$YBa_2Cu_3O_{7-\delta}$ thin films deposited by pulsed laser deposition and radio-frequency assisted pulsed laser deposition

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Epitaxial High-Critical Temperature Superconducting thin films are obtained by pulsed laser deposition only at very high substrate temperatures (≥ 780 °C) and using post-deposition treatments, which restrict their applicability and common substrates integration possibilities. In this work, we report on $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films growth at two different substrate temperatures, the classic 780 °C and 730 °C. The layers have been deposited by pulsed laser deposition. For lower deposition temperature experiments (730 °C), a radio-frequency oxygen plasma discharge working at 200 W has been added. Morphological (atomic force microscopy), structural (X-ray diffraction), optical (spectrometric ellipsometry) and electrical investigations have been performed for films characterization, as well as AC magnetic susceptibility measurements. A correlation between the deposition conditions and $YBa_2Cu_3O_{7-\delta}$ thin films functional properties has been performed.

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1. Introduction

Since the discovery in 1986 of the superconductivity phenomena in cooper-based oxide compounds, the close understanding of these materials has become a priority for scientists, because of their numerous applications in electronics and telecommunications industry [1]. The High-Critical Temperature Superconducting (HTSc) devices for microwave application require epitaxial thin films [2, 3]. They can be obtained by various chemical and physical techniques including chemical vapor deposition (CVD), co-evaporation, pulsed laser deposition (PLD) and sputtering [3]. Pulsed laser deposition is one of the most versatile and reproducible technique for the growth of superconducting thin films. However, one of the main disadvantages of the PLD technique is the appearance of particles (droplets) on thin film surface during deposition. This problem could be solved by an accurate control of the deposition parameters like substrate temperature, laser fluence, distance between target-substrate, oxygen pressure and post-annealing treatments. Also, several attempts have been reported to reduce the density of droplets by optimizing the deposition conditions: changing the deposition geometry or using different laser wavelength beams. The use of a freshly polished target can also improve the film's morphology [4, 5]. By selecting the proper substrates with similar crystal structures and thermal expansion coefficient with the ones of the film, the epitaxial strain induced by substrate in the film is reduced, favoring in the 2D growth mode with few or no 3D islands, reducing the film roughness [6].

$YBa_2Cu_3O_{7-\delta}$ (YBCO) with p-type conduction was extensively studied in the last twenty years due to the relatively simple producing process and its excellent superconducting properties. In superconducting phase it has an orthorhombic symmetry with cells parameters (a = 3.823 Å, b = 3.887 Å and c = 11.680 Å) and the maximum critical temperature (T_C) ≈ 93 K for the optimum oxygen doping. Two symmetry phases can be observed when δ varied between $0 \leq \delta \leq 1$. For $\delta = 1$ YBCO became insulator with a tetragonal phase and for $\delta \approx 0.1$ this compound is superconductor with an orthorhombic phase [3, 7]. In thin films form, *c*-axis oriented YBCO films are thermodynamically preferred to the *a*-axis ones and are most often used for the construction of electronic devices for microwave applications [7, 8]. Epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films have been obtained at deposition temperatures of at least 780 °C by pulsed laser deposition. Moreover, a post-deposition thermal treatment in oxygen atmosphere was found to be necessary to achieve high quality layers [8, 9].

In this paper, the influence of substrate temperature and radio-frequency (RF) oxygen plasma addition on the YBCO thin films properties has been studied. The YBCO thin films have been grown on (001) $SrTiO_3$ (STO) single-crystal substrates by PLD at 780 °C while for the layers grown at 730 °C a beam containing excited and ionized oxygen species produced by a RF (RF-PLD) discharge in oxygen was directed to the substrate [10, 11].

