FOURTH EURO CERAMICS - Vol. 6 - pp. 423–428
High Tc Superconductors
Edited by A. Barone, D. Fiorani, A. Tampieri.

EFFECTS OF ANNEALING CONDITIONS ON STRUCTURAL AND SUPERCONDUCTING PROPERTIES OF $YBa_2Cu_3O_x$ EPITAXIAL FILMS

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$YBa_2Cu_3O_x$ films, grown by sputtering on $LaAlO_3$ (100) substrates in different deposition conditions, were characterized by x-ray diffraction, Raman spectroscopy and magnetization measurements. The results show that the best deposition conditions, allowing the growth of high quality epitaxial films (T_c=90 K), are realized by single target and *in-situ* annealing. The effect of the deposition conditions on the final oxygen stoichiometry and its relationship with T_c and J_c values are discussed.

INTRODUCTION

High quality superconducting films are very important for a better understanding of the mechanism of high T_c superconductivity and for device applications. A careful control of their microstructure and stoichiometry is then required, implying the optimization of deposition conditions. It is well known that oxygen stoichiometry plays a very important role in determining the superconducting properties, ruling the carriers concentration and the actual dimensionality of the flux line lattice. For this reason the study of the relationship between oxygen stoichiometry and T_c and J_c values is a subject of current interest [1-4]. In this context we have grown by sputtering a series of $YBa_2Cu_3O_x$ films changing the deposition conditions (e.g. starting from one or two targets, with *in-situ* or *ex-situ* annealing ...) and we have characterized them from a structural and superconducting point of view by X-ray diffraction, Raman spectroscopy and magnetization measurements. The effect of the deposition conditions on the final oxygen content and on the T_c and J_c values will be discussed.

SAMPLES PREPARATION

Superconducting films of $YBa_2Cu_3O_x$ were deposited on $LaAlO_3$ (100) substrates using a 90° planar magnetron sputter gun mounted in a cryopump vacuum chamber; the base pressure was $3x10^{-8}$ Torr. The targets were prepared by pyrolysis of citrates of the corresponding elements. The sputtering atmosphere varies between 40 to 60 Torr O_2 and from 160 to 240 mTorr Ar.

An RF power of 100 W generates a cathode self-bias of -70 V and gives a deposition rate for the off-axis geometry of about 0.1 Å/s, which depends on the total pressure and the Ar/O_2 ratio. In our case it is 200 mTorr with 20% O_2 and 80% Ar. The substrate was bonded by silver paste on the holder. During film growth the substrate block temperature was held

constant at 780°C. Different YBCO films, reported in Tab. 1, were deposited under different annealing conditions. The films 0793, 1194, 1594, 2294 were prepared by using two stoichiometric targets, whereas the films 0295 and 0495 by using a single target. The film thickness is approximately 0.7 μ and 0.2 μ for the samples prepared from two and one target respectively. For the 1194 and 0793 films after deposition the chamber was immediately vented to 20 Torr of pure oxygen and the substrate was allowed to slowly cool to room temperature. For the 1594 film the growth was followed by an *ex-situ* annealing (20 Torr of pure oxygen at 700°C and a slow cooling to room temperature).

Table 1- T_c, *c*-axis length, $FWHM_{005}$ and oxygen stoichiometry estimated by eq. (1), for different YBCO films.

Sample	T_c(K)	*c*-axis(Å)	FWHM(°)	x
0495	90	11.673(7)	0.317	7.0
0295	90	11.685(3)	0.426	7.0
1194	85	11.697(5)	0.696	6.9
0793	84	11.710(4)	0.538	6.8
1594	83	11.735(2)	0.864	6.7

Films were characterized by X-ray diffraction and Raman spectroscopy and by means of magnetic measurements.

