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Defects Analysis of *in situ* Grown BiSrCaCuO Thin Films

L. Ranno*, R.M. Defourneau*, J.P. Enard*, J. Perrière* and D. Martinez-Garcia°

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

°Departamento de Fisica Aplicada, Universitat de Valencia, 46100 Burjassot, Valencia, Spain.

Abstract

Using the *in situ* laser ablation deposition technique, we have grown thin superconducting films of the "2212" phase of the Bi compound (i.e. $Bi_2Sr_2Ca_1Cu_2O_{8+y}$). Depending upon the precise growth conditions, various kinds of defects can be observed in such films : disturbed surface morphology, intergrowth of various phases and crystalline defects which can degrade the transport properties of the films. The nature and density of these defects in the films have been studied, and possible ways to obtain defect free epitaxial BiSrCaCuO thin films are presented and discussed.

1. Introduction

In situ grown BiSrCaCuO films are presently obtained by the pulsed laser deposition technique[1]. Their transport properties and in particular their transition temperature strongly vary (between 20 and 80 K) with the preparation conditions. This is related to the nature and density of defects which are present in these *in situ* grown films. In fact, differences with respect to the ideal 2212 cationic stoichiometry, or to the precise oxygen content lead to strong decrease in T_c. In the same way, the intergrowth of various semiconducting or insulating phases with the superconducting "2212", or a disturbed surface morphology can be the origin of the low values of critical current densities observed in the Bi films. In this work, using RBS, SEM and X-Ray diffraction, we have studied the elemental composition, the atomic profile along the growth direction, the surface morphology and the precise crystalline phase composition, as a function of the experimental deposition conditions, in order to determine possible ways to grow defect free BiSrCaCuO films.

2. Experimental

Thin BiSrCaCuO films were deposited using the pulsed laser deposition technique[2]. In our experimental set-up, a frequency tripled Nd:YAG laser (B. M. Industries), with λ = 354 nm and τ = 7 ns, is focused via a quartz lens onto a rotating BiSrCaCuO target which is placed in a vacuum chamber. (100) oriented MgO single crystals were used as substrates, and the film growths were carried out at high substrate temperature (700°C) under pure oxygen atmosphere (P= 0.1 mbar).

The elemental composition and the in-depth atomic profiles were obtained by Rutherford Backscattering Spectrometry (RBS). Moreover, RBS in channeling geometry gave us information on the crystalline quality of the films, by determining the ratio of aligned to random spectra (i.e. the χ_{min} value). The different phases present in the films were identified using X-ray diffraction in the Bragg-Brentano geometry and rocking curves were also measured on (00l) peaks. The surface morphology was studied by scanning electron microscopy.

3. Results

At first, the precise cationic composition of the films depends upon the laser deposition conditions[2]. The laser parameters (photon wavelength, pulse energy and beam focalisation)

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and the target parameters (composition, density and grain size) mainly determine the flux and angular distribution of the elements reaching the substrate. Therefore, in general, films with a different composition from that of the target are obtained using the laser ablation process. Moreover, the substrate temperature and the oxygen pressure play the most important roles on the cationic fixation rate, especially for Bi, for which a slight decrease in the oxygen pressure leads to a severe decrease of the sticking coefficient at high substrate temperature[2,3]. As a result, multiphased materials are generally grown, this behaviour being reinforced by the lamellar character of Bi compounds which allows the intergrowth of various semiconducting or insulating phases with the superconducting 2212 phase. In fact, the optimised deposition conditions are critical : a too low substrate temperature gives badly crystallised 2201-2212 materials, while a too high one induces surface roughness and undesirable impurity phase formation (CuO and others). As shown by the X-ray diffraction pattern presented in Fig. 1, pure 2212 films are grown at 700°C under 0.1 mbar oxygen pressure.

An improved surface quality is also observed on the BiSrCaCuO films grown using the *in situ* method. In fact SEM analysis shows that such films are smooth and uniform, while *ex situ* films present a considerable surface roughness. However, outgrowths can be observed on *in situ* films. These morphological defects are due to a Cu excess, with respect to the ideal 2212 cationic composition, that can be reduced using a non

