Solid State Communications, Vol. 83, No. 1, pp. 67-71, 1992.
Printed in Great Britain.

0038-1098/92$5.00+.00
Pergamon Press Ltd

RBS STUDY OF *IN SITU* GROWN BiSrCaCuO FILMS

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(Received 11 December 1991 by M. Balkanski)

BiSrCaCuO thin films have been grown *in situ* on MgO single crystals by pulsed laser deposition under 0.1 mbar oxygen pressure, the substrate temperature being around 700 °C. These films are nearly pure 2212 phase, highly textured with a full c-axis orientation, and Rutherford backscattering spectrometry (RBS) in channeling geometry has been used to obtain precise information on their crystallinity. Although the X_{min} values were found higher (about 35%) than those measured on bulk single crystals, they show partial epitaxy of the films, which was not observed with post annealed films. The comparison of backscattering yield in random and aligned orientations evidences the fact that all the cationic elements behave in a similar way in the channeling experiments, while differences are observed for the oxygen species according to their precise location in the network. These *in situ* grown films were found very sensitive to the ion irradiation, and showed large dechanneling effect with increasing ion dosis.

Discovered in 1986 [1] , high Tc superconducting phases were at first synthetised in bulk, but it is obvious that thin films of this material are more important especially for devices. While at the beginning a two step process (i.e. film deposition followed by a high temperature oxygen annealing treatment) was used to obtain superconducting transitions with films of this material, now several groups perform growth of *in situ* superconducting films, and even junctions and superlattices are realised [2,3]. Yet to optimise these *in situ* epitaxial growths, a better understanding of the growth mechanism is expected, i.e. the influence of the formation conditions on the various properties of the films must be determined. That is why we have used several methods to characterise the atomic composition, surface morphology, structural and superconducting properties of BiSrCaCuO films grown by the *in situ* laser ablation method. In particular we have used Rutherford backscattering spectrometry in channeling geometry to investigate the epitaxy of thin films (70 nm thick) of the 2212 phase on MgO substrates. RBS in channeling geometry has been widely used for YBaCuO films, but at this time only a few reports mention its application to BiSrCaCuO films. In this paper, we lay emphasise on the results of such experiments on *in situ* grown BiSrCaCuO films, and on the interpretations for the different channeling behaviours of cations and oxygen that we have evidenced.

Thin films of the BiSrCaCuO compound were deposited onto MgO (100) single crystal substrates using the pulsed laser evaporation technique [4]. The laser used in this work was a Nd : YAG (supplied by BMI) delivering pulses with a 5 ns duration at a 5 Hz repetition rate. All the films were deposited using the second harmonic wavelength (532 nm), which was generated by a frequency doubling KDP crystal, and the available laser intensity at the surface of the target was typically in the 50 to 200 MW/cm^2 range. The evaporations took place in a high vacuum chamber (10^{-8} mbar base pressure), and the target was a polycrystalline ceramic pellet with a $Bi_4Sr_3Ca_3Cu_4O_y$ composition. This target was rotating during laser irradiations. The *in situ* formation of superconducting films was achieved by deposition onto heated substrates (in the 650 to 750°C range) under 0.1 mbar oxygen pressure. After deposition, the films were cooled at 50°C/min under oxygen (between 0.1 and 1 mbar) down to a plateau where the films stayed half an hour at 400°C under higher oxygen pressure (up to 1 bar) and finally cooled down to room temperature.

By the complementary use of Rutherford backscattering spectrometry, scanning electron microscopy and X-ray diffraction analysis, the atomic composition, surface morphology and crystalline state of the *in situ* grown films were studied. The superconducting properties of these films were determined by the standard dc four probe resistivity measurements. Moreover to gain additional information on the crystalline quality of the films, RBS experiments in channeling geometry were performed, i.e. RBS spectra recorded in channeling geometry (when the incident He ion beam is aligned with a crystallographic direction) are compared to those taken in random geometry. The ratio of the aligned to random contribution (i.e. the minimum yield X_{min}), is a measure of the structural quality of the films : the smaller X_{min}, the better the structure.

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As noted previously [5], whatever the deposition conditions the film composition was found different from that of the target, and was not uniform through the overall deposited area (due to different spatial distributions of the four cations). That is why only the uniform central area of the deposition was studied using 1 cm^2 substrates. The film composition determined by RBS was found to depend upon the deposition conditions, especially a Bi deficiency was often observed for film deposition at high temperature (>600°C) and low oxygen pressure. Superconducting transitions were obtained with films showing a composition close to that of the 2212 phase, i.e. for films deposited at 700°C under 0.1 mbar oxygen pressure. Lower temperatures lead to incomplete crystallisation of the film, while at higher temperature large Bi losses were often observed. As shown in Fig. 1, the resistivity curves of films grown at 700°C present a broad transition, with a temperature for zero resistivity depending upon the precise cooling down. In fact, for the 2212 phase the T_c value is strongly affected by the oxygen concentration and/or oxygen distribution in the lattice. Thus a careful optimisation of the cooling down (the oxygen incorporation) would lead to an enhancement in T_c, as it has been shown for post annealed films [6].

