Role of the oxygen on the initial growth mechanism and microstructure of $YBa_2Cu_3O_{7-\delta}$ thin films

G. STANCIU[a,*], N. D. SCARISOREANU[b], R. BIRJEGA[b], M. DINESCU[b], E. ANDRONESCU[a]
[a]*University Politehnica of Bucharest, Faculty of Applied Chemistry and Material Science, Bucharest, Romania*
[b]*National Institute for Lasers, Plasma and Radiation Physics, Magurele, Romania*

Superconducting *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ thin films were grown on (001) $SrTiO_3$ single crystals by PLD and RF-assisted PLD in order to investigate the role of the atomic oxygen concentration used during growth on the microstructural and electrical transport properties of the films. The results show a better oxygen distribution in the out-of-plane direction and better superconducting properties for the films grown by means of RF-assisted PLD, with a better morphology and microstructure for the PLD grown films.

(Received September 27, 2012; accepted October 30, 2012)

Keywords: $YBa_2Cu_3O_{7-\delta}$ thin films, PLD, RF-assisted PLD, oxygen distribution, XRD, AFM, transport properties

1. Introduction

Development of new technologies based on high critical temperature (T_C) superconductors (HTSc) requires knowledge of physico-chemical properties of these compounds and a better understanding of the interdependence between synthesis methods and their microstructural and transport properties [1-5]. Since its discovery in 1987 by Wu *et al*. [6], $YBa_2Cu_3O_{7-\delta}$, a p-type HTSc with T_C ~ 93 K, has been intensively studied for potential applications in electronic devices, as well as for theoretical investigation on the microscopic mechanism of superconductivity in cuprates [7,8]. The use of $YBa_2Cu_3O_{7-\delta}$ as thin films for superconducting electronics requires high quality epitaxial films with sharp interfaces and smooth surface [1,9,10]. Such properties can be achieved by a better control of the way the film growth proceeds, associated with further development of the growth methods. Under typical growth conditions (temperature and pressure) the as-deposited non-superconducting $YBa_2Cu_3O_{7-\delta}$ films have a tetragonal symmetry, with the CuO_x planes neighboring the BaO planes containing (mainly) oxygen vacancies. As a general approach, superconductivity is obtained in these films after a post deposition annealing step of ~ 450 ^oC, under 1 bar O_2, required for oxidation to the superconducting phase, with an orthorhombic symmetry [11,12].

Due to its versatility, pulsed laser deposition (PLD) is one of the most used physical deposition method for growth of complex oxides [1,3,4,13]. By this method, the material is stoichiometrically transfered (under optimum growth conditions) from a target to a substrate via a plasma plume formed as a result of the interaction of a laser beam with the target. In this paper we discuss the results of experimental studies on the role of the oxygen on the growth mechanism and microstructure of $YBa_2Cu_3O_{7-\delta}$ thin films grown by PLD and radio-frequency (RF) assisted PLD. In both cases O_2 was selected as the oxidant during growth, with a higher concentration of atomic oxygen being yielded in the latter case by an increased dissociation of oxygen molecules by the RF plasma [14,15]. In this way, the distribution of the oxygen inside the film can be better controlled during growth and not only by the post-deposition oxidation step.

The microstructural properties of the films were studied by X-ray diffraction (Panalytical X'Pert PRO MRD diffractometer), while their morphology by atomic force microscopy (Park Systems XE 100 Atomic Force Microscope). The electrical transport measurements (variation of resistance with temperature) were performed in a liquid He cryostat, in the 30-300 K range.