EXPERIMENTAL

X-ray diffraction measurements have been performed on a Seifert XRD 3000P diffractometer operating in the Bragg-Brentano geometry using Cu-Kα radiation (λ=1.5418 Å). The diffracted intensities were collected in a θ-2θ scan mode in the range $3<2\theta<90°$ with step size 0.01° and scanning time 2s at each step. The full width at half maximum (FWHM) of (005) reflection was derived from θ-scans (i.e. "rocking curves") made in fixed 2θ mode.

The Raman spectra were recorded with a SPEX TRIPLAMATE spectrograph equipped with an optical multichannel CCD detector by EG&G PARC. The 514.5 nm line of an Ar^+ laser was used for excitation with 15 mW at the sample. The measurements were performed in a backscattering geometry. The Raman spectra were subjected to data reduction procedure (base line removing and curve fitting) by GRAMS/386 software by Galactic. Frequency positions and intensities of the Raman bands were obtained through this data treatment by the deconvolution of the Raman spectra in mixed lorentzian-gaussian components.

DC magnetization measurements were performed using a commercial SQUID ($2<T<400$ K, H_{max}=5.5 T) and a VSM magnetometer ($20<T<300$ K, H_{max}=1 T). The magnetic field was applied parallel to the c-axis. From the low-field (H=10 Oe) ZFC measurements the T_c values (taken as the onset of the diamagnetism) reported in Tab. 1 were derived.

RESULTS AND DISCUSSION

a) X-ray diffraction measurements.

The diffraction spectra show that the films are epitaxial with the *c*-axis perpendicular to the film surface (only 00l reflections are present in the diffraction pattern). Moreover, the absence of any other peak shows that no impurity phases are present. A typical diffraction pattern of

YBCO film deposited on $LaAlO_3$ (100) substrate (sample 0295) is reported in Fig. 1. The inset shows the rocking curve of the (005) reflection and its FWHM calculated from the Lorentzian fit of the data after $K\alpha_2$ subtraction.

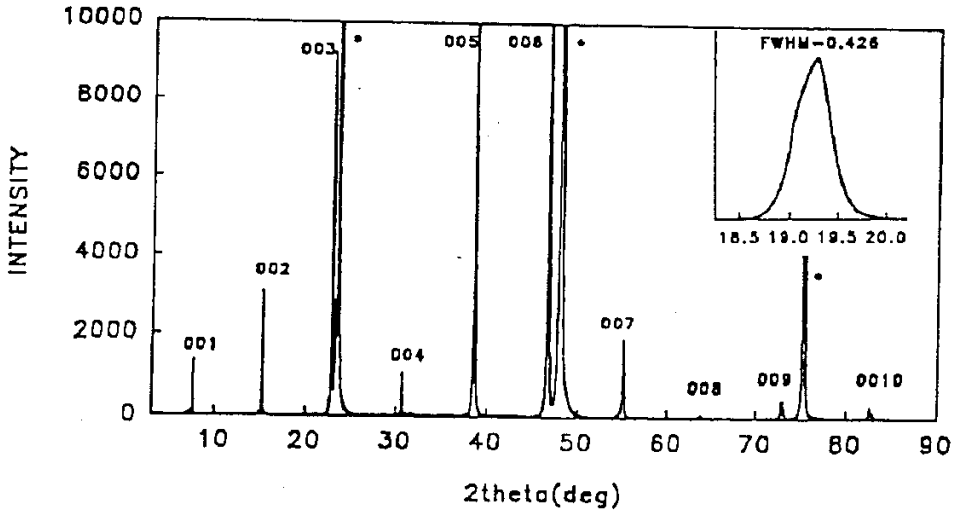

Fig.1 - X-ray diffraction pattern of sample 0295. The * indicates the substrate peak. The inset shows the (005) rocking curve.