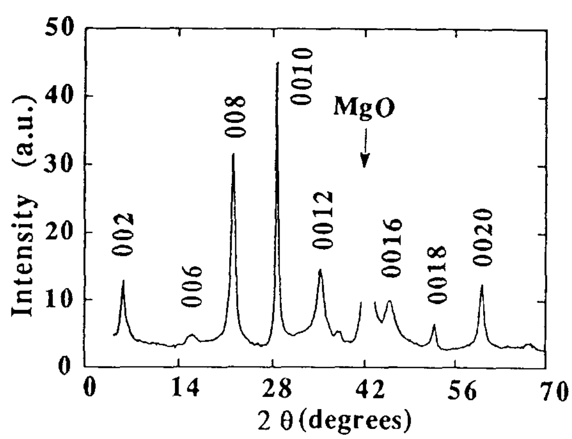

Fig 1 : Pure 2212 film θ-2θ diffraction pattern

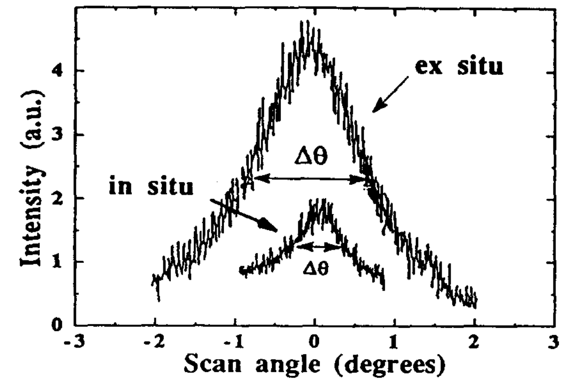

Fig 2: (0010) rocking curves of *ex situ* (Δθ=1.6°) and *in situ* (Δθ=0.5°) grown films

stoichiometric target. The oxygen pressure during the deposition plays also an important role on the surface morphology of the films, since a too low pressure induces a non continuous film growth. As a matter of fact, Fig. 3 shows RBS spectra for films grown at different oxygen pressures. These spectra show, for pressures lower than 0.08 mbar, the presence of tails towards low energies on each peak. These tails are characteristic of a non uniform growth, as checked by the presence of macroscopic defects in the SEM images.

The very strong (00l) reflections observed on the θ-2θ diffraction patterns (Fig. 1), indicate that the films are oriented with their c-axis normal to the MgO substrate. This textured growth was further studied by the measurements of the (0010) rocking curves FWHM (see Fig. 2). For comparison purpose we show also a typical rocking curve

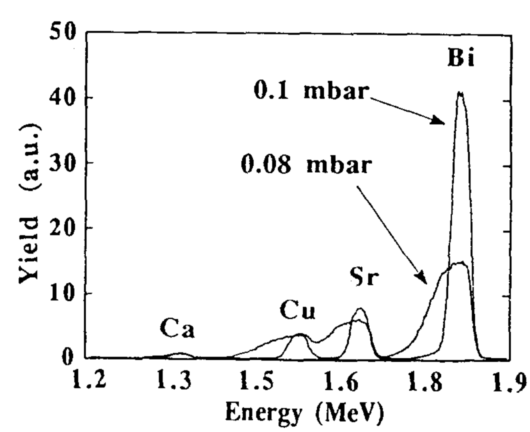

Fig. 3 : Effect of oxygen pressure on morphology

recorded on *ex situ* films (post annealed films). The FWHM of these rocking curves evidence the fact that the *in situ* growth process induces a narrower angular spread of the c-axis, 0.5° to compare to 1.6° measured on *ex situ* films.

RBS in channeling geometry has been used to check the crystalline quality of the BiSrCaCuO films, and Fig. 4 represents typical aligned and random backscattering spectra observed in this work. The best χ_{min} values obtained were 35 % for the cationic species, and to our knowledge better results have not been reported in the litterature for *in situ* grown films. This value can be compared to that reported for channeling in 2212 single crystals, i.e. 25 % [4]. This high χ_{min} value (even for single crystals) seems to be due to the presence of the incommensurate modulation in the Bi double layer, which induces large atomic displacement (up to 0.04 nm), and therefore, this can be the origin of the important dechanneling effect in this material. This idea is confirmed by the fact that Pb substituted 2212 single crystals present a better χ_{min} value, i.e. 10 % [5], and the presence of Pb atoms is known to reduce the extent of atomic displacements, and to improve the modulation coherence along the c direction.

The measurements of the χ_{min} value for oxygen, although less precise than the cationic ones, gave higher values (about 70%). This behaviour seems to be related to the structure of the BiSrCaCuO compound. In fact, the lack of channeling for oxygen may be the result of the presence in the c-axis direction of rows of low Z atoms (oxygen) embedded in a matrix of high Z atomic rows (cations). This structure should then induce weaker channeling effects for oxygen[5].

The nature of defects present in the *in situ* grown BiSrCaCuO films was also studied by measuring the χ_{min} variation as a function of the energy of the incident He ion beam. In fact, it is known that the dechanneling caused by point defects (displaced atoms) decreases with increasing ion energy. An opposite trend is characteristic of extended defects (dislocations), while stacking-faults do not induce any variation[6]. As shown in Fig. 5, a slow decrease is observed with decreasing energy for the χ_{min} values measured on the Bi signal in films of different thicknesses (30 and 80 nm). Since the incommensurate modulation is equivalent to intrinsic point defects (displaced atoms), extrinsic defect free films would give a pure $\chi_{min} \propto E^{-1/2}$ relationship characteristic of the intrinsic punctual defects[6]. Therefore, the slight decrease observed in Fig. 5 means that the main defects in our films may be dislocations and stacking faults. This last point being related to the two-dimensional character of the Bi compound.