2. Experimental

$YBa_2Cu_3O_{7-\delta}$ thin films with a thickness of 100-125 nm were grown on single crystal (001) $SrTiO_3$ substrates by PLD and RF-assisted PLD using an ArF excimer laser (λ = 193 nm), at a repetion rate of f = 5 Hz. Before use the substrates were ultrasonically cleaned in acetone and ethanol (10 minutes each) and then annealed for 1 h at 950 ^oC, in O_2 flow (400 sccm) in order to get a preferentially SrO termination [16]. From the possible surface treatments methods used for this type of substrates (chemical etching [16-19], thermal annealing [16,19], or growth of a buffer layer [3]), we have selected thermal treatment. By using a SrO terminated surface formation of CuO_{2-x} precipitates, observed for the $YBa_2Cu_3O_{7-\delta}$ films grown on chemically etched substrates with a TiO_2 termination [16], is avoided. After annealing the substrates were attached to the substrate holder by Ag paste then brought to the deposition temperature under vacuum conditions, kept for about 30 minutes at these conditions, then the O_2 pressure was increased to the deposition pressure and the films deposited. During growth the substrate temperature was kept at T_d = 730 ^oC, while de pressure inside the PLD chamber was P_d = 0.22 mbar O_2. In order to get a stoichiometric deposition and a low concentration of droplets the substrate to target distance was d_{ts} = 3.5 cm, and the laser energy on target (fluence) of E_d = 1.75 J/cm^2. For the films deposited with the addition of the radio-frequency oxygen plasma, the beam was working at 200 W discharge power. After deposition, the PLD grown films were annealed for 15 minutes at 600 ^oC, under 0.10 bar O_2 and then for 1 h at 450 ^oC, under 1 bar O_2, while the RF-assisted PLD grown films were cooled down with 25 ^oC/min under 1 bar O_2 directly from deposition temperature, without any annnealing steps. After growth the films were studied by atomic force microscopy (AFM) and X-ray diffraction (XRD). The T_C value was determined last.

3. Results and discussion

In Fig. 1 AFM images of two selected $YBa_2Cu_3O_{7-\delta}$ thin films grown by PLD (Fig. 1a) and by RF-assisted PLD (Fig. 1b), respectively, are presented. The micrographs show a lower surface roughness (smaller RMS - Root Mean Square - value) for the film grown by PLD. This is an indication of difference in growth mode of the films grown under different oxidizing conditions. The presence of higher atomic oxygen concentration during growth by RF-assisted PLD leads to formation of the orthorhombic structure already during growth which, on the $SrTiO_3$ substrate with cubic symmetry, results in an increased level of epitaxial strain and as a result, a lower surface diffusion length of the ad-atoms in this case. During film's growth, beside strain the evolution of the growth front will be determined by deposition parameters, such as T_d and P_d, E_d, d_{ts}, substrate surface morphology, as well as by the miscut angle of the substrate. These parameters will determine the diffusion length of the ad-atoms on the surface and finally, a bidimensional (2D) or island (3D) growth mode. In the case of these two YBCO films, due to the relatively low deposition temperature (~ 730 ^oC) and high deposition pressure (0.22 mbar O_2), the diffusion length of the ad-atoms will be short, resulting in low mobility on the surface between pulses and limited or no inter-layer diffusion, as well as low intra-layer mobility. As a result, during a pulse small islands will form on the surface and due to low mobility, they do not attach to other islands to form large, 2D islands. The ad-atoms do not have enough energy to diffuse to the edge of the islands they arrive on and as a result, a 3D growth mode take place, with the film growing as relatively small crystallites. The 3D growth mode is enhanced in the case of the RF-assisted PLD grown films due to an increased level of epitaxial strain, as will be discussed next.