SEM analysis shows that rather smooth and uniform films are grown by the *in situ* method, while post annealed films present an appreciable surface roughness [5]. For *in situ* and *ex situ* films, the X-ray diffraction patterns present very strong (001) reflections which indicate that the films are oriented with their c-axis normal to the surface of the MgO substrates. For the *in situ* films grown at 700°C, these patterns yield essentially a c-axis lattice parameter of 3.09 nm, meaning that single phase $Bi_2Sr_2Ca_1Cu_2O_y$ films are grown under these conditions. Impurity phases if present were not identified by X-ray diffraction. Although the diffraction patterns indicate a preferred c-axis orientation for *in situ* and *ex situ* films, RBS analyses show diffferences between these two methods of growth.

RBS in channeling geometry has been used to check the crystalline quality of the BiSrCaCuO films. Of course, the X_{min} values were found to depend upon the deposition conditions, and one of the best results is shown in Fig. 2, by the random and aligned spectra recorded with 1 MeV He ions on 70 nm thick BiSrCaCuO films deposited at 700°C under 0.1 mbar O_2. Immediatly after the surface peak in the Bi contribution a X_{min} value equal to 35% is measured, while the appreciable increase in the dechanneling effect in the Bi spectrum for decreasing energies indicates that the crystalline quality of the film is degraded towards the interface with the substrate. The disorder at this interface may be due to the 10% mismatch which exists between the 0.412 nm MgO crystalline parameter and a and b crystalline parameters of BiSrCaCuO which are around 0.38 nm. The X_{min} values measured on *in situ* films are very different from those observed with BiSrCaCuO films annealed at high temperature after laser deposition. In this last case, the channeling experiments do not evidence a large epitaxy of the films, since for the best result we have obtained, we have measured a X_{min} value equal to 90%. The value obtained in this work for the *in situ* formation of BiSrCaCuO films on MgO is similar to the result reported for BiSrCaCuO deposited onto $SrTiO_3$ substrate [7], but appears rather better than the one previously reported (60%) for a film deposited onto MgO [8] which was grown at a substantially higher substrate temperature (850°C) than ours.

However, this X_{min} value is largely higher than those routinely measured on YBaCuO films (less than 5%) [9]. This can be due to various reasons which are related to the material itself and to the growth process. A first singularity of the BiSrCaCuO compound is the presence of an incommensurate modulation in the BiO double layer, which breaks the periodicity and leads to dechanneling. In fact, atomic displacements resulting from this incommensurate phase modulation are present and variations in the atomic location up to 0.04 nm for Bi and Sr atoms in the a and c directions, and 0.03 nm for the Cu in the c direction have been reported [10]. As a result, the best X_{min} value for BiSrCaCuO single crystal is around 10% [11], which must be compared to the 2% found for YBaCuO single crystal. Moreover, the BiO layers in the

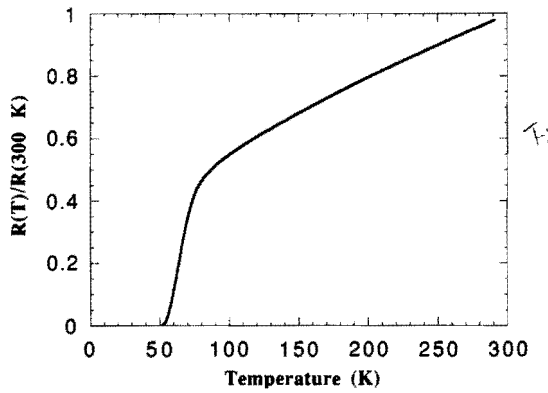

Fig. 1 : Resistivity curve of an *in situ* film deposited at 700°C on MgO under 0,1 mbar O_2

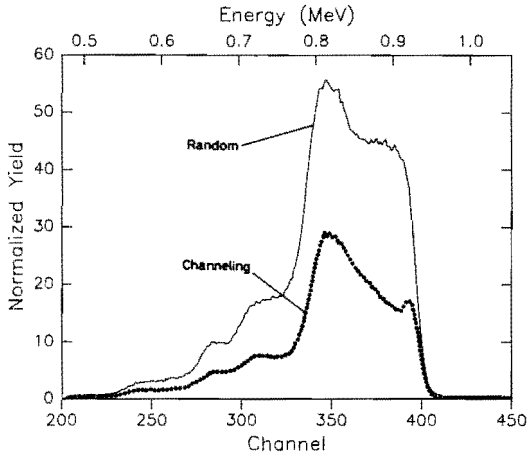

Fig. 2 : RBS spectra in random (—) and channeling (···) geometries recorded with 1 MeV He^+ : X_{min} = 35 %