2. Experimental

The YBCO thin films have been obtained using a commercially available target (CHEMCo, Germany). The used substrate was (001) $SrTiO_3$ (STO) single-crystal. The ArF excimer laser working at a wavelength of 193 nm, repetition rate 5 Hz was used as irradiation source. The PLD experiments have been done using the following experimental parameters: laser fluence 1.5 J/cm^2, gas deposition pressure 0.22 mbar (O_2), target-substrate distance 50 mm, substrate temperature of 780 ^oC. Also, post-annealing treatments have been performed in 1 bar O_2 at 650 ^oC for 15 minutes, followed by another 1 hour at 450 ^oC in 1 bar of oxygen. This set of samples identified as YBCO1 was used as a reference for the RF-PLD deposited samples. The second set of samples identified as YBCO2, has been done at 730 ^oC substrate temperature and with the addition of the radio-frequency oxygen plasma beam working at 200 W discharge power, all other experimental parameters being unchanged. For YBCO2 experiments the post-annealing treatments have been performed as for the YBCO1 samples.

The morphology of the surfaces was studied with an XE 100 Atomic Force Microscope from Park Systems: the surface features and the roughness (RMS) of the films surfaces, for areas of 2 × 2 μm^2,were measured.

Diffraction spectra were acquired using a Panalytical X'Pert PRO MRD diffractometer in Bragg-Brentano geometry (θ-2θ). For information about thin films texture the omega measurements (rocking curves) spectra have been recorded.

Optical measurements were done with a Woollam Variable Angle Spectroscopic Ellipsometer (VASE) system, equipped with a high pressure Xe discharge lamp incorporated in an HS-190 monochromator. Measurements were performed in the range of wavelength between 250 and 1700 nm at 45, 60 and 75^0 angles of incidence.

The electrical properties of the thin films were measured in the 4.2-300 K range, using the standard dc four-probe method in a cryostat with liquid helium, for the R (Ω) vs. T (K) data [6].

For RF-PLD deposited sample, YBCO2, AC magnetic susceptibility measurements as a function of temperature have been performed using a Vibrating Sample Magnetometer system (VSM). With the VSM system a small AC field is applied on the sample with a so-called primary coil and the sample response is acquired with an astatic pair pick-up or second coil [12-14].

3. Results and discussion

3.1 Surface morphology

The influence of the depositions parameters such as substrate temperature and RF-oxygen plasma addition on the morphology of YBCO/STO (001) thin films was revealed by AFM investigation. All samples present uniform, droplets free surfaces and by the addition of RF to PLD process an increase of roughness value can be observed (from 2 nm for sample deposited by PLD to 5 nm for samples deposited by RF-PLD) (Fig. 1).