In spite of the presence of such numerous defects in the films, the epitaxial growth of the BiSrCaCuO films on MgO substrates is possible. Moreover, the epitaxial relationship between the a and b axes of the BiSrCaCuO film and the ones of MgO substrate can be studied by channeling experiments using the special configuration of

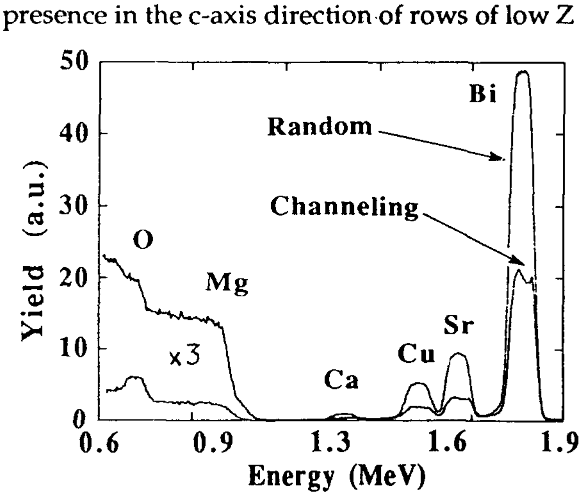

Fig. 4 : Aligned and random RBS spectra

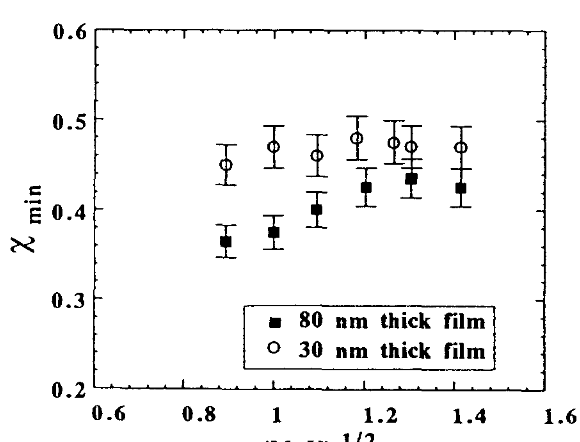

Fig. 5 : χ_{min} as a function of ion energy

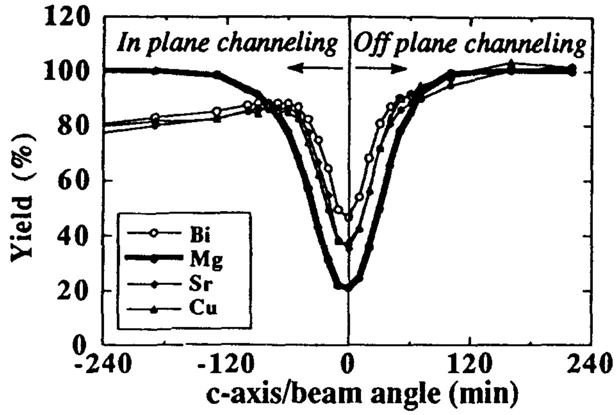

Fig. 6 : In plane and off plane RBS scans

planar channeling. 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 (i.e. χ_{min} = 100%). These conditions correspond to planar channeling characterised by a planar χ_{min} value higher than the one measured in axial channeling but lower than 100%. Thus by tilting the beam in various directions, and measuring the RBS yield on MgO and on the film, it is possible to determine their relative orientation. As a matter of fact, Fig. 6 represents tilts into planes, 13 and 20° off the MgO (100) plane. For the 20° scan, all the elements RBS yields reach the random value, and this direction does not represent a planar channeling direction for the film or the substrate (off plane channeling). On the contrary, for the 13° direction, the Mg yield reaches the random value, while the yields of the elements of the BiSrCaCuO film do not reach the random level. This means that this direction does not correspond to a crystallographic plane for the MgO, while it does for the film. By this way, we characterise the existence of epitaxial directions, and a RBS ω-scan using planar channeling has evidenced two distinct directions of epitaxy (13° and 45°). This result agrees with the results of X-ray precession and X-ray ω-scan.

4. Summary

In order to grow, using laser ablation, *in situ* epitaxial thin films of BiSrCaCuO reaching the crystalline quality of YBaCuO ones, several points have to be mastered to keep the defect density at the lowest possible level : an ideal cationic composition of the films (2212), a perfect surface of the MgO substrate, a controlled epitaxial growth based on optimised substrate temperature and oxygen pressure during deposition. However, some studies still remain, especially the origin of the epitaxial orientations between the film and the substrate have to be determined. The nature of this epitaxial growth itself (layer by layer or island growth) has to be specified. Finally the superconducting properties of the *in situ* films have to be related to the defects in order to improve them.

Acknowledgements

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