structure are not strongly bound and practically each unit cell along the c axis behaves independently of the others. Therefore during the film growth it does not exist a memory effect for the orientation of the a and b axis, i.e. the films are highly textured but the epitaxy is not actually realised, a and b axis being randomly oriented in the planes which are perpendicular to the well defined c axis. That is quite different from lead substitued films because in these films the lead atoms serve as substitutes for bismuth atoms, which leads to extra electronic bondings between these two layers. As a consequence the a-b orientation can persist on longer distances along the c axis, even if a and b can always be exchanged. These two intrinsic problems leads to a high channeling yield and an extra increase is due to some characteristics of our growth process. As a matter of fact, the case presented in Fig. 2 correspond to an atomic composition $Bi_2Sr_{1.8}Ca_{1.2}Cu_{2.2}$. Thus, this is not a pure 2212 film meaning that other phases may be present, and the intergrowth of these chemical phases is possible in the BiSrCaCuO family. This intergrowth of different phases, even in small proportion, can therefore break the atomic periodicity along the c axis, leading to a dechanneling effect. Furthermore, the substrate can be also at the origin of these high value for the X_{min}. In fact, we have observed that BiSrCaCuO films deposited under the same conditions on MgO substrates of different origins, do not present the same X_{min}, the difference being important in some cases (40% and 90%). Taking into consideration the fact that no special surface treatment was carried out on the MgO substrates, better results for the epitaxy of the BiSrCaCuO films can be expected, as it has been observed for the YBaCuO case [12].

The spectrum in Fig. 2 has been recorded at 1 MeV, and the mass separation is not sufficient to draw reliable informations on the individual Sr, Cu, Ca and O contributions. Additional insights are obtained with a 2 MeV ion beam as it is shown in Fig. 3a. In this case, the single masses of the film are practically resolved, and moreover, the backscattering yield from the substrate is also well separated. As a result, this Fig. 3a shows that the X_{min} value is the same for all the cationic elements of the film (about 40%), while the X_{min} value for the oxygen is largely higher (about 70%) as it is measured on the extended low energy part of the spectrum in Fig. 3b. This is a general result which has been observed for films deposited under various conditions and presenting different X_{min} values. At first, this result characterises a large structural disorder in the oxygen sublattice, when compared to the cationic behaviour. Once again, the incommensurate modulation in the Bi compound may be the origin of this disorder. The oxygen atoms in the BiO layers can occupy all the positions between the center of square defined by the Bi atoms and the midpoint of the square side. Thus they do not actually participate to the channeling effect of the incident ion beam.

Another possible interpretation of this difference in behaviour of oxygen and cations in the channeling experiments is related to the precise location of the various atoms in the crystalline structure of the 2212 superconducting phase. In this structure, there are two different kinds of atomic rows parallel to the c axis. The atomic sequences of the two rows are represented below :

(i) Bi - O - Cu - Cu - O - Bi - O - Sr - Ca - Sr - O
<---------- 3.09 nm ---------->

(ii) ----- O - O ---------- O - O --
<-------- 1.54 nm ------->

The second row (ii) consists only of oxygen atoms with very different interatomic spacings, since these oxygen atoms are localised in the copper oxide planes. Thus, two kinds of oxygen atoms can be defined, those in the (i) row, and the ones in the (ii) row, and these two kinds of oxygen atom are in the same quantity. For the channeling of the incident He^+ ions, the second kind of row will play a minor role with respect to the effects of the first one, since the low atomic number of oxygen and the large interatomic distance give very weak channeling effects. Therefore, the Bi, Sr, Ca, Cu and the oxygen

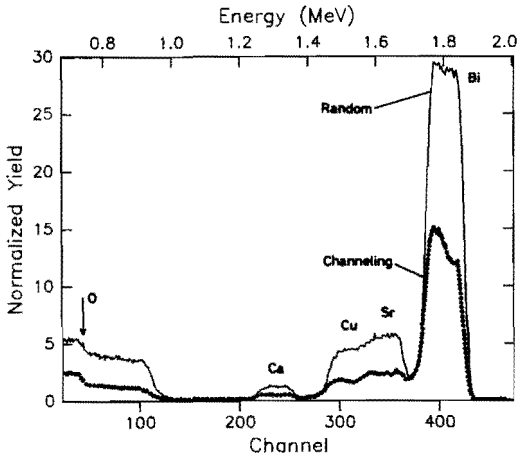

Fig. 3a : RBS spectra in random (—) and channeling (···) geometries recorded with 2 MeV He^+ : X_{min} cations = 40%