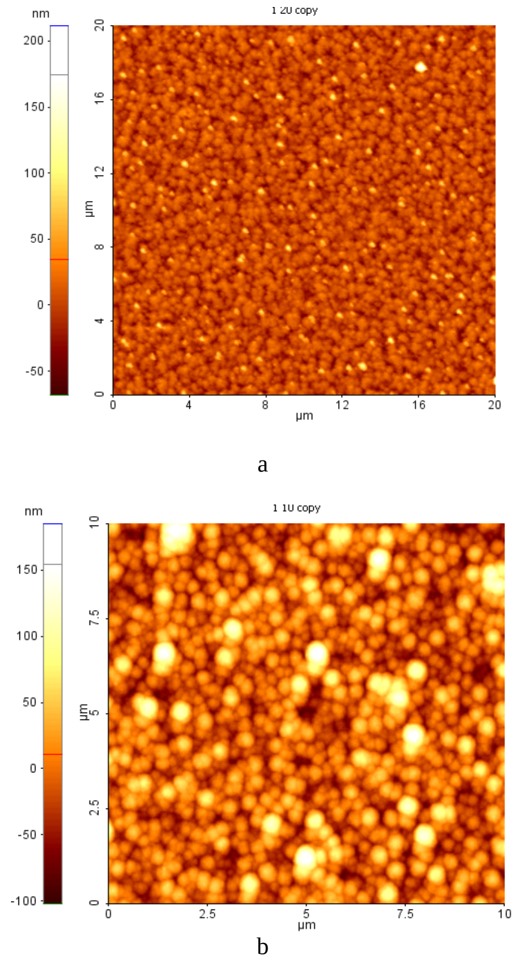
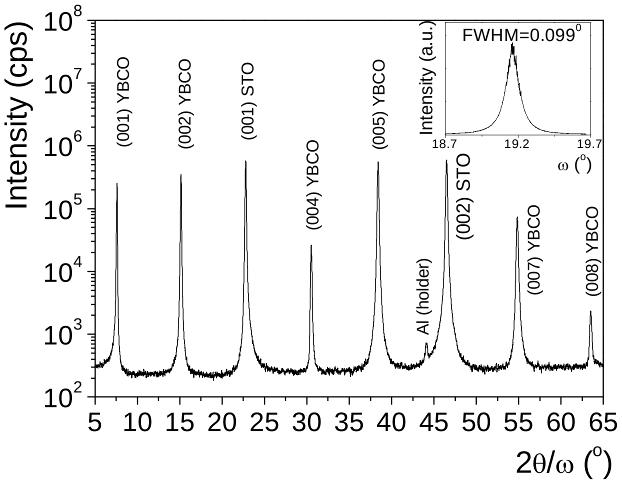


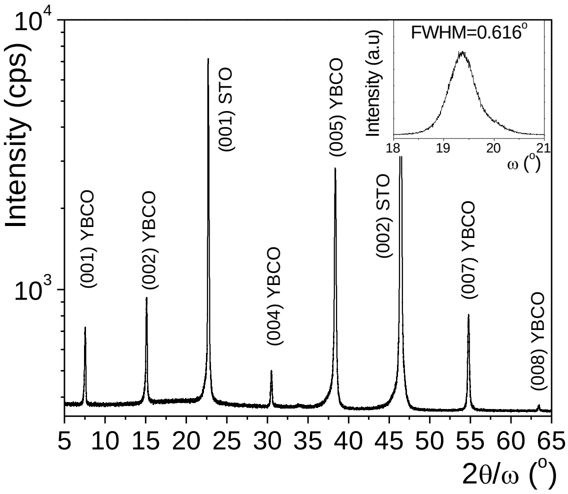
Fig. 1. AFM micrographs of a) $YBa_2Cu_3O_{7-\delta}$ film grown by PLD (RMS ~ 10 nm), and b) $YBa_2Cu_3O_{7-\delta}$ film grown by RF-assisted PLD (RMS ~ 18 nm).

The 2θ/ω scans from Figs. 2 show that the $YBa_2Cu_3O_{7-\delta}$ thin films are single phase, epitaxialy grown, *c*-axis oriented. However, the presence of secondary phase may not be ruled out, as nano-clusters of a secondary phase might not be detected by XRD [20,21]; the same for the case when the growth of the secondary phase is not epitaxial. The in-plane cell parameters, calculated from several (hkl) reflections (namely, 204, 024, 105, 015, and 115) are a ~ 3.825 Å, and b ~ 3.882 Å, while out-of-plane cell parameter was calculated from the (00*l*) reflection as c ~ 11.685 Å, for PLD grown films, and c ~ 11.680 Å, for RF-assisted PLD film, respectively. The values for the cell parameters indicate good oxidation of the films, with a small oxygen deficiency ($\delta > 0$) for the former film.

