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EXPERIMENTS ON PULSED LASER DEPOSITION AND CHARACTERIZATION OF EPITAXIALLY *IN-SITU* GROWN $YBa_2Cu_3O_{7-x}$ THIN FILMS

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Experimental results concerning the pulsed laser deposition parameters of in-situ epitaxially grown high crystalline quality $YBa_2Cu_3O_{7-x}$ thin films are reported. The structural and morphological properties of the deposited films analyzed by transmission electron microscopy, selected area electron diffraction, X-ray diffraction, and Raman spectroscopy are also presented. The $YBa_2Cu_3O_{7-x}$ thin films, predominantly *c*-axis oriented had required the smallest oxygen pressure during the cool-down time reported to date.

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1. Introduction

Presently most of the high temperature superconductor thin films for electronic applications are made of $YBa_2Cu_3O_{7-x}$ (YBCO) and related 123 materials. Of paramount importance for the superconducting properties of YBCO films is their crystalline quality. To prepare these films reliably and on large scale represents a combination of challenges in multidisciplinary technology. The pulsed laser deposition (PLD) process is one of the most convenient methods to obtain thin films of these relatively complicated materials. High quality thin films with maximum critical temperature T_C of the 123 phase (i.e., 92 K), could be obtained provided the substrate with the minimum lattice mismatch to YBCO (as, for example, $LaAlO_3$ or $LaGaO_3$) and the PLD conditions favoring the growth along the *c*-axis are used [1]. To date there is still a lot of variability in the PLD conditions and parameters; different conditions have been used by different working groups [1]. Therefore it is necessary to determine the PLD conditions specific for each laboratory. Understanding the growing mechanism and the ability to control the microstructure are key issues for obtaining materials with good properties for device applications. This work was aimed to determine specific experimental conditions for in-situ PLD YBCO thin films growth with high crystalline quality by using our available equipment. It is known that the correct oxygenation of the YBCO film during PLD process is important for its superconducting properties. However, the presence of high oxygen pressure introduces a number of technical problems for the PLD process. In our experiment we used during the cool-down time an oxygen pressure several times lower than the usual one (see Section 2). Good superconducting properties ($T_C \approx 87$ K) were obtained for our film without a high temperature post-deposition annealing process.

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Section 2 describes our experimental conditions of in-situ PLD epitaxially grown, highly oriented YBCO thin films. In Section 3 an analysis of the structural features and of the crystallographic microstructure of the grown film is made. The methods used to characterize the structure of the as-grown YBCO films and reported here are: transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD), and Raman spectroscopy. Section 4 provides some concluding remarks.

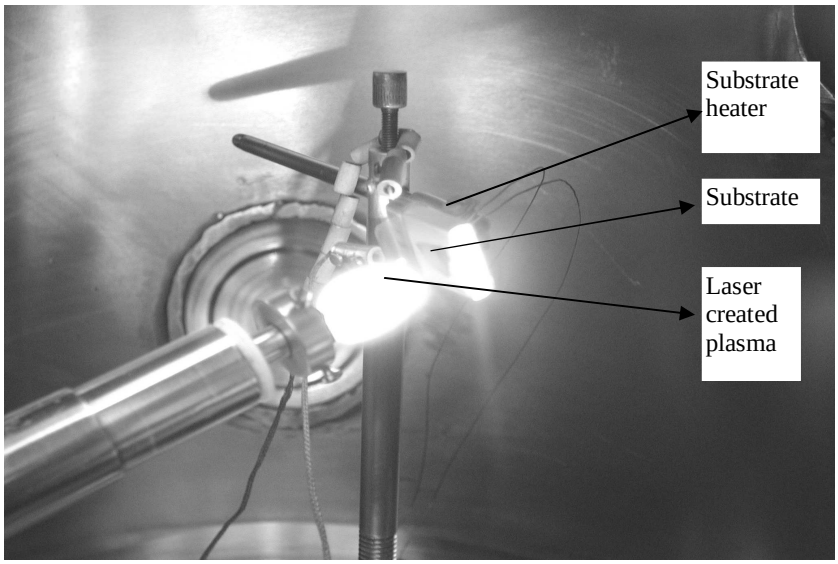

Fig. 1. Experimental setup.