The *c* lattice parameter has been determined for each sample from the 2θ value of the diffraction peaks through a least-squares refinement process. Table 1 reports the *c*-axis values and the FWHM of the (005) diffraction peaks obtained from ω-scans. With the exception of sample 1594, the low FWHM values indicate that the mosaic spread is quite small, evidencing a good epitaxial growth. The higher value found for 1594, the only *ex-situ* annealed film suggests the presence of increasing amounts of defects and worse epitaxial quality. Samples 0495 and 0295 have the shortest *c*-axis lengths and the highest T_c values (see Tab. 1). Then these films are expected to have the highest oxygen content. It is known that the *c*-axis length in high T_c superconductors is closely related to the oxygen content, decreasing with increasing it. However in films, unlike in powders and single crystals, the *c*-axis length may be influenced by other parameters too (e.g. defects, disordered distribution between Y and Ba atoms, type of substrate) and then its correlation with the oxygen content is not straightforward [5]. An approximate relationship between the *c*-axis length and the oxygen stoichiometry x has been reported in literature and applied to thin films too [6]:

$$x = 74.49 - 5.78 * c[\text{Å}]. \qquad (1)$$

The x values calculated from (1) are reported in Tab. 1. The increase of the oxygen content with decreasing the *c*-axis length follows the same trend as the data reported by J.Ye et al. [5] for YBCO thin films, based on the experimental determination of either the *c* lattice parameter and the oxygen fraction. Our results show that the *c*-axis length in the different films is mainly influenced by the variation of the oxygen content. Films 0295 and 0495, prepared by using single target are the best samples from the structural point of view and have the highest oxygen content.

b) Raman spectroscopy measurements.

Raman spectra show for all films the characteristic phonon frequencies of $YBa_2Cu_3O_x$ material. However some extra bands are also present. The spectrum of the film 0295 (T_c=90 K)

is discussed in detail. In Fig. 2 the Raman spectrum of this film in the range 300-700 cm^{-1} is shown. The phonon bands at 340 (in-plane O) and 500 cm^{-1} (apex O), typical of orthorhombic phase, are recognised. Since the typical sampling depth in the Raman measurements is 50 - 100 nm for high T_c materials [8], not significant signal from the substrate was detected. Other Raman bands present in the spectrum (see e.g. the quite strong one at 630 cm^{-1} with a shoulder around 600 cm^{-1}) can be attributed to impurity phases (e.g. $BaCuO_2$,Y_2BaCuO_5)present in the film as small inclusions at the boundaries of the $YBa_2Cu_3O_x$ domains [7]. Such impurities were not detected by X-ray diffraction. This would suggest that they are mainly present on the film surface.

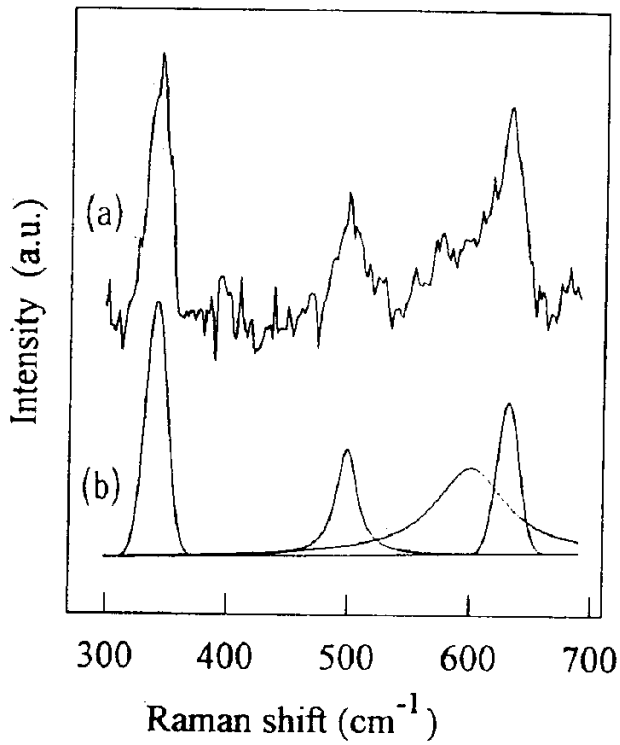

Fig. 2 - (a) Raman spectrum of sample 0295 in the range 300 - 700 cm-1.
(b) Deconvolution of the same spectrum by the curve fitting procedure showing the main Raman components.