In case of the film from Fig 2b, from the ratio of the (005)/(001) and (002)/(001) XRD peaks some structural disorder seams to be present due to partial, random substitutions between Ba and Y. The possible reason for this is the influence of the RF-plasma on the PLD plume and on kinetic energies of the plume particulates. The low peak intensities for this film may be explained by the small crystallites of the film and a higher level of epitaxial strain. This is confirmed by the rocking curve measurements of the (005) plane, indicating a much higher FWHM (Full Width Half Maximum) value (so, much smaller crystallites) for the film grown by the RF-assisted PLD method. The 2θ/ω scan from Fig. 2b also shows the presence of small amount of amorphous phase; however, the position of this phase (at the substrate-film interface, or inside the film) is unknown.



a

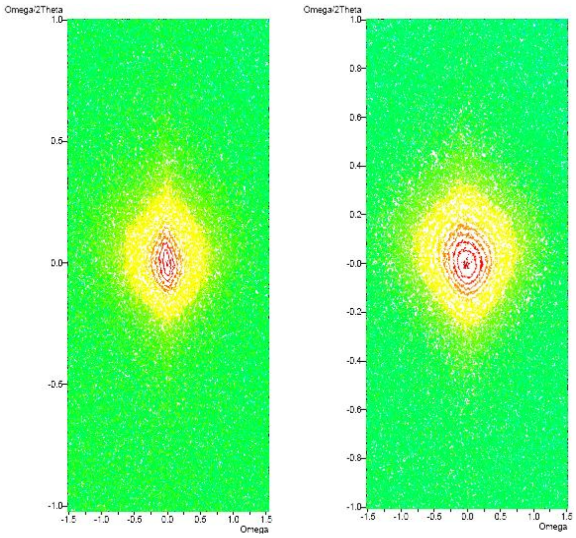


b

Fig. 2. XRD 2θ/ω scans of a) $YBa_2Cu_3O_{7-\delta}$ thin film grown by PLD, and b) $YBa_2Cu_3O_{7-\delta}$ thin film grown by RF-assisted PLD. Insets: ω scan (rocking curve) of (005) plane.

Fig. 3 shows reciprocal space map (rsm) measurements for the (005) reflection of both films. The scans were done with steps of 0.01° for the ω axis, and 0.005° per step for the ω/2θ axis; they show a better crystallographic structure and/or a lower level of epitaxial strain for the PLD grown film (Fig. 3a), indicated by smaller width in omega direction. Also, the short diffraction streaks (the short tails in the ω/2θ direction) indicates a rough substrate-film interface for both films. This may be due to the presence of a high level of strain at the interface and/or due to the presence of structural defects, such as dislocations or amorphous regions.

A slightly better interface is observed for the PLD grown sample (slightly longer diffraction streaks), probably as a result of a lower level of strain.

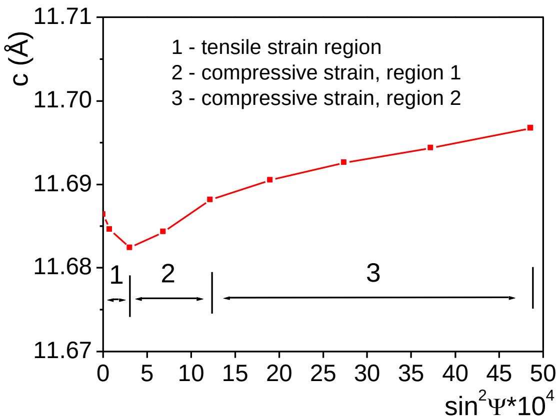


a) b)