2. The PLD process

The primary YBCO material was prepared as a bulk target to be ablated by a pulsed excimer laser beam, as reported elsewhere [2]. A KrF excimer laser with the following parameters was used: wavelength 248 nm, average fluence 2.7 J/cm^2, pulse repetition rate 1.8 Hz, pulse length (full width at half maximum) 20 ns. The laser beam was focused onto the rotating YBCO target in a vacuum chamber at 0.67×10^{-4} Pa. Molecular oxygen at 133 Pa was added before the deposition processes. Fig. 1 shows the experimental setup during the PLD process. The target-substrate distance is about 3.5 cm, the substrate being few mm away from the laser-created plasma, allowing a good deposition of the YBCO films [3]. As substrates, polished plan-parallel plates (1 mm thickness, 5-10 mm on sides) of <001> well oriented $LaAlO_3$ cubic single crystals were used. Before deposition, they were cleaned in an ultrasonic bath in acetone and then cemented to the heater with silver paint. A copper-constantan thermocouple cemented to the other part of the heater was used in a feedback loop to control the temperature. The substrate was heated at 800 °C. The deposition time varied between 10,000 and 25,000 laser pulses. With 0.014 nm/pulse typical deposition rate, obtained from preliminary previous experiments, the films' thickness was in the range of 150 nm to 350 nm. The film subjected to the present analysis has a thickness of ≈ 350 nm obtained by using 25,000 laser pulses. After deposition, the pressure of the molecular oxygen was increased continuously up to 1.3×10^4 Pa. The substrate temperature was slowly reduced (5 ^{o}C/min) to 470 ^{o}C and then fixed for one hour in order to allow a complete oxygenation of the film. During that hour the oxygen pressure was increased continuously from 1.3×10^4 Pa to 2.7×10^4 Pa. Fig. 2 shows the substrate temperature and the oxygen pressure during the PLD process as a function of time. Note that, for the oxygen pressure during the cool-down time, much higher values, in the range of 6.7×10^4 Pa - 11×10^4 Pa are usually reported for the YBCO PLD process without post-deposition annealing [1].

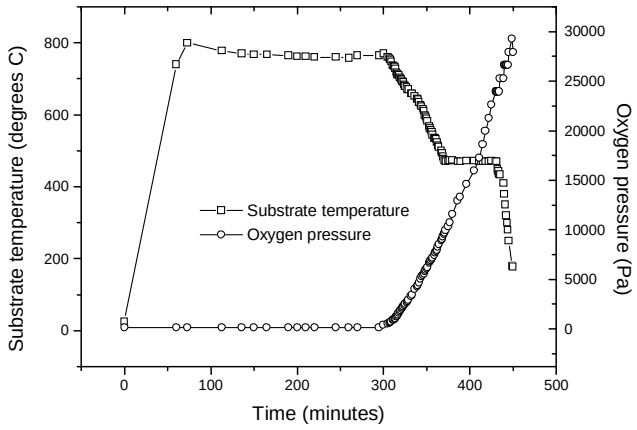

Fig. 2 Oxygen pressure and substrate temperature during the PLD.

3. Structural and crystallographic quality characterization of the YBCO thin films

Good superconducting properties of the thin film were obtained. A sharp transition at ≈ 87 K was observed by using an ac susceptibility measurement on the film. However, this work is focused on measurements concerning the crystalline quality of the films, which is essential for good superconducting properties and does not discuss the superconducting measurements. The results of the following methods to characterize the structural features of the YBCO thin films are reported here: TEM, SAED, XRD, and Raman spectroscopy.