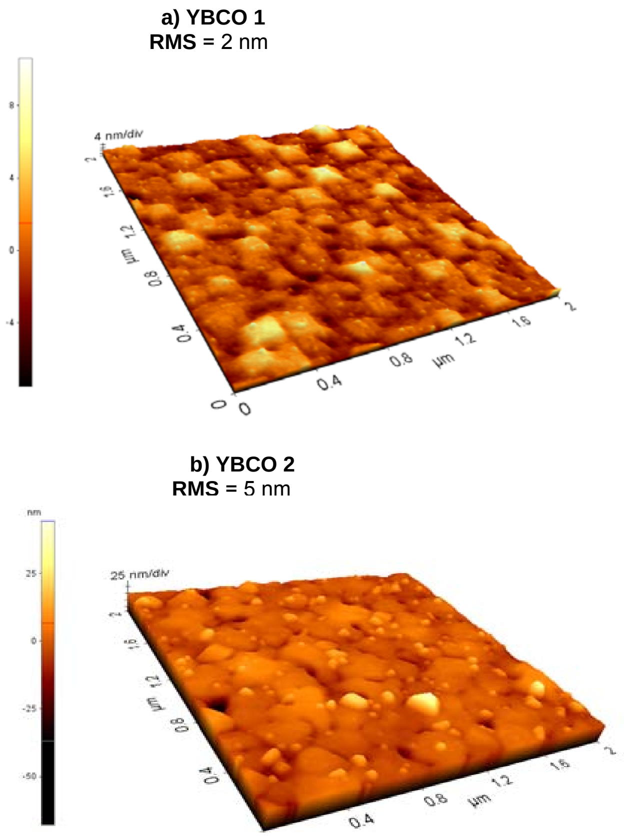

Fig. 1. AFM images for YBCO/STO (001) thin films deposited by: a) PLD at a substrate temperature of 780 ^oC and post-annealing treatment in 1 bar O_2 for 15 min. at 650 ^oC and 1 h at 450 ^oC respectively (YBCO 1); b) RF-PLD at a substrate temperature of 730 ^oC and post-annealing treatment in 1 bar O_2 for 15 min. at 650 ^oC and 1 bar O_2 for 1 h at 450 ^oC respectively (YBCO 2).

3.2 Structural analysis. X-ray Diffraction

A typical 2θ XRD pattern for $YBa_2Cu_3O_{7-\delta}$ thin films grown by PLD and RF-PLD on (001) $SrTiO_3$ is given in Fig. 2. The XRD data showed that the PLD films are epitaxial, with *c*-axis perpendicular to the substrate surface; they have an orthorhombic symmetry, with *c*-axis cell parameter value found to be $c \sim 11.69$ Å, similar with previously reported values [9]. The RF-PLD grown YBCO films are highly crystalline, exhibiting the value of $c \sim 11.685$ Å. From omega scans (not shown here), values of full width at half maximum (FWHM) for (005) reflection were measured, resulting that the RF-PLD films (YBCO2) have a higher mosaicity, which usually mean a higher strain level and/or smaller crystallite size. Noticeably, for the sets of RF-PLD samples a small amount of *a*-axis oriented crystallites can be observed. (Fig.2 b).

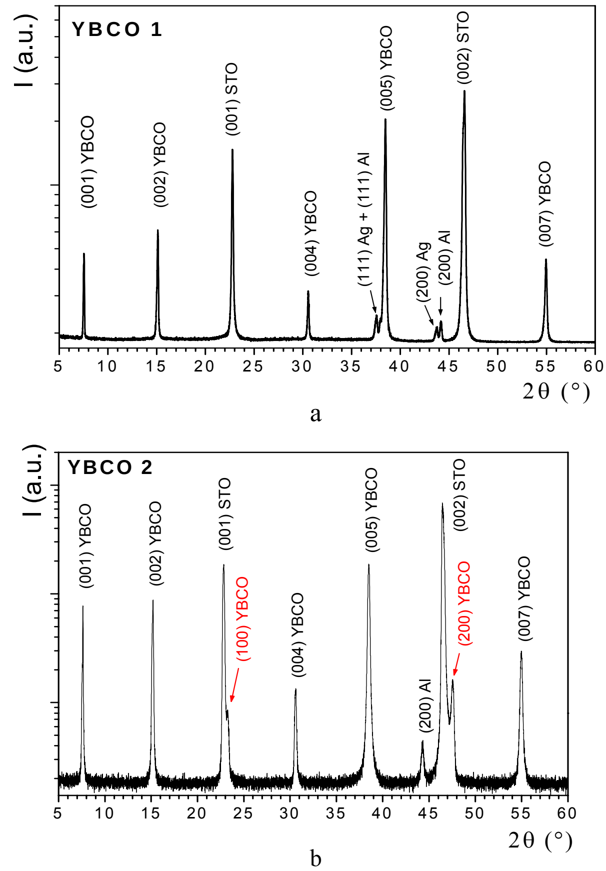

Fig. 2 - XRD difractograms obtained for YBCO/STO (001) epitaxial thin films deposited by PLD (a) and RF-PLD (b); The Al reflection is coming from the sample holder, while Ag (used to glue the sample during deposition) is from the back of the substrate.

3.3 Optical properties

In ellipsometry, the change of the polarization state of linearly polarized light is measured upon reflection at the surface. Because is a comparative method an accurate optical model is required for the system under consideration, which enables simulation or fitting of the results.