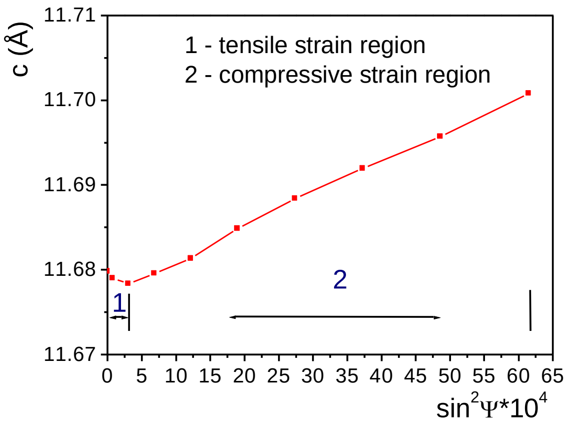
Fig. 3. XRD rsm scans of (005) plane for: a) $YBa_2Cu_3O_{7-\delta}$ film grown by PLD and b) $YBa_2Cu_3O_{7-\delta}$ film grown by RF-assisted PLD.

Next, we have determined the type and level of strain from changes in position of the (005) peak in 2θ/ω direction with the sample tilt angle (Ψ). The results, shown in Fig. 4, indicate the presence of two regions within the *c*-axis direction with different type of strain: close to the substrate-film interface the film is under tensile strain and on top of this region there is the one characterized by compressive strain. Within the compressive strain region the PLD grown film shows two regions with different level of strain (Fig. 4a), the most relaxed part of the film being close to the film surface. These results may be explained as follow: first, the as-deposited film has a tetragonal symmetry as the oxygen content is about 6 ($YBa_2Cu_3O_6$), with cell parameters of the films smaller than the ones of the substrate. During oxidation part of the film become orthorhombic, with cell parameters smaller than the corresponding one of the tetragonal phase. Second, at the initial phase of growth the film follows a 2D growth mode then, via structural defects, the film relaxes and the growth becomes 3D (island growth). During oxidation the relax part of the film oxidizes easier than the strained part (the one close to the substrate-film interface), this substrate-film interface (strained) part of the film acting as a buffer layer between the substrate and oxidized part of the film. Therefore, the difference in level of strain in the compressive part of the films may be explained by oxygen gradient in the *c*-axis direction. Also, the film grown by RF-assisted PLD shows only one compressive strained region, with higher level of strain (as indicated by higher slope) than in the case of the PLD grown film, confirming the above XRD data.

In this case, the strain evolution shows a better distribution of the oxygen in the *c*-axis direction (no compositional gradient in the relaxed part of the film). The difference in compressive strain may also be explained by the fact that the post-deposition annealing steps help strain relaxation. This is confirmed by the observation that if the RF-assisted films are further annealed post-deposition, the rocking curves FWHM value decreases, but it is always larger than the one for the PLD grown films, an indication that the growth mode is determinant on the final microstructure.



a



b

Fig. 4. Evolution of out-of-plane strain for: a) $YBa_2Cu_3O_{7-\delta}$ film grown by PLD, and b) $YBa_2Cu_3O_{7-\delta}$ film grown by RF-assisted PLD. The scans were done by tilting the sample (Ψ angle) with steps of 0.5^o and measuring the resulted $2\theta/\omega$ angle of the (005) peak, with steps of 0.001^o. The c-axis parameters was then calculated from $2\theta/\omega$ angle and plotted against $sin^2\Psi$.

The electrical transport measurements showed that the films were superconducting, with $T_{C,zero}$ values of 80-88 K, for the PLD grown films, and of 82-89 K, for the RF-assisted PLD grown ones, respectively. The slightly better superconducting properties of the latter films may be explained by a better oxygenation and/or a better oxygen distribution inside these films.

4. Conclusions

$YBa_2Cu_3O_{7-\delta}$ thin films were grown by PLD and RF-assisted PLD in order to have a better understanding of the role of the atomic oxygen during growth on their morphological, microstructural, and superconducting properties. While the PLD grown films show better surface morphology and better microstructural properties, the RF-assisted PLD grown films have a more homogeneous oxygen distribution in the out-of-plane direction, and better superconducting properties. These latter films could be obtained without the need of post-deposition annealing steps. Improvement of the microstructure for the film grown with the addition of the RF-plasma may be obtained by using as a template a substrate with an orthorhombic symmetry, such as (001) $NdGaO_3$, which should permit yielding films with lower level of strain and as a result, better microstructure.