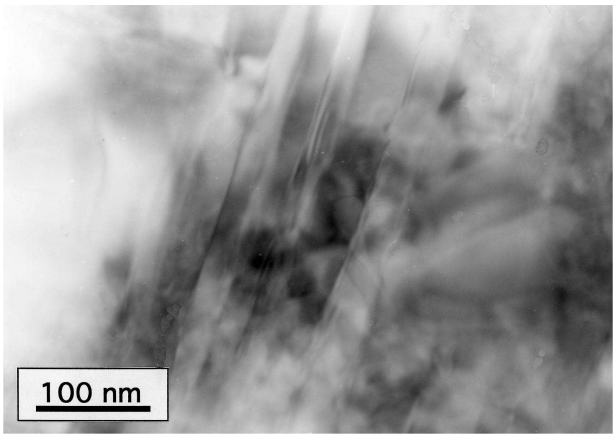

Fig. 3. TEM image of <110> oriented micro-twin lamella of 25 nm in the orthorhombic structure.

The structure of the grown YBCO thin film was examined by TEM and SAED [3, 4]. Fig. 3 shows the characteristic TEM contrast of the <110> oriented micro-twinned structure in the orthorhombic supraconducting phase, consisting of several lamellae with a width of about 25 nm. Fig. 4 shows the TEM plan view and the corresponding SAED pattern images, showing the high order <100> orientation in the film plane. Both pictures are taken on the same film with the thickness of about 350 nm, but using different orientations of the probe under the electron microscope. The texture of the film is strongly *c*-axis oriented.

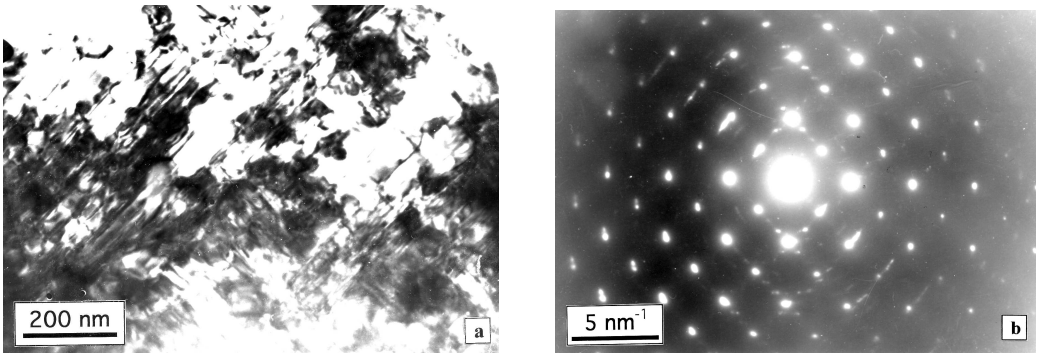

Fig. 4. Plan-view of the YBCO film on the ‹001› axis corresponding to: a) TEM image and b) SAED image.

X-ray diffraction analysis was used to assess the crystal quality, the degree of the out-of-plane of the epitaxy, the phase composition and purity, as well as the degree of the inhomogeneous strain and the lattice parameters of the YBCO film. The X-ray diffraction pattern of YBCO film was determined using the CuKα radiation from a computer-controlled diffractometer type Bruker AXS D8 ADVANCE using the proprietary software (DIFFRAC^{plus} EVA). Fig. 5 shows the X-ray diffraction pattern of the YBCO film. The values 1.169 nm, 0.383 nm, 0.388 nm of the *c*, *a*, *b*-lattice constants and the 0.005 nm of the orthorhombic strain (*b*-*a*) of the YBCO film (rounded to three decimals) were automatically calculated from the YBCO film X-ray diffraction pattern by the diffractometer's software. An oxygen deficiency $x = 0.13$ was estimated from the *c*-lattice constant using data from Refs. [2] and [5], so we conclude that the film has sufficient oxygen. The X-ray diffraction pattern of the YBCO film contains the <001>, <002>, and <003> peaks caused by the substrate (indicated with S), several strong and weak peaks of the superconducting orthorhombic $YBa_2Cu_3O_{6.87}$ phase, as well as two weak peaks of some impurities (other than the above phase) located approximately at $2\theta = 21^o$ and 43^o respectively. From the relative amplitude of these peaks we conclude that the impurity percentage is very low in comparison to the main superconducting orthorhombic YBCO phase.