In a paper by V.N. Denisov et al. [7], the intensity ratio, N , between the 500 cm^{-1} band and the 340 cm^{-1} band was used to estimate the preferable orientation of the film and was correlated with the T_c transition width, ΔT_c, (e.g. for a sample with $\Delta T_c<2$, N was found in the range 0.5-1). Following their arguments, we should expect for sample 0295, having N=0.5, a small ΔT_c and crystals with the 0xy orientation mostly parallel to the film surface. Both these results are confirmed by X-ray diffraction measurements, showing (00l) reflections only with small FWHM, and by magnetic measurements showing a sharp superconducting transition for this film.

It is known that the frequency of the Raman band around 500 cm^{-1} (apex-O phonon) can be correlated to the lattice constant, *c*, and hence to the oxygen content, x [9]. From the frequency position of this band we obtain for 0495, 0295 and 0793 films *c*-axis values of 11.694 ± 0.004, 11.710 ± 0.004 and 11.723 ± 0.004 Å respectively. The *c* values are consistent with those obtained by X-ray diffraction and with the T_c values measured by magnetization measurements (Tab. 1). According to equation (1) they correspond to the oxygen stoichiometry

7.0 and 6.9. However the *c* values are slightly shifted with respect to those obtained from diffraction measurements. This could in principle indicate small differences in the oxygen content on the surface layers with respect to those closer to the substrate.

c) Magnetic measurements.

It is well known that T_c is related to the number of carriers in the Cu-O planes and that in YBCO it is expected to increase with increasing the oxygen content [3, 4]. The measured T_c values are consistent with the oxygen content estimated from the *c*-axis lengths obtained by X-ray diffraction measurements and Raman spectroscopy (Tab.1). The films having the highest T_c's (0295 and 0495) correspond indeed to those with the smallest *c*-axis lengths.

The width of the superconducting transition is also well consistent with the FWHM values of the (005) diffraction peaks, the transition being broader for the film having the highest FWHM value. The very large separation between the FC and ZFC branches of the susceptibilities for the 0295 film reveals a stronger flux trapping with respect to the other films (Fig. 3).