The complex reflection coefficient ρ is defined as:

$$\rho = \frac{R_p}{R_s} = \tan(\Psi)e^{i\Delta} \tag{1}$$

- where *Rp* and *Rs* are the reflection coefficients for the parallel and perpendicular polarizations, respectively. The quantity ρ is expressed in the two angles Ψ and Δ [15]. In ellipsometry measurements are relatively simples but the analysis of the results are more complicated. An accurate model is required for the system under consideration, which enables simulation or fitting of the results. In the present work we make use of WVASE 32 software, which is designed to handle data modeling and fitting multi-layers samples. In order to obtain the optical constants (refractive indices and extinction coefficients), thickness and roughness of the YBCO thin films was necessary an accurate optical model to generate Ψ and Δ data. These generate curves was compared with experimental Ψ and Δ curves. The difference between experimental data and fitted data is given by MSE (Mean-Square-Error) which is expressed by:

$$MSE = \frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\psi_i^{\mathrm{mod}} - \psi_i^{\mathrm{exp}}}{\sigma_{\psi,i}^{\mathrm{exp}}}\right)^2 + \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right] \tag{2}$$

- where *N* is the number of (Ψ, Δ) pair, *M* is the number of variable parameters in the model, and σ are the standard deviations on the experimental data points.

The MSE as shown in equation represents a sum of the squares of differences between the measured and calculated data, with each difference weighted by the standard deviation of that measured data point.

The optical model consists of 3 layers for films deposited on STO (001): the substrate, the YBCO layer and a *rough* top layer which is set to have half air and half STO. The optical response of the rough layer is approximated in the Bruggeman effective medium theory [15]. The bulk dielectric function for the STO substrate is taken from literature [16].

For YBCO in normal state the dielectric functions described by Kumar et al. [17], is written as a sum of Lorentz term, a Drude term and a high-frequency constant (εinf) and are given by equations 3-5.

In this work for the YBCO thin layer, the same model in order to fit the experimental data and to obtain a minimum MSE was used.

$$\varepsilon = \varepsilon_\infty + \varepsilon_{n\_Lorentz} + \varepsilon_{Drude} \tag{3}$$

$$\varepsilon_{n\_Lorentz} = \frac{A_n Br_n E_n}{E_n^2 - E^2 - iBr_n E} \tag{4}$$

$$\varepsilon_{n\_Drd} = -\frac{A_n Br_n}{E^2 + iBr_n E} \tag{5}$$

- where E_n is energy of oscilation, A_n is amplitude and B_r is oscilator broadening.

In Fig. 3 are presented the experimental data and the fit results using the model decrisbed by Kumar et al. [17], for the sample YBCO1 obtained by PLD at 780 °C substrate temperature. The calculated MSE value is relatively small (MSE 24.4), which is a good agreement with the reported one [17]. The thickness of YBCO thin films was found to be aprox. 120 nm and the thicknes of rough top layer is around 4.2 nm.

