Journal of Alloys and Compounds, 195 (1993) 239-242
JALCOM 7457

Structural Defects in YBaCuO Thin Films Grown on MgO Substrates

L. Ranno‡, J. Perrière‡, M.C. Bernard*, A. Hugot-Le Goff*, D. Keller°+, D. Chambonnet+ and C. Belouet+

‡Groupe de Physique des Solides, Universités Paris VII et Paris VI, URA 17, Tour 23, 2, Place Jussieu, 75251 Paris Cedex 05, France.

*Laboratoire de Physique des Liquides et Electrochimie, Université Paris VI, UPR 15, Tour 22, 4, Place Jussieu, 75252 Paris Cedex 05, France.

°Laboratoire de Minéralogie Cristallographie, Universités Paris VI et Paris VII, URA 9, Tour 16, 4, Place Jussieu, 75252 Paris Cedex 05, France.

+Alcatel Alsthom Recherche, Route de Nozay, 91460 Marcoussis, France.

Abstract

YBaCuO thin films grown using the *in situ* laser ablation deposition technique, were studied using several complementary analyses : X-ray diffraction, RBS in channeling geometry and micro Raman spectrometry, in order to obtain complementary data on the crystalline quality of the films and on the nature of the intrinsic defects due to the growth process or induced by the RBS analysis.

1. Introduction

YBaCuO thin films are now routinely and reproducibly *in situ* grown on MgO single crystals by pulsed laser deposition. These films present high quality superconducting properties, i.e. a transition temperature T_c greater than 90 K and critical current densities in the 10^6 to 10^7 A/cm^2 range at liquid nitrogen temperature in zero magnetic field[1]. However, numerous questions are not solved out about the growth mechanisms of these compounds, and the nature and the density of defects present in the films as a result of the growth process. Thus, in this paper we report on the structural characterisation of *in situ* grown YBaCuO films. X-ray diffraction, RBS in channeling geometry and micro Raman analysis were used to obtain nearly exhaustive information about the film crystalline perfection.

2. Experimental

The YBCO thin films were grown on (100) MgO substrates using the well known pulsed laser deposition technique. The experimental set-up and the precise deposition process were previously described [1]. Briefly, the depositions were carried out under a pure oxygen pressure (0,2 mbar) on heated substrates (740°C). The cooling rate was 10°C/min under an oxygen pressure of 300 mbar. Under these conditions, the growth of pure c-axis films was always observed.

X-ray diffraction in the Bragg-Brentano geometry was performed on all films. Special attention was paid on the (0 0 3L) peaks in order to determine the existence of a-axis and c-axis orientations. To distinguish 0° and 45° orientations of the c-axis grains with respect to the substrate axes, the in-plane relative orientation ($(100)_{YBCO}$ // $(100)_{MgO}$ versus $(100)_{YBCO}$ // $(110)_{MgO}$) of the YBaCuO cell, was determined using the asymmetrical reflection on the (108) plane of the YBaCuO structure. Rocking curves were also performed on the (006) peak. RBS experiments in channeling geometry were carried out, and the ratio of aligned to random spectra (the minimum yield χ_{min}) was used as a measure of the film crystalline quality. In addition to the estimation of the oxygen content of YBaCuO films,

0925-8388/93/$06.00

micro Raman analysis was used to characterise the defects induced in the films by the MeV ion irradiation. The Raman spectra were recorded at room temperature with the 514.5 nm line of an argon laser focused onto the sample through a microscope and a selected area of 1 μm^2 was observed.

3. Results

The analyses of X-ray diffraction peaks showed that all the *in situ* grown (at 740°C) YBaCuO films have their (a,b) planes parallel to the MgO (100) substrate surface. This highly textured growth was further evidenced measuring the (006) rocking curve. Typical curves recorded on YBaCuO films show FWHM in the range 0.45° to 0.6°, which is close to the ones reported in literature. Moreover, differences in the FWHM were not observed for films having different oxygen contents evidenced by shifts of the rocking curves.