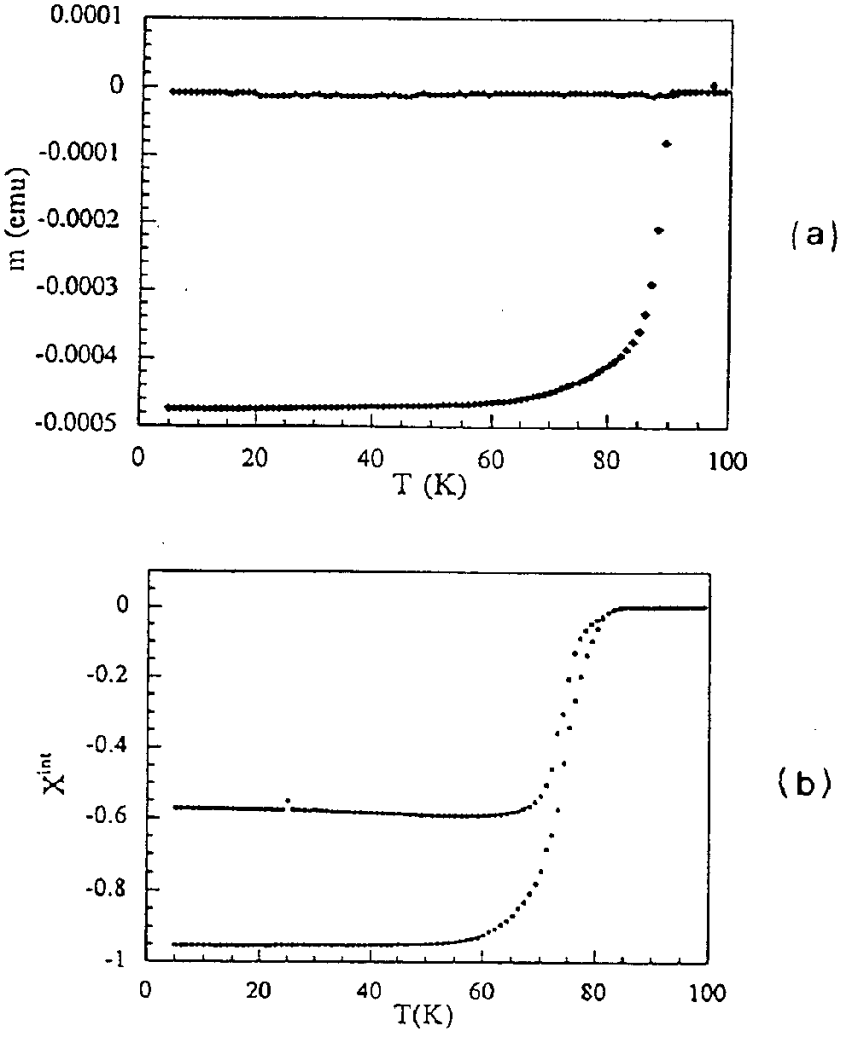

Fig. 3 - Magnetization (H= 10 Oe) applied parallel to the *c*-axis vs temperature for 0295 (a) and 0495 (b) films.

Critical current J_c values were derived from the hysteresis loops, measured by vibrating sample magnetometer (sweep time: 20 min), by using a modified Bean formula for the critical

state [10]. At low temperature J_c does not show significative differences between the different films (e.g. J_c (T=20 K, H=1 KOe) = 1.2 - 1.5x10^6A/cm^2).

On the other hand at high temperature remarkable differences are observed: e.g., comparing the films 0295 (grown from single target) and 1194 (grown from two targets), J_c (77 K, H=1 KOe) is 1.7x10^5 A/cm^2 and 8.8 x10^4 A/cm^2 for the first and second one respectively.

Comparing the films, both grown from two targets, 1194 (*in-situ* annealed) and 1594 (*ex-situ* annealed), J_c (60 K, H=1 KOe) is 4.5x10^5 A/cm^2 and 2.5x10^5 A/cm^2 for the first and the second one respectively. It is well known that oxygen vacancies (dimensions ≈ 0.4 nm) act as weak point pinning centers effective at low temperatures [3, 11]. Small differences are then expected at low temperature, depending on the oxygenation degree of the sample. This is consistent with the J_c values measured at 20 K. At high temperature twin boundaries, acting as strong extended pinning centers, play a dominant role in determining J_c for YBCO samples as well as the actual flux lattice dimensionality, ruled by the oxygen content [3, 4, 12]. Due to the lack of three-dimensional diffraction data (only 00l reflections can be collected in θ-2θ scan) and of further microstructural investigations, we do not know whether the films have different density of twin boundaries. The smaller J_c value at high temperature for the films with lower oxygen content should be related to the weakening of the coupling between CuO_2 planes, determining a lower actual flux lattice dimensionality (decrease of 3D behaviour).

CONCLUSIONS

The results show that the best deposition conditions allowing the growth of high quality epitaxial films are realized by a single target and *in-situ* annealing (samples 0295 and 0495). This is confirmed by X-ray diffraction and Raman spectroscopy measurements, which also give an estimation of the oxygen content (the oxygen stoichiometry is 7.0 for 0295 and 0495). Magnetization measurements show that both T_c and Jc increase with increasing oxygen content (for 0295, T_c=90 K, J_c(T=77 K; H=1 KOe)= 1.7x10^5 A/cm^2).

ACKNOWLEDGEMENTS

We would like to thank C. Veroli and L. Filaci for technical assistance during X-ray diffraction and magnetization measurements.

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