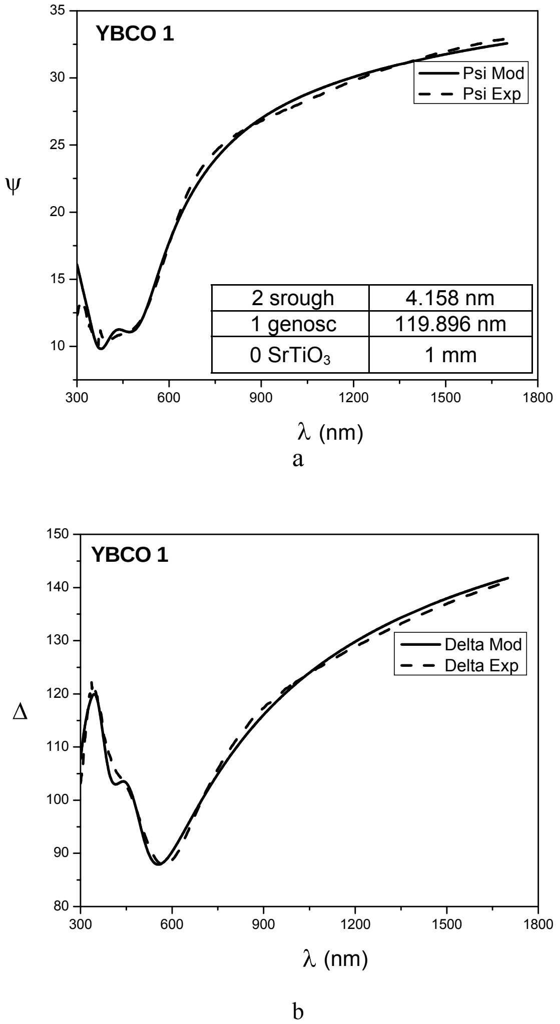

Fig. 3 - The experimental Ψ (a) and Δ (b) and fitted data using a Lorentz-Drude model for the sample YBCO1 obtained by PLD at a deposition temperature of 780 °C.

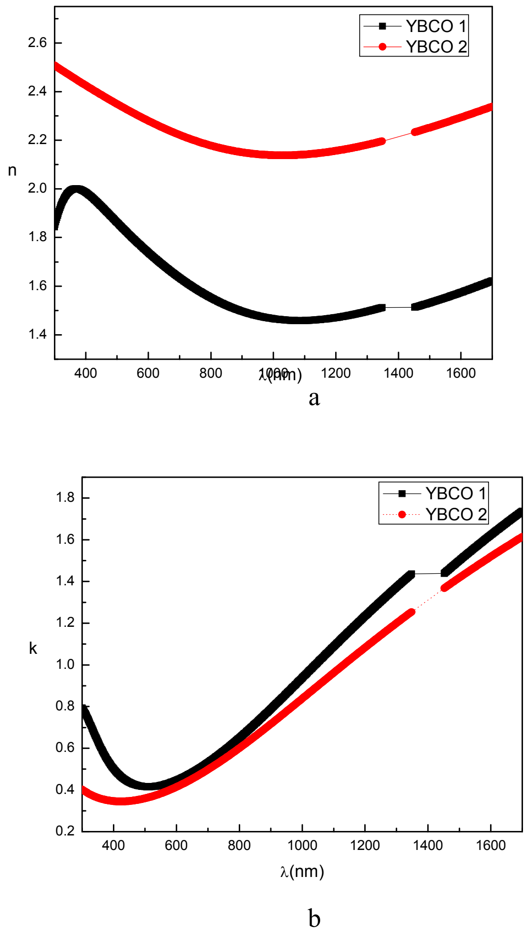

Fig. 4. The refractive indices (a) and extinction coefficients (b) for YBCO/STO (001) thin films deposited by PLD and RF-PLD.

For the sample YBCO2 grown at 730 °C substrate temperature, the same fitting procedure was used. The dependence of refractive indices and extinction coefficient (*n*, *k*) for both samples YBCO 1 and YBCO 2 are presented in Fig. 4 and show a typically dispersion for YBCO layers. It can be noticed a similar behavior of the two curves in the range of 500-1700 nm wavelength and slight differences in the 250-500 range.

3.4 Electrical and AC magnetic susceptibility measurements

Electrical measurements were performed in the 4.2-300 K range using a dc four-probe method (two current contacts and two voltage contacts). The onset critical temperatures for the two sets of samples have been measured at the intersection of the tangents with the R (T) curve and the transition halfway, following the method published by J. J. Scholtz *et al* [18].

The obtained values were T_C^{onset} ~ 88 K for the YBCO1 thin film deposited by PLD and T_C^{onset} ~ 89 K for the YBCO2 deposited by RF-PLD. For a complete characterisation of our films, the offset critical temperature recorded at the intersection of the R(T) curve and the abscissa is presented in Figure 5 [19]. The measured value of T_C^{offset} ~ 80 K have been obtained for the sample YBCO1 deposited by PLD at 780 °C (Fig 5a). For the films grown by RF-PLD at 730 °C, the best T_C^{offset} values obtained was 88 K (Fig 5b). The influence of the oxygen plasma addition on electrical properties can be observed from Figure 5 a, b. The results show that the RF-assisted PLD grown films have slightly better superconductive properties, most probably due to a better oxidation.