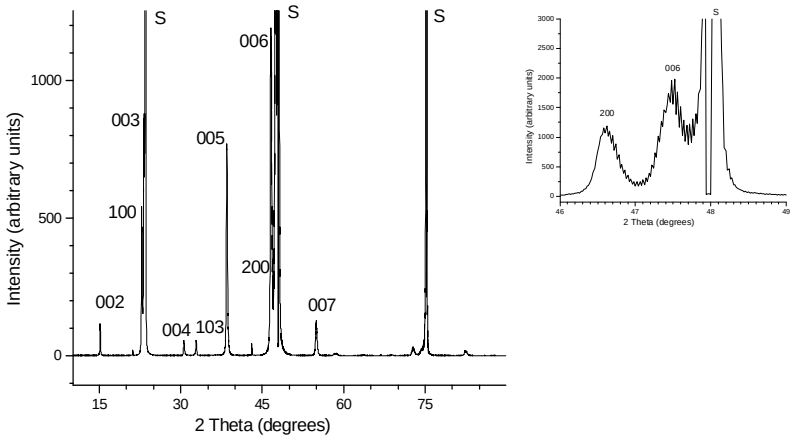

Fig. 5. X-ray diffraction pattern of YBCO thin film. The small inset shows the (200) and (006) peaks.

The film shows strong <00l> orientation, where l = 1-7, and also <h00> orientation, where h = 1, 2. The ratio between the area under the <200> peak and the area under the <005> peak of the film allows us to estimate a percentage of about 27 % of the *a*-axis oriented grains from the mainly *c*-axis oriented grains.

The rocking curves' FWHM of the <002> substrate reflection and of the <005> YBCO film reflection show a mosaic spread close to 0.45^o and $\approx 1^0$, respectively. The latter curve is shown in Fig. 6. This proves the perfection of the out-of-plane epitaxially grown film on the substrate.

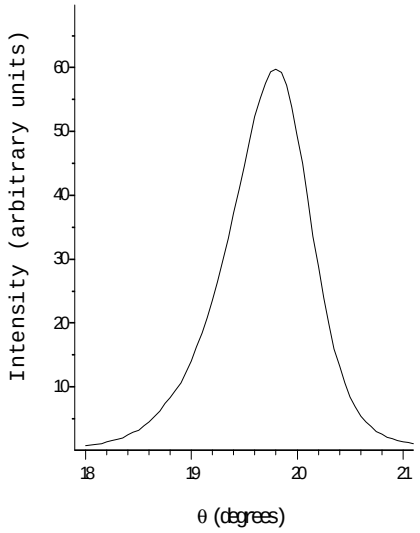

Fig. 6. Rocking curve on the (005) XRD peak.

The evaluation of the oxygenation and of the local crystallographic orientation of YBCO thin film was carried out by Raman spectroscopy analysis. We used a Renishaw Raman Imaging Microscope, with the proprietary software WIRE^{TM} accompanying the spectrometer. The Raman scattered light was excited by a 633 nm, 17 mW, continuous wave HeNe laser emitting a $TEM_{00,}$ single mode, linearly polarized beam. The laser light is delivered through the focusing optics of the microscope becoming an incident polarized light on the thin film under test. The detector is an array of 578 x 385 Si elements CCD camera with pixel size 22 μm x 22 μm. It operates at - 70 °C by using thermoelectric cooling, with no expensive cryogenic coolants. We measured the spectral range of 25 cm^{-1} - 1000 cm^{-1} Raman shift with a resolution < 1 cm^{-1}. The Renishaw Raman system was used in the confocal mode with a 10 μm pinhole to acquire data from that part of the sample most strongly irradiated by the laser, allowing a depth of spatial resolution of 50 nm. The grating spatial frequency is 2400 mm^{-1}. The characteristic Raman spectrum for the orthorhombic YBCO phase has maxima at 118 cm^{-1}, 150 cm^{-1}, 340 cm^{-1}, 435 cm^{-1}, and 500 cm^{-1}, corresponding to the vibrations along the *c*-axis of Ba, Cu, planar oxygen in CuO_2 plane out of phase, planar oxygen in CuO_2 plane in phase, and apical oxygen, respectively [6].

