenching procedure. Thus, we will not discuss the unexpected continuo increase of T_c with distance found for samples prepared at $P_{O_2} = 0.4$–0.5 mbar, whose origin is probably related to the presence of the a-axis oriented phase within the films.

4.3. Dependence of T_c on P_{O_2}

It is observed in Fig. 2 that for a constant target–substrate distance, T_c presents a maximum at $P_{O_2} = 0.3$–0.4 mbar and decreases by lower (0.2 mbar) or higher (0.5 mbar) oxygen pressures. As stated above, the enhanced oxygenation of growing films is probably due to the production of atomic oxygen during metal–atom reactions with background oxygen. Therefore, the amount of diatomic oxide present in the plume should also present a peak as a function of the O_2 pressure. This effect has been observed by Otis et al. [21,23] in their study of the gas-phase production of CuO during laser ablation of YBaCuO. The CuO concentration initially increases with increasing background pressure, reaches a maximum in the range of 0.13–0.33 mbar of O_2 and then fall to negligible level by 0.5–0.6 mbar. These values are in very good agreement with our experimental results, which reinforce the idea that the atom–O_2 collisions play a very important role in the oxidation mechanism of YBaCuO.

4.4. Influence of oxygenation process on the morphological and structural properties

In a pulsed process like PLD the instantaneous deposition rate can be as high as 10^{19} species/cm^2 s [3]. Thus, to obtain good quality films, it is not sufficient to satisfy the thermodynamic stability criteria. In addition, it is necessary to meet the high kinetic requirement during growth [3]. In that respect, the presence of reactive oxygen plays an important role in the process that governs the reaction kinetics of the YBaCuO phase formation, due to the mobility enhancement of species incident on the substrate. This leads to an important improvement of the morphological and structural properties, in agreement to our experimental observation that the quenched films with higher T_c (i.e., stronger oxygenation during growth) present the lower $\chi_{\min}$ value and the best surface morphology. These results make clear that the origin of an optimal target/substrate distance for YBaCuO growth is strongly related to the spatial dependence of the density of reactive oxygen which, as stated before, is associated to the velocity distribution of the various species through the energy-dependent cross-section of the dissociation reaction.

4.5. Effect of the atomic oxygen lifetime

The decrease of T_c with the laser repetition rate (Fig. 4) can be understood if we consider the decay of the atomic oxygen density after the plasma has been switched off. Two dominant loss mechanisms for the O atoms are wall recombination and volume recombination. The latest process requires a three-body collision to carry away the energy released, and the probability of such collisions is low at typical pressures used during PLD [20]. This leaves wall recombination as the main loss mechanism. The exact decay time of O is critically dependent on the wall recombination efficiency, whose value taken from literature ranges between 10^{-4} and 5×10^{-3} [24,25]. Calculations based on these values give an estimate of the atomic oxygen lifetime of about 1–10^{-2} s. This time is of the same order of magnitude that the interval between laser pulses ($\tau = 0.1$–1 s) but much longer than the diffusion time to reach

the thermodynamic equilibrium ($\sim 10^{-4}$ s, see above). Therefore, the decrease on T_c with laser frequency simply reflects the diminution of atomic oxygen density between laser pulses and the subsequent oxygen outdiffusion from the films. When the next pulse arrives, providing new ablated material and atomic oxygen, the oxygen content of the film increases, and then decreases again due to recombination of O. As a result of these processes, the average oxygenation of the films during growth by PLD reaches a stationary value, which is in general higher than that predicted by the (P_{O_2}, T) thermodynamic diagram. Note that films grown at 1 Hz were found to be not superconductors, which implies that within 1 s most of the atomic oxygen disappear, in agreement with the above estimations. It is also important to notice that, even when the laser is operated at 10 Hz, the atomic oxygen concentration can decrease considerably between pulses. Thus, it would be possible to increase T_c of the quenched films simply by increasing the laser repetition rate. Unfortunately, our laser system can not produce pulses at frequencies higher than 10 Hz, and this hypothesis could not be demonstrated.

Finally, we would like to point out that the results obtained in this study could also be of importance for the understanding of the growth mechanism of new oxide materials using PLD or other techniques, like sputtering and MBE, in which important amounts of reactive oxygen are present during film deposition.

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 intercalation during the cooling down procedure is not necessary to form superconducting films, contrary to predicted from the (P_{O_2}, 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, as deduced from T_c measurements and XRD data, on both the target-to-substrate distance and the oxygen pressure, supports

the mechanism by which atomic oxygen produced during collision of atoms ejected from the target with O_2 is responsible for the enhanced oxygenation of the films. Furthermore, we have experimentally demonstrated that atomic oxygen plays an important role in the process that 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.

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