The high structural quality of the films was also observed by RBS in channeling geometry. As a matter of fact, Fig. 1 shows the random and aligned backscattering spectra of a (001) oriented film with a 0.55° c-axis angular spread measured on the (006) rocking curve. The χ_{min} values measured at 2 MeV in the case of axial channeling along the c axis, are 8% for the Ba and Y atoms, while a value of 11% is found for the Cu. These values, which are the best results obtained in this work, can be favourably compared to the best published values for laser deposited YBCO films on MgO substrates [2]. The differences observed in the χ_{min} values between Cu and the other cations are related to the fact that along the c-axis two different kinds of cationic rows exist in the YBaCuO structure, i.e. Cu rows and (Ba, Y) rows. Thus, according to the fact that the Cu rows have a lower average atomic number (i.e. a lower linear charge) with respect to the (Y, Ba) rows, weaker channeling effects, therefore a higher χ_{min} value, are expected for this element. Let us note that the precise χ_{min} values measured on YBaCuO films with the same c-axis angular spread, depend upon the oxygen content. In fact, higher χ_{min} values are observed on the films having a higher value of c parameter (characteristic of a low oxygen content).

Whatever the crystalline quality of the YBaCuO films, we observed a decrease of χ_{min} values with decreasing He ion energy (Fig. 2). Since dechanneling caused by extended defects (like dislocations) decreases with decreasing beam energy [3], such extended defects appear as the main cause of dechanneling in the YBaCuO *in situ* grown layers. Moreover, for the best films, the extrapolation of the χ_{min} variation goes to zero, showing that only extended defects are present. Thus, the question arises on the correlation between these defects and the spiral structure observed by scanning tunnel microscopy during the growth of YBaCuO films on MgO [4]. The screw dislocations which can be present in the spiral surface microstructure may be at the origin of the dechanneling effects in the films.

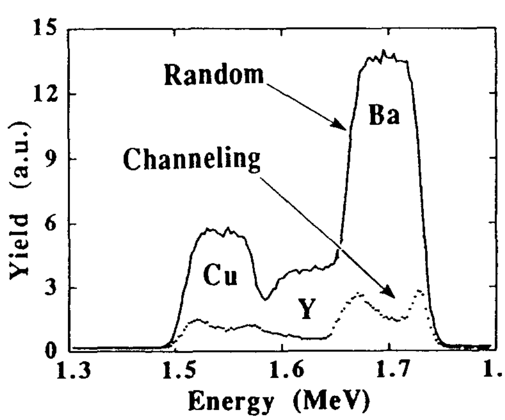

Fig. 1 : Aligned and random RBS spectra

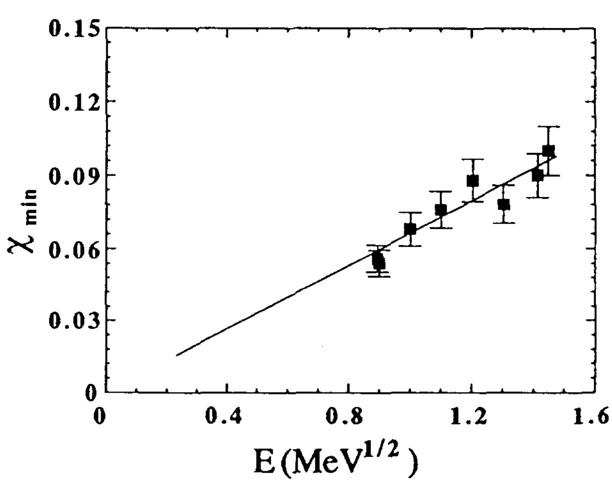

Fig. 2 : Energy dependence of χ_{min}

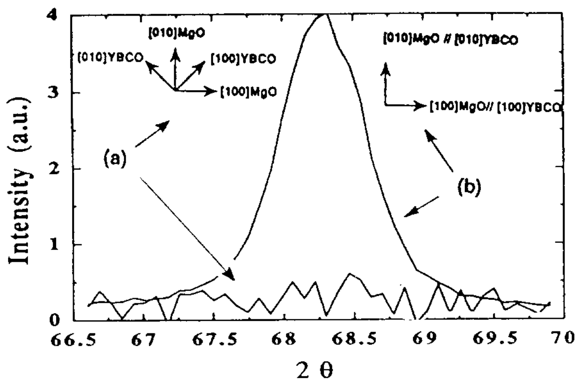

Fig. 3 : Asymmetrical reflections on (108) plane

The epitaxial relationship between the a and b axes of YBaCuO films and the ones of the MgO substrate has been determined using the asymmetrical X-ray reflections. Fig. 3 shows the diffraction patterns of the (108) reflection when the X-ray beam is parallel to the (100) (curve a) and (110) (curve b) substrate directions. The $(100)_{YBCO}$ // $(100)_{MgO}$ is the only in plane orientation which is observed in this YBaCuO film.