Fig. 7 shows the non-fitted Raman spectra (100 cm^{-1} -1000 cm^{-1}) of our YBCO thin film. Fig. 7a is typical for most of the film area and is taken somewhere in the middle of the substrate (similar spectra were obtained at different locations on the film, excepting the specially prepared corner described below). The film whose spectrum is in Fig. 7b corresponds to a corner of the substrate (representing about 25% of the substrate area) that purposely was not cemented on the heater, allowing for a tiny air gap between the substrate and the heater. We estimate that this corner had, during the PLD process, a temperature about 50 ^oC smaller than the substrate. The comparison between the amplitude of the 340 cm^{-1} and 500 cm^{-1} shifts is used to determine the local crystal orientation [7]. The higher amplitude of the signal in the neighborhood of the 340 cm^{-1} shift in comparison to that in the neighborhood of the 500 cm^{-1} shift in Fig. 7a indicates an epitaxially grown predominantly *c*-axis oriented textured film. The smaller amplitude of the 340 cm^{-1} shift in comparison to that of the 500 cm^{-1} shift in Fig. 7b corresponds to a Raman spectrum typical to *a*-axis oriented grains of the film. Correlating the XRD and Raman data we conclude that the lower temperature corner contains the most part of the *a*-axis oriented grains determined by XRD pattern. Since the *a*-axis nucleus is smaller than the *c*-axis one, *a*-axis should be predominant at lower temperatures. We presume that the cause for the different alignment growth on the corner is its lower temperature during the PLD process. Therefore, the *c*-axis grown film corresponds to all but the corner area of the substrate.

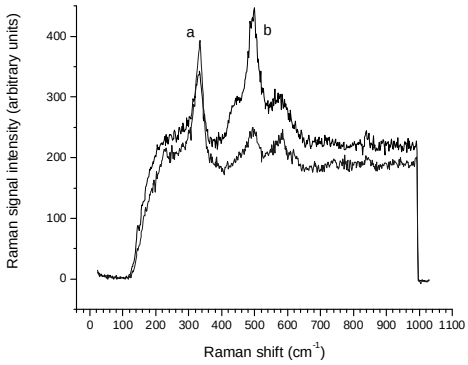

Fig. 7. Raman spectrum of the YBCO film: a) on most of film area; b) on corner

4. Conclusion

We determined the feasibility of our available equipment to obtain YBCO thin films with good structural and superconducting properties. Some of our specific experimental conditions are different than the published ones. We found that good quality YBCO thin films can be obtained using a different oxygenation regime than reported before. To our knowledge we used the smallest oxygen pressure reported to date (several times smaller than the reported values) during the cool-down time. In-situ PLD epitaxially grown YBCO thin films with predominantly *c*-axis oriented texture were obtained. A post-deposition annealing was not necessary. In this way we avoid some undesirable precaution measures and technical issues: a) loss of film stoichiometry after annealing due to the film-substrate interaction; the surface evaporation; barium and/or copper deficiency, and also b) mechanical defects as cracks and/or the increase of surface roughness during the thermal cycling [8].

By correlating the XRD information on the whole film surface with the local information from TEM, SAED, and Raman spectroscopy, it is possible to obtain relevant information on the local oxygenation and the local crystal orientation of a textured film.

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