Acknowledgements

This work has been partially funded by the Sectoral Operational Programme Human Resources Development 2007 - 2013, POSDRU/88/1.5/S/61178.

References

[1] J. M. Dekkers, G. Rijnders, S. Harkema, H. J. H. Smilde, H. Hilgenkamp, H. Rogalla, D. H. A. Blank, Appl. Phys. Lett., **83**, 5199 (2003).
[2] S. Bals, G. van Tendeloo, G. Rijnders, M. Huijben, V. Leca, D. H. A. Blank, IEEE Trans. Appl. Supercond., **13**, 2834 (2003).
[3] V. Leca, S. Bals, G. Van Tendeloo, D. H. A. Blank, G. Rijnders, Appl. Phys. Lett., **89**, 92504 (2006).
[4] J. Tomaschko, V. Leca, T. Selistrovski, S. Diebold, J. Jochum, R. Kleiner, D. Koelle, Phys. Rev. B**85**, 024519/(2012).
[5] Ariando, D. Darminto, H. J. H. Smilde, V. Leca, D. H. A. Blank, H. Rogalla, H. Hilgenkamp, Phys. Rev. Lett., **94**, 167001 (2005).
[6] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, C. W. Chu, Phys. Rev. Lett., **58**, 908 (1987).
[7] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, D. Werder, Phys. Rev. B, **36**, 5719 (1987).
[8] H. J. H. Smilde, A. A. Golubov, Ariando, G. Rijnders, J. M. Dekkers, S. Harkema, D. H. A. Blank, H. Rogalla, H. Hilgenkamp, Phys. Rev. Lett., **95**, 257001 (2005).
[9] V. Leca, D. Neagu, E. Stefan, E. Andronescu, Rom. J. Mater., **40**, 365 (2010).
[10] H. J. H. Smilde, Ariando, D. H. A. Blank, G. J. Gerritsma, H. Hilgenkamp, H. Rogalla, Phys. Rev.

Lett., **88**, 057004 (2002).
[11] R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, D. Werder, Phys. Rev. B, **36**, 5719 (1987).
[12] X. G. Qiu, H. Koinuma, M. Iwasaki, M. Kawasaki, Y. Segawa, Phys. Rev. B, **60**, 707 (1999).
[13] V. Leca, E. Andronescu, Rom. J. Mat., **40**, 149 (2010).
[14] G. Dinescu, D. Matei, D. Brodoceanu, N. Scarisoreanu, M. Morar, P. Verardi, SPIE, **5448**, 136 (2004).
[15] N. Scarisoreanu, D. G. Matei, G. Dinescu, G. Epurescu, C. Ghica, L. C. Nistor, M. Dinescu, Appl. Surf. Sci., **247**, 518 (2005).
[16] J. M. Huijbregtse, J. H. Rector, B. Dam, Physica C, **351**, 183 (2001).
[17] M. Kawasaki, K. Yoshimoto, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, H. Koinuma, Science, **266**, 1540 (1994).
[18] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. A. Blank, H. Rogalla, Appl. Phys. Lett., **73**, 2920 (1998).
[19] V. Leca, E. Andronescu, Rom. J. Mater., **41**, 127 (2011).
[20] R. Werner, C. Raisch, V. Leca, V. Ion, S. Bals, G. Van Tendeloo, T. Chassé, R. Kleiner, D. Koelle, Physical Review B, **79**, 054416/1 (2009).
[21] S. Bals, G. van Tendeloo, G. Rijnders, D. H. A. Blank, V. Leca, M. Salluzzo, Physica C, **372-376**, 711 (2002).

*Corresponding author: georgestanciu00@yahoo.com
george.stanciu@inflpr.ro