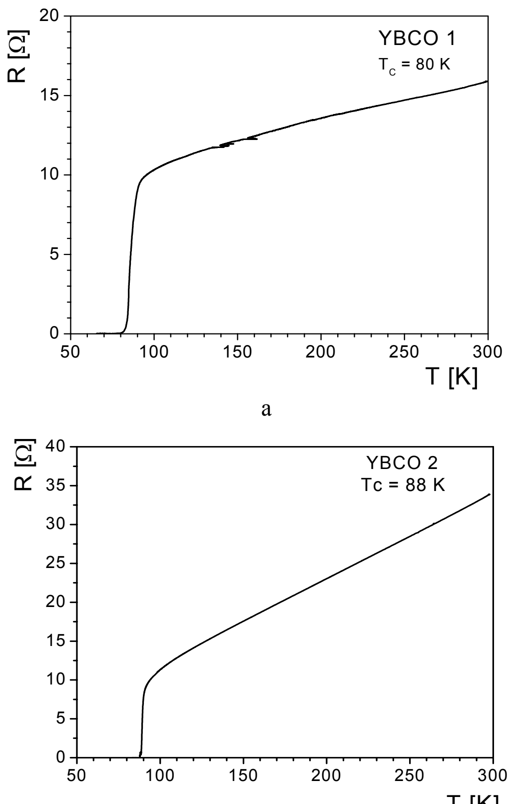

Fig. 5. Temperature dependence of resistance for a YBCO/STO (001) thin films deposited by PLD (a) and RF-PLD (b).

For the YBCO films grown by RF-PLD, AC magnetic susceptibility measurements as a function of temperature have been performed using a Vibrating Sample Magnetometer system (VSM): this analysis have been done to cross-check (confirm) the electrical measurements. The AC magnetic susceptibility measurements indicate a T_C^{onset} value around 87.5 K, which is in good agreement with the dc-four probe method result of 88 K.

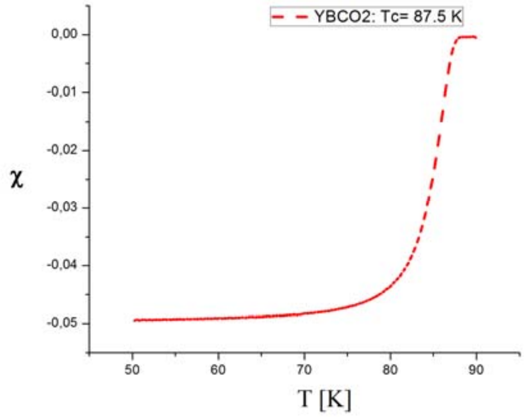

Fig. 6. Temperature dependence of AC magnetic susceptibility for a YBCO/STO (001) thin film deposited by RF-PLD.

4. Conclusions

$YBa_2Cu_3O_{7-\delta}$ thin films have been deposited by pulsed laser deposition and radio-frequency assisted pulsed laser deposition and a correlation between the deposition conditions and their functional properties has been performed. Within this approach, we have demonstrated the possibility of obtaining YBCO thin films by RF-PLD technique at a lower deposition temperature (≈ 730 °C), exhibiting similar electrical properties with the previously reported YBCO films deposited at higher temperatures (≈ 780 °C). From the electrical measurements made in the 4.2-300 K range using a dc four-probe method (two current contacts and two voltage contacts), slightly better T_C values have been recorded for the YBCO2 sample (T_C^{onset} = 89 K). For this sample, the AC magnetic susceptibility measurements indicate a similar T_C value of around 87.5 K, which is in good agreement with the dc-four probe method result.

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