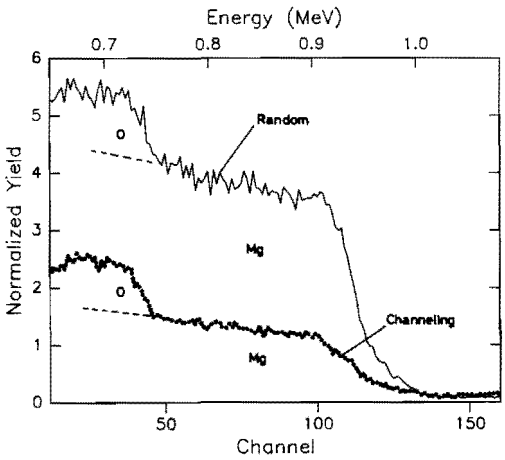

Fig. 3b : RBS spectra in random (—) and channeling (···) geometries recorded with 2 MeV He^+: X_{min} oxygen = 70%

atoms present in row (i) will be determinant for the channeling of the He ions, and they will behave in an identical way for the channeling experiments, i.e. the same X_{min} value will be observed, and this is indeed observed for the cationic constituents. On the contrary, one can consider the oxygen atoms of row (ii) as atoms in interstitial positions with respect to the channel defined by the row (i). So due to the structure along c axis, half of the oxygen of the structure is "naturally" in dechanneling sites, and therefore contribute to the high value of X_{min} observed for oxygen.

Let us note that this X_{min} behaviour must be also true for channeling experiments on a BiSrCaCuO single crystal. Such experiments have been previously reported, but a particular behaviour for the oxygen has not been mentionned in the publications. However, in single crystal it is difficult to obtain precise values of the X_{min} for oxygen since the backscattering oxygen signal is overwhelmed by the high masses contribution. Increasing the He^+ dosis can seem a good solution to improve the precision on the spectra but then one can observe that BiSrCaCuO is a very sensitive crystal. This can be shown in Fig. 4 which represents RBS spectra recorded after increasing doses. In the 10^{15}-10^{17} He^+/cm^2 range X_{min} evolved from good channeling to ramdom type spectrum. Moreover X_{min} is a linear function of the dosis in this range and the four cations behave the same way. The effect of several 10^{15} He^+/cm^2 has already been reported [13] but then total dechanneling was achieved with a smaller dosis.

In summary, we show here the benefit of growing in situ BiSrCaCuO films, which leads to smoother surfaces and a better epitaxy. The crystallographic state of the films and the nature of the chemical phases are strongly affected by the substrate temperature and oxygen pressure during the pulsed laser deposition, while the superconducting properties largely depend upon the cooling down. In fact for Tc, which is very sensitive to the oxygen incorporation, the post deposition temperature decrease has to be performed under a sufficient pressure of oxygen, which has to be optimised, to keep a high Tc without high temperature post-annealing. To improve the epitaxy of these *in situ* films and come closer to YBCO films and

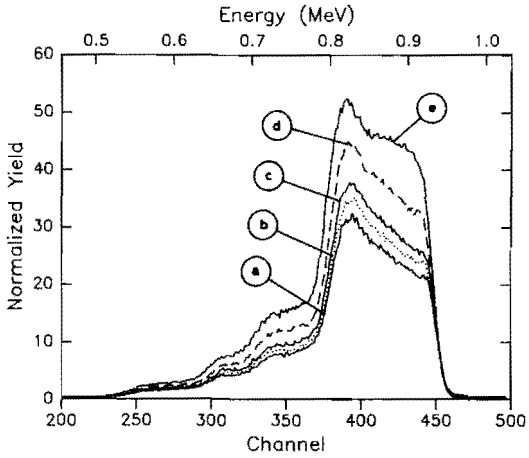

Fig. 4 : RBS channeling spectra recorded after the sample was irradiated with (a) 2.10^{15}, (b) 8.10^{15}, (c) 16.10^{15}, (d) 80.10^{15} He^+/cm^2 doses compared with the random spectrum (e).

BiSrCaCuO single crystal X_{min}, the conditions of growth have to be improved. This means that the ideal cationic composition of the 2212 phase must be reached in the deposited films, in order to avoid any formation of undesirable impurity phases, and that surely higher quality MgO substrates will have to be used. As a consequence, multilayers and even superlattices of the different phases of BiSrCaCuO may soon be realised. Finally, the RBS experiments in channeling geometry have evidenced the lack of channeling for oxygen which may be the result of rows of low Z oxygen imbedded in a matrix of high Z rows. Moreover, the high sensitivity of the BiSrCaCuO films to the He ion irradiation has been also observed. The correlation between this last point and the various properties of the films are now studied.

Acknowledgements - The authors wish to express their thanks to A. Chéenne, R.M. Defourneau, F. Queyroux, and M. Nanot. Part of this work was supported by the CNRS (GDR n° 86).

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