These epitaxial relations were also studied by channeling experiments using the special configuration of planar channeling. In fact, when the incident ion beam is tilted from the c-axis direction to a direction included in a major crystallographic plane, the RBS yield does not increase up to the random value but only up to the planar χ_{min} value. Therefore, by tilting the beam in the (100) or (110) plane of the MgO substrate, the respective positions of the (100) and (110) YBaCuO planes can be studied. Fig. 4 represents the χ_{min} variation for scans in the (100) and (110) YBaCuO planes. It is worth noting that the χ_{min} values in (100) planar channeling are different for Ba and Cu, while a single value is observed for the (110) planar channeling. This is due to the YBaCuO structure. In fact, two kinds of cationic planes are present in the (100) family (Cu planes and (Y, Ba) planes), while for the (110) family, only one kind of cationic plane (with Y,Ba and Cu species) exists. In the latter case, only one χ_{min} planar value is observed, while for the (100) plane, the lower average atomic number plane (the Cu one) induces weaker channeling effects. Thus, it seems possible via planar channeling studies to define the epitaxial orientation of the film with respect to the substrate axes.

High T_c superconducting oxides are particularly sensitive to radiation damage. The MeV He ion beam used to record RBS and nuclear microanalysis spectra induces measurable changes of transport properties (T_c and J_c) of epitaxial YBaCuO thin films as previously reported [4]. As a result, during the channeling experiments reported in this study, the charge deposited by the incident ion beam was kept at a minimum dose (i.e. 10^{16} He^+/cm^2) for each spot. This value was deduced from the analysis of the χ_{min} evolution with ion dose as presented in Fig. 5. The increase of χ_{min} with ion dose characterises the creation of defects in the films

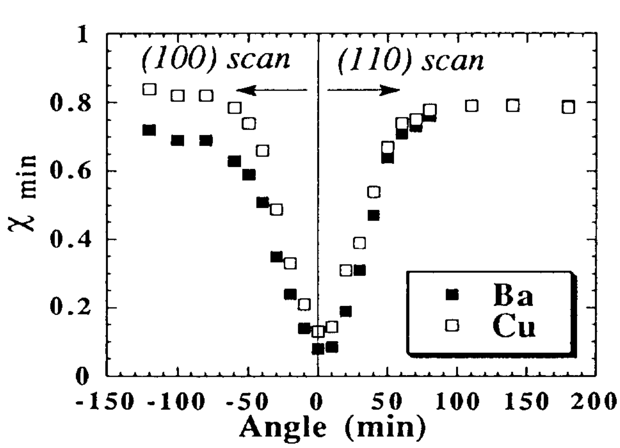

Fig. 4 : Scans along (100) and (110) YBaCuO planes

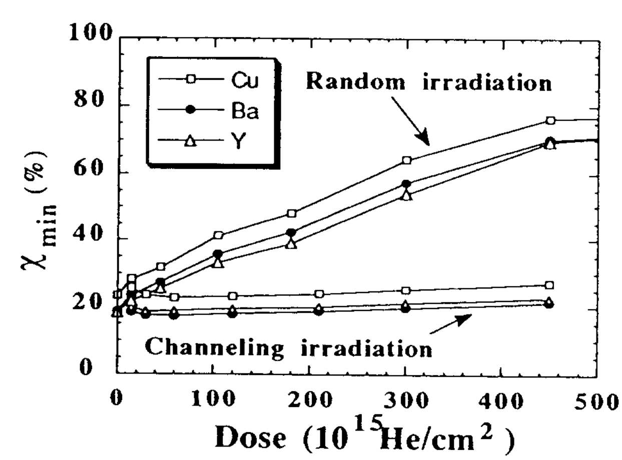

Fig. 5 : Effect of the He dose on χ_{min}

due to the incident ion beam. Irradiation in random geometry is far more destructive than the one in channeling geometry because of the larger amount of He interactions with the film atoms.

The structural defects created by the 2 MeV He ion irradiation were studied using micro Raman spectroscopy. As shown in Fig. 6, the Raman spectrum for as grown YBaCuO films (spectrum a) exhibits three main lines at 497, 336 and 145 cm^{-1} [5]. The 497 cm^{-1} band is assigned to the axial O (1) stretching vibration, its rather weak intensity (with respect to the other bands) is due to the preferential orientation of this film, with the c-axis normal to the MgO substrate. When the sample is irradiated along a random direction i.e. not along a major crystallographic axis, a broad band near 565 cm^{-1}, appears in the corresponding Raman spectrum (curve b in Fig. 6.) This band is very similar to the one observed on badly crystallised or amorphous YBaCuO thin films for which the Raman spectrum is also presented for comparison purpose (spectrum c). The intensity of this 565 cm^{-1} band increases with increasing ion dose, so does the film amorphisation leading to the dechanneling effect observed in Fig. 5.

The gradual amorphisation of the film does not induce any large effect on the 336 and 145 cm^{-1} lines (corresponding to atomic vibrations in the CuO plane). At the same time, the appearance of a characteristic line at 470 cm^{-1} indicates a partial orthorhombic to tetragonal transformation

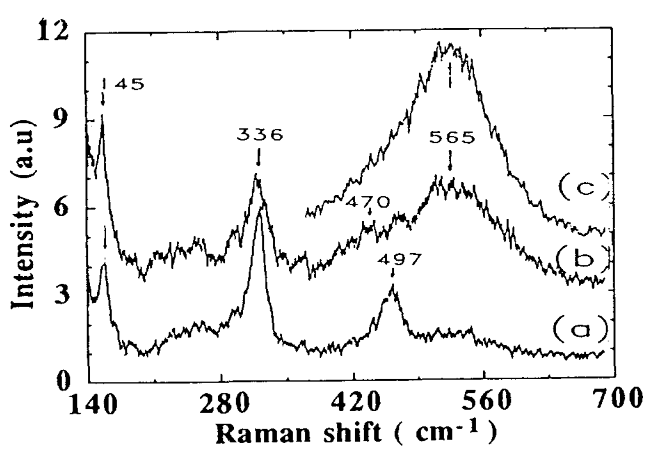

Fig. 6 : Raman spectra of an *in situ* film before (a) and after (b) RBS irradiation, amorphous film (c)

(spectrum b) [6]. This ion induced transformation represents a loss of oxygen during irradiation, which can explain the observed related decrease in T_c, as well as the change in the c parameter measured after irradiation.

Summary

We have evidenced the high crystalline quality of our laser ablated YBaCuO films, measuring low χ_{min} values (8%) and narrow rocking curves. Conditions to obtain pure c-axis perpendicular to MgO surface films have been determined. 0° and 45° epitaxial growths on MgO are obtained, further studies are under way to eliminate the 45° orientation. The possibility to study these epitaxial relations using RBS is demonstrated and the sensitivity of YBCO to ion irradiation is discussed. Intrinsic and induced defects are commonly monitored by microRaman spectroscopy.

Acknowledgements

The help of M[rs] C. Audry (LDIS Alcatel Alsthom Recherche) for X-ray diffraction analyses was much appreciated. This work was supported by the CNRS (GDR 86).

References

1 D. Chambonnet, C. Fages, D. Sinobad, C. Belouet, A. Chéenne, J. Perrière, C. Vignolle, A. Gervais, "High T Superconductor Thin Films", L. Correra Ed., p. 407 (1992), Elsevier.

2 O. Meyer, T. Kroener, J. Remmel, J. Geerk, G. Linker, B. Strehlau, TH. Wolf, Nucl. Instr. Meth. B 65, (1992), 539.

3 E. Rimini, "Materials Characterization Using Ion Beam", p. 455, Eds. J.P. Thomas and A. Cachard, Plenum Publishing Corporation 1978.

4 D.P. Norton, D.H. Lowndes, X.Y. Zheng, Shen Zhu, R.J. Warmack, Phys. Rev. B 44, (1991), 9760.

5 R. Feile, Physica C 159, (1989), 1.

6 M. Stavola, D.M. Krol, W. Weber, S.A. Sunshine, A. Jayaraman, G. A. Kouroulis, R.J. Cava, E.A. Rietman, Phys. Rev. B 36, (1987), 850.